



(51) International Patent Classification:

C01G 41/02 (2006.01) *B82Y 30/00* (2011.01)
C03C 17/23 (2006.01) *B01J 23/30* (2006.01)
G02B 5/23 (2006.01)

(21) International Application Number:

PCT/AU2017/050262

(22) International Filing Date:

24 March 2017 (24.03.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2016901115 24 March 2016 (24.03.2016) AU

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: SMART WINDOW COATING

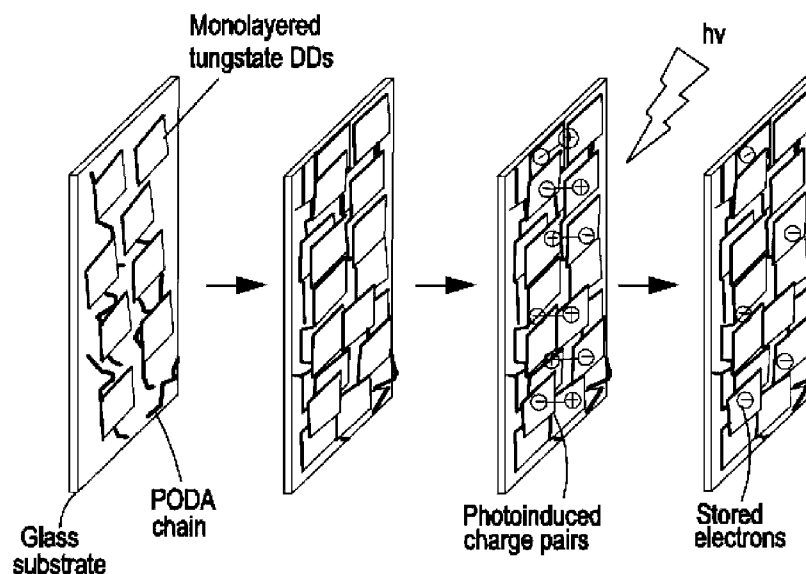


Figure 1

(57) Abstract: A functional coating for a substrate comprising at least one functional layer formed from a plurality of tungstate nanodots. The functional coating is formed by providing a substrate, preferably a glass substrate and depositing at least one functional layer including a monolayer of tungstate nanodots onto that substrate.

SMART WINDOW COATING

CROSS-REFERENCE

[001] The present application claims priority from Australian provisional patent application No. 2016901115 filed on 24 March 2016, the contents of which should be understood to be incorporated into this specification by this reference.

TECHNICAL FIELD

[002] The present invention generally relates to a functional coating for a substrate, and more particularly a functional coating for a transparent or semi-transparent substrate to form a smart window coating. The invention is particularly applicable as a coating of a window substrate, such as a transparent material like glass or the like and in particular a self-cleaning window coating and it will be convenient to hereinafter disclose the invention in relation to that exemplary application. However, it is to be appreciated that the invention is not limited to that application and could be used as a coating in other functional coating applications on various substrates including non-transparent substrates.

BACKGROUND OF THE INVENTION

[003] The following discussion of the background to the invention is intended to facilitate an understanding of the invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge as at the priority date of the application.

[004] The discovery of two dimensional (2D) nanosheets (NSs) such as graphene and monolayered transition metal oxide crystallites has sparked new findings in areas such as catalysis, nanoelectronics, biomedical sciences, etc., and also opened up great possibilities of constructing new nanostructures. Compared to their bulk counterparts, 2D NSs not only possess significantly expanded surface area, but also exhibit some unique optical, electrical, and chemical properties. For example, NSs can be assembled to ultrathin photoactive films with excellent transparency. Moreover, the nearly completely exposed surface of NSs provides abundant active sites for many reactions owing to the existence of numerous under-coordinated

atoms, making NSs highly active for a number of applications such as hydrogen production and photocatalysis.

[005] One of the applications of nanostructures based on semiconductor NSs is solar-driven photocatalysis, which is considered to be a prospective pathway to production of useful chemicals and fuels and decomposition of pollutants. However, conventional photocatalysts are only active under light illumination and they will stop functioning once external irradiation ceases, as the lifespan of photogenerated charge carriers is generally around a few nanoseconds or shorter. Thus, no activity without light. This drawback limits the application of solar-driven photocatalysis to strictly daytime only as no solar light is available at night time. In order to retain photocatalytic activity after light ceases, a few attempts have been made to combine TiO_2 photocatalysts with carbon nanotubes (CNTs) or PdO nanoparticles. Photoinduced electrons in TiO_2 migrate to CNTs or PdO under irradiation and diffuse back to TiO_2 forming radical species to extend activity in the dark. However, their large sizes make the composites unsuitable for the synthesis of transparent ultrathin films with memory photocatalytic activity, which is vital for many practical applications such as functional glass coatings.

[006] Other applications of nanostructures and/or functional films include:

[007] *Full-day photocatalytic air purification and water treatment:* Full-day servicing antibacterial films is conventionally achieved by incorporating additional functioning particles into a TiO_2 film, such as Ag. In such films, the TiO_2 photocatalyst and Ag particles are active for antimicrobial effect under UV light irradiation and in dark condition, respectively. However, these properties require the expense of incorporating one or more additional material components into the coating.

[008] *Self-cleaning induced by superhydrophilicity:* Superhydrophilicity-induced self-cleaning window is currently achieved by coating window panels with a layer of semiconductor particles such as TiO_2 . Under irradiation, the semiconductor's surface exhibits light-induced superhydrophilicity because of the generation of oxygen vacancies. Therefore, the surface absorbed dirt can be easily washed away.

However, the light-induced superhydrophilicity will gradually attenuate in the dark, that is, they lack the long term self-cleaning capability.

[009] *Smart window effect (UV spectrum blockage, visible spectrum transparency and switchable IR spectrum transmission):* To build smart windows, a layer of chromogenic materials is incorporated into windows including thermochromic (VO_2 , etc.), electrochromic (WO_3 , NiO , etc.), and photochromic (WO_3 , etc.) materials. These materials have switchable IR spectrum transmission, that is, the optical properties of smart windows can be controlled via heat, electricity, and light. This will allow the blockage of IR light in summer to isolate heat transfer, and penetration of IR light in winter to warm up buildings. The problem with the conventional smart windows is that the coating materials generally have absorption in the visible range, and therefore the smart windows are not very transparent in the visible range.

[010] *Anti-fogging:* anti-fogging is a desired property for functional films in many applications, e.g. car windows, glasses.

[011] It would therefore be desirable to provide a new and/or improved window coating which can reduce and/or overcome one or more of the above disadvantages of current smart window coatings.

SUMMARY OF THE INVENTION

[012] A first aspect of the present invention provides a functional coating for a substrate, preferably a glass substrate comprising at least one functional layer formed from a plurality of tungstate nanodots (TND).

[013] Advantageously, the coating of the present invention can simultaneously introduce three important functions: 1) Full-day photocatalytic activity; 2) Self-cleaning and anti-fogging induced by superhydrophilicity; and 3) Smart window effect (UV spectrum blockage, visible spectrum transparency, and switchable IR spectrum transmission). The present invention achieves the three abovementioned important functionalities concurrently using a facile method, and also improves all individual

functionalities compared to existing technologies. These advantages are outlined in more detail below:

[014] *Full-day photocatalytic activity:* The present invention provides a single-component film which provides photocatalytic antimicrobial effect upon irradiation (having similar properties to TiO_2 coatings), and also store photonic energy in the form of trapped electrons, which can then be used to drive antibacterial reactions in the dark.

[015] *Self-cleaning induced by superhydrophilicity:* The tungstate nanodot coating of the present invention can exhibit superhydrophilicity due to its unique surface chemistry and surface nanostructures. The film of the present invention typically retains its inherent superhydrophilicity properties. The superhydrophilicity results in a self-cleaning property.

[016] *Smart window effect (UV spectrum blockage, visible spectrum transparency and switchable IR spectrum transmission):* The tungstate nanodots used in the smart coating of the present invention are arranged in a manner that preferably has no visible absorption due to its large band gap and small size, thus the coated window shows great visible transparency. Moreover, the tungstate nanodots exhibit clear photochromism and associated switchable IR light absorption. In addition, the tungstate nanodots can effectively block UV light owing to their excellent absorption in the UV region.

[017] *Anti-fogging:* The tungstate nanodots film/ coating can also achieve excellent anti-fogging property due to its superhydrophilicity which lets water droplets quickly spread on the surface.

[018] The film of the present invention also shows a “memory” photocatalytic activity. Photoinduced electrons are quickly stored in the ultrathin film upon irradiation due to the reduction of W^{6+} to W^{5+} , and discharged to produce superoxides and hydrogen peroxide, enabling post-irradiation antibacterial activities.

[019] It should be appreciated that nanodot refers to a nanometer-scaled structure, 50 nm and smaller, in the case of the present invention formed from tungstate.

[020] Tungstate nanodots (TND) typically comprise Tungsten oxides and mixed oxide containing Tungsten, for example Cesium Tungstate (CsWO) and Rubidium Tungstate (RbWO).

[021] Each functional layer comprises a layer of tungstate nanodots. In some embodiments, each functional layer may comprise a monolayer formed from a plurality of tungstate nanodots.

[022] The tungstate nanodots are preferably applied to the substrate to preferably form ultrathin layer over the substrate surface. That layer can be a monolayer of tungstate nanodots or a multilayer of tungstate nanodots. In preferred embodiments, each functional layer is formed from a monolayer of tungstate nanodots.

[023] The nanodots can have a variety of characteristics. In embodiments, the nanodots preferably comprise small lateral sizes of from 1 to 50 nm, preferably from 1 to 30, more preferably from 5 to 20 nm and thickness of between 1 and 3 nm, preferably between 2 and 3 nm, more preferably about 2.5 to 2.8 nm. In embodiments, the nanodots can be characterised by an absorption edge at 300 to 400 nm and a band gap of 3.2 to 4.0 eV, preferably 335 nm and band gap of 3.42 eV. Preferably, the tungstate nanodots have a negative charge of between -30 and -70 mV, preferably -40 and -50 mV, preferably about -45 mV. In embodiments, the tungstate nanodots have a flat band potential of -0.51 V vs. NHE. It should however be appreciated that the flat band potential may change if the synthesis conditions are changed.

[024] A number of tungstate nanodots can be used in the present invention. In some embodiments, the tungstate nanodots are selected from at least one of caesium tungstate or rubidium tungstate. The tungstate nanodots preferably comprise caesium tungstate, preferably $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$) with hexagonal tungsten bronze (HTB) $Cs_4W_{11}O_{35}$ structure.

[025] In some embodiments, the functional layer or layers are formed using a binding polycation layer. In these embodiments, the function layer preferably comprises a bilayer comprising a monolayer formed from a plurality of tungstate nanodots and a binding polycation layer preferably selected from polydiallyldimethylammonium chloride (PDDA) or other cationic polyelectrolytes such as diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI).

[026] In some embodiments, the functional layer or layers are formed using a self-assembly layer by layer method. The tungstate nanodots preferably self-assembled to form each layer of nanodots. This method and other production methods may arrange the tungstate nanodots in a substantially spaced apart relation to each other within each layer. The tungstate nanodots of each applied layer in this layer by layer method typically overlap the tungstate nanodots of another layer, eventually forming a full coating of tungstate nanodots over the substrate surface.

[027] In other embodiments, the functional layer or layers are formed using at least one of spin coating, spray coating, dip coating, chemical vapour deposition, plasma deposition, or electrodeposition processes. These processes are described in more detail later in this specification.

[028] The functional coating can have a number of characteristics. In some embodiments, functional coating has a surface roughness R_{RMS} of from 5 to 6 nm, preferably from 5.2 to 5.7 nm. In some embodiments, the functional coating comprises a ten layer tungstate-polycation multilayer film, and can have a thickness of less than 30 nm.

[029] In some embodiments, the functional coating has a clear n-type photo-response. In some embodiments, the functional coating has an open circuit potential from +0.88 V to +0.25 V. In some embodiments, the functional coating has a solar energy storage capacity of at least $1 \cdot 10^{-4} \text{ C/cm}^2$ after 20 mins of irradiation. In some embodiments, the functional coating has a post-illumination “memory” catalytic antibacterial activity. In some embodiments, the functional coating has a water contact angle of less than 10 degrees, preferably less than 7 degrees.

[030] Again, the tungstate nanodots forming the functional coating of the present invention preferably have no visible absorption due to its large band gap and thus the coated window will show great visible transparency. In some embodiments, the tungstate-PDDA film is at least 90%, preferably at least 95%, more preferably at least 99% optically transparent in the visible light range. Preferably, the functional coating exhibits at least one of photochromism or associated switchable IR light absorption. In some embodiments, the functional coating substantially blocks UV light.

[031] It should be appreciated that the functional coating can be applied to any suitable substrate. The substrate preferably comprises a transparent substrate suitable for use in a window or the like. In embodiments, the substrate comprises a glass substrate. However, it should be appreciated that other suitable transparent substrates can also be used, for example Perspex or other transparent polymer. In other embodiments, non-transparent substrates can also be used. The substrate can have any suitable form and configuration. In some embodiments, the substrate comprises a pane, preferable a flat pane. However, it should be appreciated that the functional coating could be applied to any shape, configuration or form that the substrate is formed or shaped.

[032] A second aspect of the present invention provides method of forming a functional coating for a substrate, comprising:

providing a substrate, preferably a glass substrate;

depositing at least one functional layer on the surface of the substrate, each functional layer formed from a plurality of tungstate nanodots;

thereby forming a functional coating of tungstate nanodots on the substrate.

[033] The method of the present invention produces a transparent coating comprising monolayered tungstate nanodots, which are built up to form the functional coating/ film. The depositing step can be repeated until the number of desired coating is deposited onto the substrate.

[034] It should be appreciated that the nanodots can form a layer of that material on the substrate. Preferably, each functional layer includes a monolayer of tungstate

nanodots. The morphology of that layer is a monolayer which includes tungstate nanodots which are built up via the method of the second aspect of the present invention to form the functional coating/ film.

[035] The depositing step can be achieved using a number of techniques, including at least one of:

- a layer-by-layer (LBL) method, preferably a self-assembly layer-by-layer method;
- spin coating;
- spray coating;
- dip coating;
- electrophoretic deposition;
- chemical vapour deposition; or
- plasma deposition.

[036] It should be appreciated that more than one functional layer can be deposited on the surface of the substrate to form the functional coating. In embodiments, at least two functional layers are deposited on the surface of the substrate. In other embodiments, at least three functional layers are deposited on the surface of the substrate. In yet other embodiments, at multiple functional layers are deposited on the surface of the substrate.

[037] The method of the present invention produces a transparent coating by depositing monolayered tungstate nanodots, which are built up to form the functional coating/ film. The deposition process is repeated until the number of desired coating (preferably tungstate-polycation bilayers) is deposited onto the substrate.

[038] Each functional layer is preferably formed using a binding polycation, preferably selected from polydiallyldimethylammonium chloride (PDDA) or other cationic polyelectrolytes such as diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI). Accordingly, each function layer would comprise a bilayer comprising a monolayer formed from a plurality of tungstate nanodots and a binding polycation layer preferably selected from polydiallyldimethylammonium chloride (PDDA) or other

cationic polyelectrolytes such as diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI). It should be appreciated that the use of polycation is dependent on the substrate and coating method. In some substrate (positively charged) and coating methods (for example plasma deposition, electrophoretic deposition, chemical vapour deposition) the use of a polycation is not necessary.

[039] Each functional layer can be formed by a number of techniques including dipping, spraying, spin coating, immersion, painting or the like. In embodiments each functional layer is formed by:

- applying a binding polycation solution to the substrate;
- drying the binding polycation coated substrate; and
- applying a tungstate nanodots suspension to the binding polycation coated substrate.

[040] Again, the binding polycation is preferably selected from polydiallyldimethylammonium chloride (PDDA) or other cationic polyelectrolytes such as diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI).

[041] In some embodiments, the functional coating is formed by a layer-by-layer (LBL) method, preferably a self-assembly layer-by-layer method. The present invention therefore provides a coating, preferably an ultrathin film of monolayered tungstate nanodots that can be deposited onto glass panels using a layer-by-layer self-assembly method.

[042] For the layer-by-layer method, each functional layer is preferably formed by:

- immersing the glass substrate in a binding polycation solution;
- drying the binding polycation coated substrate; and
- immersing the binding polycation coated substrate into a tungstate nanodots suspension.

[043] In this method, the glass substrate is alternately immersed in a binding polycation solution and a nanodots suspension to form each functional layer of

tungstate nanodots bilayer and binding polycation layer. In some embodiments, the glass substrates were cleaned by deionised water and dried by an air gun after each deposition cycle.

[044] In other embodiments, the depositing step comprises a spin coating process. In such embodiments each functional layer can be formed by:

- spin coating the substrate with a binding polycation solution;

- drying the binding polycation coated substrate; and

- spin coating the binding polycation coated substrate with a tungstate nanodots suspension.

[045] These steps can be repeated at least two times, preferably three times to produce the functional coating.

[046] In some embodiments, the depositing step comprises a spray coating process. In embodiments each functional layer is formed by:

- spray coating the substrate with a binding polycation solution;

- drying the binding polycation coated substrate; and

- spray coating the binding polycation coated substrate with a tungstate nanodots suspension.

[047] The thickness of the functional layer can be tuned by controlling the time of spraying time, for example a spray time of at most 1.5 seconds, preferably between 0.1 to 1 seconds, more preferably between 0.5 to 1 seconds.

[048] In embodiments, the depositing step comprises an electrophoretic deposition process. In embodiments, the substrate comprises an electrically conductive glass arranged as an anode and each functional layer is formed by applying an electric field (for example an electric field with a voltage of 3V) to a tungstate nanodots suspension or dispersion to cause negatively charged tungstate nanodots to migrate to the substrate and self-assemble into the functional coating. The thickness of the film or the transparency of the glass can be adjusted by changing the applied voltage and the deposition time.

[049] In some embodiments, the depositing step comprises a chemical vapour deposition process. In such embodiments, volatile tungstate precursors, such as $(W(CO)_6)$, WF_6 , $W(OEt)_x$, or the like, can be used to produce a tungsten oxide vapour which can be deposited on the surface of the substrate.

[050] The substrate may also undergo a pretreatment process in some instances where the tungstate nanodots are applied to the substrate by plasma deposition to improve the surface properties of the substrate to enhance adhesion or bonding between the functional coating and the substrate. In embodiments, the pretreatment step comprises:

treating the surface of the substrate with oxygen plasma to produce oxygen vacancies on the surface.

[051] Typically, immediately following pretreatment, the glass substrate is immersed in TND suspension solution, and a plurality, preferably 3 to 10 cycles of polycation (e.g. PDDA)/TND adsorption are performed. These steps may comprise immersing the glass substrate in a binding polycation solution, preferably a polydiallyldimethylammonium chloride (PDDA) solution or other cationic polyelectrolytes such as diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI); drying the binding polycation coated substrate; and immersing the binding polycation coated substrate into a tungstate nanodots suspension. However, any of the other described methods (for example spray coating, spin coating or the like) could also be used if desired.

[052] In some embodiments, the functional coated substrate undergoes secondary treatment, in particular where the functional coating is formed by layer-by-layer deposition, spin coating or spray coating techniques. This secondary treatment can be to improve the properties of the functional coating, substrate, bond therebetween or a combination thereof. In some embodiments, the functional coated substrate undergoes a thermal treatment process which aims to improve adhesion and/or wear resistance of the coating on the substrate. In such embodiments, the process further includes the step of:

heat treatment of the coated substrate at 300 to 600 °C, preferably 350 to 550 °C for at least 30 mins, preferably at least 1 h, more preferably at least 3 h.

[053] In embodiments, the tungstate nanodots suspension comprises tungstate nanodots suspended in a dispersion solution, preferably tetrabutylammonium hydroxide (TBAOH) solution. The tungstate nanodots suspension preferably has a concentration of tungstate nanodots of from 0.01 to 5 g/L, preferably from 0.05 to 1 g/L, more preferably from 0.05 to 0.1 g/L. The polydiallyldimethylammonium chloride (PDDA) solution preferably has a concentration of from 0.1 to 2 g/L, preferably from 0.5 to 1.5 g/L, more preferably about 0.8 g/L. In relevant embodiments such as the layer-by-layer method, the substrate is immersed in one or both of the binding polycation solution, or the tungstate nanodots suspension for at least 1 min, preferably at least 3 mins, more preferably at least 5 mins.

[054] The tungstate nanodots can be synthesised or produced by any suitable method or process. The tungstate nanodots are preferably produced by exfoliation of layered tungstate nanocrystals. In some embodiments, the tungstate nanodots are synthesized by exfoliating nanocrystals (NCs) of a layered precursor comprising $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$) with hexagonal tungsten bronze (HTB) $Cs_4W_{11}O_{35}$ structure.

[055] It should be appreciated that functional coating for a glass substrate according to first aspect of the present invention can be formed by a method according to the second aspect of the present invention. Equally, it should be appreciated that the method of the second aspect of the present invention can be used to form a functional coating according to the first aspect of the present invention. Features discussed in relation to the first aspect of the present invention therefore are applicable to the second aspect of the present invention and vice versa.

[056] The functional coating is preferably stable in a broad temperature range from 4 °C up to 550° C, preferably retaining its superhydrophilicity with the water contact angles in the range of 5 to 8° in these temperature ranges.

[057] The functional coated glass preferably retains its superhydrophilicity even under an intensive stirring in water (850 rpm) for more than two days (water contact angle = 7° after stirring), indicative of a firm mechanical combination between the glass and the TNDs.

[058] The functional coating has shown a great long-term stability in a more than 1-year time period. The water contact angles for TND-coated glass have been experimentally found to remain in the range of 6 to 8° after 12 months, preferably after 18 months.

[059] Given the above, the functional coating of the present invention can in embodiments provide a novel ultrathin full-day self-cleaning smart window film that exhibits several clear advantages over the current technologies:

1) The coating/film of the present invention provides a single coating which simultaneously incorporates three important aspects to smart windows, namely: i) Full-day photocatalytic activity; ii) Self-cleaning and anti-fogging induced by superhydrophilicity; and iii) Smart window effect (UV spectrum blockage, visible spectrum transparency, and switchable IR spectrum transmission). In comparison, conventional smart window technology uses different technologies to impart these three individual functions to window panels.

2) Every functionality of the smart window has been improved, that is, full-day air purification performance without addition of extra antimicrobial agent, long-term superhydrophilicity, and switchable IR transmission with excellent visible transparency.

3) Significantly reduced fabrication cost. The film developed in the present invention does not involve any costly chemicals, complex techniques, or expensive apparatus. Moreover, the fabrication process is simple.

BRIEF DESCRIPTION OF THE DRAWINGS

[060] The present invention will now be described with reference to the figures of the accompanying drawings, which illustrate particular preferred embodiments of the present invention, wherein:

[061] Figure 1 provides a schematic of the LBL self-assembly of the monolayered tungstate NDs and the electron storage upon irradiation.

[062] Figure 2 shows a) TEM and b) High-resolution TEM images of the monolayered tungstate NDs. The observed lattice fringes of 0.338 nm corresponded to the (460) plane. c) AFM image of the NDs deposited on a silicon wafer with height profile from point A to point B. d) UV-Visible absorption spectra of (tungstate-PDDA)_n multilayer films on a glass substrate. The inset shows the peak absorbance at ca. 240 nm as a function of number of bilayers. e) Photographs of clean glass and (tungstate-PDDA)₁₀ film deposited on glass.

[063] Figure 3 shows a) Photocurrent versus time measured with (1) (tungstate-PDDA)₁₀ deposited on FTO and (2) bare FTO at 1 V vs Ag/AgCl reference electrode. b) The shift of open-circuit potential (OCP) in response to light on/off for the (tungstate-PDDA)₁₀ electrode. c) The XPS spectrum of W 4f in a (tungstate-PDDA)₁₀ film measured after the film was illuminated in water for 2 h. d) The discharging current profile of the (tungstate-PDDA)₁₀ photoelectrode after 20 mins irradiation in a two-electrode set-up. The inset is a magnified discharging current profile in the first 50 s. Experimental conditions: 300 W Xe lamp, 3wt% NaCl solution (pH=5.0), 1.9 cm² illumination area. Detailed set-up is described in supporting information.

[064] Figure 4 shows a) Concentrations of viable *E. coli* vs. reaction time under dark conditions for the unilluminated film and the photocharged film. b) Concentrations of viable *E. coli* in (1) the initial suspension and after 1 h dark reaction with (2) the unilluminated film, (3) photocharged film, (4) photocharged film in the presence of Fe(II) and (5) photocharged film in the presence of TEMPOL. TEM images of *E. coli* reacted with c) unilluminated film and d) photocharged film for 6 h. e) Schematic of the mechanism of antibacterial process under dark conditions on the (tungstate-PDDA)₁₀ film.

[065] Figure 4A1 shows the XRD pattern of the layered tungstate nanocrystal precursor $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$). The inset is a photograph of the tungstate nanocrystals dried at room temperature.

[066] Figure 4A2 shows TEM image of the monolayered tungstate nanodots. Inset shows the HRTEM image.

[067] Figure 4A3 shows a) UV-Visible absorption spectrum of the monolayered tungstate NDs suspension. Inset is a photograph of the NDs suspension. b) Tauc plot of the monolayered tungstate NDs.

[068] Figure 4A4 shows an XRD pattern of the monolayered tungstate nanodots deposited onto a glass substrate.

[069] Figure 4A5 shows an UV-Visible absorption spectra and photographs of (a) the as-prepared tungstate NDs suspension, (b) the NDs suspension after 10 mins of irradiation, and stored in dark for (c) 3 days and (d) 6 days.

[070] Figure 4A6 shows an XPS spectrum of the (tungstate-PDDA)₁₀ multilayer film.

[071] Figure 4A7 shows an SEM image of (tungstate-PDDA)₁₀ multilayer film on glass substrate.

[072] Figure 4A8 shows AFM image of (tungstate-PDDA)₁₀ multilayer film on glass substrate, and the height profile analysis taken around the white line.

[073] Figure 4A9 shows visible transmittance of clean glass substrate and (tungstate-PDDA)₁₀ multilayer film.

[074] Figure 4A10 shows (a) the shift of OCP in response to light on/off for the P25 photoelectrode; and (b) a photograph of the P25 photoelectrode.

[075] Figure 4A11 shows an XPS spectra of W 4f measured in (a) the as-prepared (tungstate-PDDA)₁₀ film and (b) the illuminated (tungstate-PDDA)₁₀ multilayer film after being stored in air for 1 week.

[076] Figure 4A12 shows a Cyclic voltammogram of the (tungstate-PDDA)₁₀ multilayer electrode (a) measured immediately after the photoelectrode was illuminated for 20 mins and (b) measured 5 mins after the first cycle was finished. The black arrows showed the scanning direction.

[077] Figure 4A13 shows a cyclic voltammogram of a bare FTO substrate. The black arrows showed the scanning direction.

[078] Figure 4A14 shows TEM images of *E. coli* cells reacted with a) unilluminated and b) pre-illuminated multilayer film for 6 h. The red arrow in b) indicates the cells with destroyed cell structure.

[079] Figure 4A15 shows a Mott-Schottky plot of monolayered tungstate nanodots. The potential was measured against an Ag/AgCl reference electrode in a 0.1 M NaH₂PO₄/Na₂HPO₄ solution (pH=7). The red dash line shows the linear fit of the plot.

[080] Figure 5 shows a schematic of the synthesis of CsWO NDs and fabrication of (CsWO-PDDA)₁₀ film for superhydrophilicity.

[081] Figure 6 shows a) TEM image of CsWO NDs, inset shows the HRTEM of CsWO NDs. b) Photograph of (CsWO-PDDA)₁₀ film deposited onto glass substrate). c) AFM image of (CsWO-PDDA)₁₀ film, inset is the height profile scanned across the black line between point A and B. d) Water contact angle change with time of freshly-prepared (CsWO-PDDA)₁₀ film and after being stored in the dark for 28 days.

[082] Figure 7 shows Water contact angle change with time for a) pure PDDA film, b) UV-irradiated (CsWO-PDDA)₁₀ film, c) (RbWO-PDDA)₁₀ film, d) (Ti_{0.91}O₂-PDDA)₁₀ film and e) (MnO₂-PDDA)₁₀ film.

[083] Figure 8 shows a) Water contact angle change with time for (CsWO-PDDA)_n films, n=1-9. b) Optical transmittance in the visible range of (CsWO-PDDA)₁₀ film. c)

Antifogging effect of the (CsWO-PDDA)₁₀ film. The left half of the glass substrate was coated while the right half was bare.

[084] Figure 8A1 shows an XRD pattern of the layered cesium tungstate precursor.

[085] Figure 8A2 provides an AFM image of monolayer CsWO NDs and the height profile scanned along the line between point A and B. Larger thicknesses (ca. 5 nm or higher) are attributed to the overlapping of CsWO NDs.

[086] Figure 8A3 shows a) UV-Visible absorption spectra of (CsWO-PDDA)_n multilayer films on a glass substrate. b) Peak-top absorption at 240 nm as a function of the number of (CsWO-PDDA) bilayers.

[087] Figure 8A4 shows an XPS spectra of (CsWO-PDDA)₁₀ film.

[088] Figure 8A5 provides a top-view SEM image of (CsWO-PDDA)₁₀ film.

[089] Figure 8A6 shows the water contact angle of (CsWO-PDDA)₁₀ film measured after water droplet was applied for 10 s of on different days after the film was prepared. The (CsWO-PDDA)₁₀ film was kept in the dark for 28 days.

[090] Figure 8A7 shows the XRD pattern of layered rubidium tungstate precursor.

[091] Figure 8A8 shows a) TEM and b) High resolution TEM images of RbWO NDs.

[092] Figure 8A9 provides an AFM image of RbWO NDs and height profile scanned along the line between point A and B.

[093] Figure 8A10 provides a) UV-Visible absorption spectra of (RbWO-PDDA)_n multilayer films on a glass substrate. b) Peak-top absorption at 243 nm as a function of the number of (RbWO-PDDA) bilayers.

[094] Figure 8A11 shows an XPS spectrum of (RbWO-PDDA)₁₀ film.

[095] Figure 8A12 shows a top-view SEM image of (RbWO-PDDA)₁₀ film

[096] Figure 8A13 provides an AFM image of (RbWO-PDDA)₁₀ film and height profile scanned along the line between point A and B.

[097] Figure 8A14 shows an XRD pattern of layered cesium titanate precursor.

[098] Figure 8A15 provides a TEM of Ti_{0.91}O₂ NDs.

[099] Figure 8A16 provides an AFM image of monolayer Ti_{0.91}O₂ NDs and height profile scanned along the line between point A and B.

[100] Figure 8A17 shows a) UV-Visible absorption spectra of (Ti_{0.91}O₂-PDDA)_n multilayer films on a glass substrate. b) Peak-top absorption at 270 nm as a function of the number of (Ti_{0.91}O₂-PDDA) bilayers.

[101] Figure 8A18 shows an XPS spectrum of (Ti_{0.91}O₂-PDDA)₁₀ film.

[102] Figure 8A19 provides an AFM image of (Ti_{0.91}O₂-PDDA)₁₀ film and height profile scanned along the line between point A and B.

[103] Figure 8A20 shows a top-view SEM image of (Ti_{0.91}O₂-PDDA)₁₀ film.

[104] Figure 8A21 shows an XRD pattern of layered sodium manganate precursor.

[105] Figure 8A22 provides a TEM image of MnO₂ NDs.

[106] Figure 8A23 shows an AFM image of MnO₂ NDs and height profile scanned along the line between point A and B.

[107] Figure 8A24 shows a) UV-Visible absorption spectra of (MnO₂-PDDA)_n multilayer films on a glass substrate. b) Peak-top absorption at 355 nm as a function of the number of (MnO₂-PDDA) bilayers.

[108] Figure 8A25 provides a XPS spectrum of $(\text{MnO}_2\text{-PDDA})_{10}$ film.

[109] Figure 8A26 shows a top-view SEM image of $(\text{MnO}_2\text{-PDDA})_{10}$.

[110] Figure 8A27 shows an AFM image of $(\text{MnO}_2\text{-PDDA})_{10}$ film and height profile scanned along the line between point A and B.

[111] Figure 8A28 provides top-view SEM images of a) $(\text{CsWO-PDDA})_1$ and b) $(\text{CsWO-PDDA})_5$.

[112] Figure 8A29 provides an AFM image of $(\text{CsWO-PDDA})_5$ film and height profile scanned along the line between point A and B.

[113] Figure 9 provides an SEM image of a tungstate nanodot (TND) multifunctional coating on glass formed by spin coating method.

[114] Figure 10 provides a plot of water contact angle vs time illustrating the stability of the functional coating over time.

[115] Figure 11 provides a plot of water contact angle vs time illustrating the stability of the functional coating when undergoing stirring for 48h.

DETAILED DESCRIPTION

[116] The present invention relates to an ultrathin transparent film produced using tungstate nanodots (NDs) as building blocks on a substrate using a suitable layer application technique. The inventors have surprisingly found that ultrathin transparent film can be produced as monolayered tungstate nanodots (NDs) using for example a low-cost layer-by-layer (LBL) method as illustrated in Figure 1 and/or Figure 5.

[117] The monolayered tungstate nanodots (NDs) can be deposited on a substrate using a number of different techniques including:

- a layer-by-layer (LBL) method, preferably a self-assembly layer-by-layer method;
- spin coating;
- spray coating;

- dip coating;
- electrophoretic deposition;
- chemical vapour deposition; or
- plasma deposition.

[118] One form of the self-assembly layer-by-layer method is described below in Example 1. This technique involves sequentially dipping (dip coating) a substrate such as clean glass into a PDDA solution for a set time, for example 20 mins and then tungstate nanodots (TND) suspension or dispersion for a set time, for example 20 mins to form a layer of tungstate nanodots on the substrate. The desired number of tungstate layers is achieved by repeating the dipping/ dip coating process.

[119] In some embodiments, the tungstate nanodots are applied to the substrate by a spin coating method. In this technique, a small amount of coating material is applied on the center of the substrate. The substrate is then rotated at high speed in order to spread the coating material by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. The higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the viscosity and concentration of the solution and the solvent. For the specific functional tungstate nanodots coating, PDDA solution can be first spin coated on a substrate, such as a clean glass substrate, followed by spin coating of the tungstate nanodots solution. Repeating the steps multiple times, for example at least 3 times, produces superhydrophilic tungstate nanodots coated glass.

[120] In some embodiments, the tungstate nanodots are applied to the substrate by a spray coating method. Spray coating is a rapid method to prepare large-area tungstate nanodots coated glass. Spray coating involves the spraying of a thin coating of material over a substrate from a spray nozzle, through which a pressurized fluid emits. Control of the direction, pressure, spray pattern, temperature and the like allow the thickness of the coating to be controlled. Application involves first spray coating a PDDA dispersion on a substrate, for example a clean glass substrate. Then, a TND dispersion is sprayed on the glass forming a TND film. The thickness of the TND film can be tuned by controlling the time of spraying time.

[121] In some embodiments, TNDs can also be coated on electrically conductive glasses by electrophoretic deposition. In this method, particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto a substrate (an electrode). For the functional coating, in a dispersion of TND, the negatively charged TNDs migrate to the anode (the substrate) and self-assemble into a film. The thickness of the film or the transparency of the coating can be simply by changing the applied voltage and the deposition time.

[122] In some embodiments, the tungstate nanodots are applied to the substrate by a chemical vapour deposition method. In typical chemical vapour deposition, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. For example, tungsten oxide layer can be deposited on glass by chemical vapour deposition using volatile precursors ($W(CO)_6$, WF_6 , $W(OEt)_x$, etc) placed in a sublimator to produce tungsten oxide vapour. The substrate is coated multi-layered tungsten oxide which is deposited on its surface.

[123] In some embodiments, the TNDs are applied to the substrate by plasma deposition. The substrates are first treated by oxygen to produce oxygen vacancies on the surface. Immediately after the plasma treatment, the glass substrate is immersed in TND suspension solution, and a plurality, preferably 3-10 cycles of PDDA/TND adsorption are performed. The resultant glass deposited with multilayer of TNDs.

[124] In some embodiments, the TNDs are applied to the substrate by a deposition method, preferably an electrodeposition process. In this particular embodiment, the tungstate nanodots may be applied or otherwise coated onto a surface of the substrate using an electrodeposition method or technique. Examples of suitable deposition methods include at least one of electrodeposition, electroplating, electrophoretic deposition or electroless deposition.

[125] Electroless deposition or electroless plating uses a redox reaction to deposit metal on a substrate without the passage of an electric current.

[126] In electrophoretic deposition (EPD) the substrate (in this case a conducting substrate) is submerged in a container which holds a coating bath or solution. A directed current is applied through the coating bath using electrodes. The conductive substrate is one of the electrodes, and a set of "counter-electrodes" are used to complete the circuit.

[127] In electrodeposition, the substrate forms the cathode of an electrolysis cell. The electrolysis cell comprises a current source, container including the cathode, an anode immersed in an electrolyte. The TNSs are deposited onto the substrate when an electrical current, electrical potential or any form of electrical modulation is applied through and between the anode and the cathode.

[128] The TND functional coatings deposited by chemical vapour deposition, electrophoretic deposition and plasma deposition are generally stable on substrates under intensive mechanical friction.

[129] A thermal or heat post-treatment is can be used for the TND functional coatings formed by layer-by-layer deposition, spin coating and spray coating. This post-treatment is particularly applicable if these coatings are intended to be used under harsh conditions to enhance the mechanical stability of the TND functional coatings. Heat treatment typically involves heat treatment of the coated substrate at 350 to 550 °C (according to softening points of the glass substrates) for at least 10 mins, preferably at least 1 to 3 h. The resulting functional (TND) coating is firmly anchored on the glass substrate and becomes very stable even under intensive mechanical friction.

[130] The ultrathin transparent film has a number of advantageous properties including:

(A). *Memory photocatalytic activity.* Different from prior TiO_2/CNTs and TiO_2/PdO nanocomposites, the TNDs generate electrons under light irradiation and also store the photogenerated electrons at the tungsten sites of themselves due to the reduction of tungsten elements from W^{6+} to W^{5+} , which simplifies the electron storage process.

The stored electrons can be released in dark forming oxidizing species via the reversible oxidation of W^{5+} to W^{6+} .

(B). *Full-day photocatalytic activities*: The TNDs provide a single-component coating or film which provides photocatalytic antimicrobial effect upon irradiation like TiO_2 , and also store photonic energy in the form of trapped electrons, which can then be used to drive antibacterial reactions in the dark.

[131] *Self-cleaning and anti-fogging induced by superhydrophilicity*: The TND coating of the present invention exhibits superhydrophilicity due to its unique surface chemistry and surface nanostructures. The TND coating/ film can keep its inherent superhydrophilicity properties regardless of the level of light irradiation, which is different to TiO_2 . The hydrophilicity results in the properties of self-cleaning and anti-fogging.

[132] *Smart window effect (UV spectrum blockage, visible spectrum transparency and switchable IR spectrum transmission)*: The tungstate nanodots used in the smart coating of the present invention have no visible absorption due to its large band gap and thus the coated window will show great visible transparency. Moreover, the tungstate nanodots exhibit clear photochromism and associated switchable IR light absorption. In addition, the tungstate nanodots can effectively block UV light owing to excellent absorption in the UV region.

[133] The distinct properties of the tungstate coating of the present invention including excellent transparency, clear photo-response, post-illumination antibacterial effect, low fabrication cost, and the like make it a promising candidate for smart window applications, and in particular full-day-servicing self-cleaning window coatings.

EXAMPLES

EXAMPLE 1 - Constructing Ultrathin Film with “Memory” Photocatalytic Activity from Monolayered Tungstate Nanodots

[134] This example demonstrates that ultrathin transparent film having memory photocatalytic activity can be produced using monolayered tungstate nanodots (NDs) as building blocks via low-cost layer-by-layer (LBL) method as illustrated in Figure 1. Different from prior TiO_2/CNTs and TiO_2/PdO nanocomposites, the tungstate NDs cannot only generate electrons under light irradiation, but also can store the photogenerated electrons at the tungsten sites of themselves due to the reduction of tungsten elements from W^{6+} to W^{5+} , which simplifies the electron storage process. The stored electrons can be released in dark forming oxidizing species via the reversible oxidation of W^{5+} to W^{6+} .

1. Experimental details

[135] *Preparation of monolayered tungstate nanodots*: The monolayered tungstate nanodots were prepared via exfoliation of layered tungstate nanocrystals according to K. Nakamura, Y. Oaki and H. Imai, *J. Am. Chem. Soc.*, 2013, **135**, 4501-4508 the contents of which should be understood to be incorporated into this specification by this reference. In a typical synthesis process of the layered tungstate nanocrystals, 300 mL aqueous solution of 20 mM sodium tungstate (IV) dehydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) and 10 mM caesium carbonate (Cs_2CO_3) was poured into 300 mL 0.1 M hydrochloric acid (HCl) at room temperature. The mixture was aged for 4 days and then the precipitates were collected by centrifuge and dried at room temperature. 1 g of the dried tungstate nanocrystals was then proton-exchanged in 100 mL HCl (1 M) for 3 days. The HCl was refreshed every 24 hours. After proton-exchange, the tungstate nanocrystals were washed with copious water and dried at room temperature. Then 1g of the proton-exchanged tungstate nanocrystals were dispersed in 250 mL tetrabutylammonium hydroxide (TBAOH) solution (7.05×10^{-3} wt%) and stirred for over 10 days. The as-prepared monolayered tungstate nanodots suspension has a concentration of ca. 1 g/L.

[136] *Lay-by-layer assembly of tungstate nanodots*: Before the layer-by-layer assembly, all substrates were immersed into 0.1 M HCl, acetone, ethanol and H_2O and sonicated for 20 mins respectively. The substrates were dried by an air blow gun before being dipped into polydiallyldimethylammonium chloride (PDPA) solution (20 g/L) for 20 mins. Then the substrates were cleaned with copious water and dried by an air blow gun, after which the substrates were dipped into the monolayered

tungstate nanodots suspension (0.08 g/L) for 20 mins. The dipping processes were then repeated until the number of desired (tungstate-PDDA) bilayers was achieved.

[137] *Photoelectrochemical test*: All photoelectrochemical tests were conducted in a quartz cell using a CH instruments 660E electrochemical workstation. The light source is a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV). In a three-electrode set-up, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. In the electrochemical discharging process, a two-electrode set-up was used with Pt as both the counter electrode and reference electrode.

[138] *Characterisation*: The as-prepared samples were characterized by X-ray diffraction (XRD, Rigaku Miniflex), UV-Vis spectrometer (Shimadzu UV-2600), X-ray photoelectron spectroscopy (AXIS Ultra DLD, Kratos Analytical Inc., Manchester, UK), transmission electron microscopy (TEM, FEI Tecnai G2 T20), scanning electron microscopy (SEM, FEI Nova NanoSEM 450), atomic force microscope (AFM, Bruker Dimension Icon), Zeta potential (Malvern Instruments, Nano ZS Zetasizer).

[139] *Antibacterial test in dark condition*: *E. coli* O1:K1:H7 (ATCC 11775), as an indicator for bacteria contamination, was inoculated in Luria Bertani (LB) medium and cultured at 37 °C in a shaking water bath until the culture reached optical density of 0.5 at 600 nm. To prepare the bacterial suspension, *E. coli* cells were harvested by centrifugation, washed, and then diluted with sterile phosphate saline buffer solution (PBS, pH 7, 0.1mol L⁻¹). The bactericidal activity was investigated by the drop test method with some modification as outlined in T. Tatsuma, S. Takeda, S. Saitoh, Y. Ohko and A. Fujishima, *Electrochem. Commun.*, 2003, 5, 793-796 and I. Y. Kim, S. Park, H. Kim, S. Park, R. S. Ruoff and S. J. Hwang, *Adv. Funct. Mater.*, 2014, **24**, 2288-2294 the contents of which should be understood to be incorporated into this specification by this reference. A 20 µL aliquot of *E. coli* suspension (10⁵ cells·mL⁻¹) was dropped onto the charged or discharged film surface. For each film, four independent replicates were done. After the exposure of the film for certain time at room temperature, the *E. coli* suspension was collected by thoroughly flushing it to centrifuge with 2 mL PBS buffer. 100 µL of the diluted suspension was then

transferred onto a LB medium plate and incubated for 18 h at 37 °C. Survival ratio of *E. coli* was evaluated on the basis of the number of colonies formed.

[140] For TEM imaging of *E. coli* cells, 0.5 ml of *E. coli* suspension (~10⁹ CFU/ml) was dropped onto the unilluminated and illuminated films. After 6 h, the cell pellets were washed off from the films by 2 ml buffer solution and then collected by centrifugation (8000 rpm, 10 min). The detailed procedure to prepare the *E. coli* samples for TEM is described in X. K. Zeng, D. T. McCarthy, A. Deletic and X. W. Zhang, *Adv. Funct. Mater.*, 2015, **25**, 4344-4351, the contents of which should be understood to be incorporated into this specification by this reference.

Discussion of Results

[141] The monolayered tungstate NDs were synthesized via exfoliating nanocrystals (NCs) of a layered precursor $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$) with hexagonal tungsten bronze (HTB) $Cs_4W_{11}O_{35}$ structure (see Figure 4A1, 4A2). The as-prepared NDs possessed small lateral sizes of 5-20 nm (Figure 2a, 2b) and thickness (Figure 2c) close to $Cs_4W_{11}O_{35}$ -phase tungstate monolayer (2.5 nm), which led to an absorption edge at 335 nm and band gap of 3.42 eV (Figure 4A3) owing to quantum size effect. Successful exfoliation also caused the disappearance of XRD peaks of the monolayered tungstate NDs (Figure 4A4), due to the loss of the 3D crystallographic characteristic of the tungstate precursor. Zeta potential measurements demonstrated that the monolayered tungstate NDs carry negative charge of -45 mV, which implies the possibility of carrying out LBL self-assembly with the monolayered tungstate NDs. More importantly, photochromic phenomenon with reversible colour change between light green and deep blue in response to UV irradiation on/off (Figure 4A5, suggested the photoinduced electron storing as reduced W^{15} and potential reduction power via freeing electrons in the dark).

[142] Photochromism and negative surface charge of the monolayered tungstate NDs inspire us to conduct LBL self-assembly using polydiallyldimethylammonium chloride (PDPA) as the binding polycation. Figure 2d showed the UV-Visible absorption spectra of (tungstate-PDPA)_n multilayer film with different number of tungstate-PDPA bilayers (n), and the peak absorbance at ca. 240 nm increase nearly linearly with n, suggesting the successful multiple layer growth of the NDs. XPS

spectrum of (tungstate-PDDA)_n multilayer film also confirmed the existence of W and Cs elements (Figure 4A6). The (tungstate-PDDA)₁₀ multilayer film has a rough surface (surface roughness Ra of ca. 5.15 nm, R_{RMS} of 5.66 nm), as shown in its top view scanning electron microscopy (SEM) image (Figure 4A7) and atomic force microscopy (AFM) image (Figure 4A8). As a result of its extraordinarily small thickness (less than 30 nm), the (tungstate-PDDA)₁₀ multilayer film exhibited excellent transparency (Figure 2e, 4A9), with little difference between the clean glass substrate and the one coated with multilayer film, which is critically important in some practical applications of photocatalysts such as self-cleaning glass coatings.

[143] To understand the fundamental mechanisms of the electron storage/release processes of the (tungstate-PDDA)₁₀ film, photoelectrochemical and electrochemical tests were performed on conductive fluorine-doped tin oxide (FTO) substrates coated with multilayer film. The (tungstate-PDDA)₁₀ photoelectrode showed clear n-type photoresponse (Figure 3a), with quick downshift of open circuit potential from +0.88 V to +0.25 V vs. Ag/AgCl upon irradiation (Figure 3b) due to electron accumulation in the conduction band of n-type semiconductors. However, after the irradiation ceased, unlike TiO₂ (P25) whose downshifted potential rapidly recovered (Figure 4A10), the potential of tungstate electrode increased slightly to +0.28 V vs. Ag/AgCl and was kept for a relatively long time (> 1000 s). This phenomenon indicates the stabilization of accumulated electrons in the tungstate presumably due to partial reduction of W elements.

[144] To verify the formation of reduced tungsten species, X-ray photoelectron spectroscopy (XPS) analysis was conducted. Only a single doublet at 37.9 eV and 35.8 eV corresponding to W⁶⁺ can be observed in the XPS spectrum of W 4f in the as-prepared film (Figure 4A11a). After exposure of the multilayer film to illumination, an extra doublet of W 4f corresponding to W⁵⁺ at 36.6 eV and 34.5 eV appeared (Figure 3c), implying the partial reduction of W preferentially near the oxygen vacancy sites. Therefore, during the illumination of the multilayer photoelectrode, the photoinduced electrons were trapped at the tungsten sites and essentially reduced the tungsten elements. Similar electron trapping process in WO₃ based systems was reported to be accompanied by intercalation of protons or alkali ions at the perovskite sites, which were often termed as “photocharging”. Prolonged exposure of the

photocharged multilayer film to air (>12 hrs) caused the potential returning to about the original value, which was possibly due to the consumption of electrons by ambient oxygen. The relaxation of the photoelectrode potential was accompanied by the change of oxidation state of the tungsten elements. W 4f doublet corresponding to W^{5+} disappeared in the XPS spectrum of multilayer film that was stored in air for a week (Figure 4A11b), indicating that the reduced tungsten elements were re-oxidized to the original state in air at the electron releasing stage. Moreover, in the cyclic voltammogram (CV) of (tungstate-PDDA)₁₀ multilayer photoelectrode measured immediately after 20 mins of photocharging (Figure 4A12a), an anodic peak at ca. -0.91 V (vs. Ag/AgCl) was observed, which was associated with the oxidation of W^{5+} to W^{6+} .^{19, 21} This anodic peak disappeared in the second CV scan cycle (Figure 4A12b), presumably due to absence of W^{5+} . The change in the W 4f XPS spectra and CV of the (tungstate-PDDA)₁₀ multilayer film agreed well with the observations from the potential shifts, indicating that the electron storage-discharge was realized via the reduction-oxidation of tungsten elements in the tungstate NDs. Such a “photocharging-discharging” phenomenon represents the capability of solar energy storage of the multilayer tungstate film. The photocharging capacity of (tungstate-PDDA)₁₀ film measured by electrochemical discharging (Figure 3d) was $1.01 \cdot 10^{-4}$ C/cm² after 20 mins of irradiation.

[145] To demonstrate whether the stored electrons in the tungstate can be used for catalytic applications, we performed antibacterial tests under dark conditions. Before use, the (tungstate-PDDA)₁₀ multilayer film on glass substrate was pre-irradiated by a Xe lamp for 2 h; then an *Escherichia coli* (*E. coli*) suspension (ATCC 11775) was applied to the film and the setup was kept under dark conditions. As shown in Figure 4a, although the concentration of viable *E. coli* exhibited certain drop in 6 h when reacted with the unilluminated film due to the natural death of *E. coli* cells at ambient conditions, apparently lower concentrations of viable *E. coli* were observed at all times if the film was photocharged. To better understand the inactivation of bacterial cells by the photocharged film, the morphology of *E. coli* cells was identified by TEM. While cells treated by the unilluminated film showed unanimous electron density, suggestive of their intact structure without environment disturbance (Figure 4c, 4A14a), remarkable electron-light regions appeared on the edge of the cells treated by the photocharged film (Figure 4d, 4A14b). Moreover, missing cytoplasm and big

gap between the cytoplasm membrane and the cell wall were observed in some cells, indicating the damage to cytoplasmic membrane and the cell wall. These results prove that the photocharged film possesses a post-illumination “memory” catalytic antibacterial activity.

[146] In the photocharged multilayer film, superoxide ($\cdot\text{O}_2^-$) and peroxide (H_2O_2) species with bactericidal effects can potentially be formed via the reduction of the oxygen molecules in the surrounding air by the stored electrons in one-electron and two-electron reactions ($\text{O}_2 + \text{e}^- \rightarrow \cdot\text{O}_2^-$, $\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$) in the dark, respectively.²³ Based on the calculations from the Mott-Schottky plot (Figure 4A15), the flat band potential of the monolayered tungstate NDs is -0.51 V vs. NHE, which is more negative than both O_2/O_2^- (-0.284 vs. NHE) and $\text{O}_2/\text{H}_2\text{O}_2$ (+0.682 V vs. NHE).^{24, 25} This demonstrates that the electrons stored in the monolayered tungstate NDs can reduce O_2 to form both O_2^- and H_2O_2 . In addition, in order to investigate which species is responsible for the antibacterial activities of the photocharged multilayer film under dark conditions, we exploited Fe(II) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) as scavengers for peroxide and superoxide species, respectively. As shown in Figure 4b, the addition of Fe(II) to the system did not affect the concentration of viable *E. coli*, indicating that the peroxide species did not play major role in the bactericidal process in the dark. On the contrary, the addition of TEMPOL decreased the activity significantly to almost the level of the un-illuminated film, unveiling the fact that superoxide species were responsible for the inactivation of *E. coli* at the post-illumination stage. Although from a thermodynamic point of view the generation of peroxide is more favourable than superoxide generation, the one-electron reaction of superoxide generation is faster in kinetics than the two-electron process of peroxide generation. In addition, the peroxide is highly likely produced via reduction of superoxide or further reaction of superoxides ($\text{H}_2\text{O} + \cdot\text{O}_2^- \rightarrow \cdot\text{OOH} + \text{OH}^-$, $2\cdot\text{OOH} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$). The superoxides might have been consumed before they are converted into hydrogen peroxides, so that superoxides are the major species for the inactivation of *E. coli*. XTT (2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide) was used to detect the generation of superoxide species as superoxide can reduce XTT to XTT-formazan with a characteristic absorption peak at 470 nm, but we failed to detect XTT-formazan by UV-Visible absorption spectroscopy after XTT solution (1 mM) reacted with a photocharged (tungstate-PDDA)₁₀ multilayer film. This

indicates that the concentration of superoxides generated is lower than the detection limit. The reason might be that only small amount of electrons are trapped in the ultrathin film. The overall mechanism of the catalytic antibacterial reaction of the tungstate nanodot ultrathin film in the dark is demonstrated in Figure 4e.

[147] Additionally, Figure 4A1 shows the XRD pattern of the layered tungstate nanocrystal precursor $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$). The inset is a photograph of the tungstate nanocrystals dried at room temperature.

[148] Figure 4A2 shows TEM image of the layered tungstate nanocrystals $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$). Inset shows the HRTEM image of a layered tungstate nanocrystal. The observed lattice fringes of 0.194 nm in the High resolution TEM (HRTEM) image of tungstate nanocrystals corresponded to the (004) plane of tungstate (inset of Figure 4A2).

[149] Figure 4A3 shows a) UV-Visible absorption spectrum of the monolayered tungstate NDs suspension. Inset is a photograph of the NDs suspension. b) Tauc plot of the monolayered tungstate NDs.

[150] Figure 4A4 shows an XRD pattern of the monolayered tungstate nanodots deposited onto a glass substrate.

[151] Figure 4A5 shows an UV-Visible absorption spectra and photographs of (a) the as-prepared tungstate NDs suspension, (b) the NDs suspension after 10 mins of irradiation, and stored in dark for (c) 3 days and (d) 6 days. The as-prepared monolayered tungstate NDs showed obvious photochromic phenomenon. The colour of NDs colloidal suspension quickly turned from light greenish to deep blue within 10 mins of UV irradiation, and then gradually shifted back to initial state under dark condition in a week. The reversible coloration/bleaching was repeated over three times to verify the photochromism effect of the NDs.

[152] Figure 4A6 shows an XPS spectrum of the (tungstate-PDDA)₁₀ multilayer film.

[153] Figure 4A7 shows an SEM image of (tungstate-PDDA)₁₀ multilayer film on glass substrate.

[154] Figure 4A8 shows AFM image of (tungstate-PDDA)₁₀ multilayer film on glass substrate, and the height profile analysis taken around the white line.

[155] Figure 4A9 shows Visible transmittance of clean glass substrate and (tungstate-PDDA)₁₀ multilayer film.

[156] Figure 4A10 shows the shift of OCP in response to light on/off for the P25 photoelectrode. Inset is a photograph of the P25 photoelectrode. Experimental condition: a 300 W Xe lamp was used as the light source, and 3wt% NaCl solution (pH=5.0) was chosen as the electrolyte. A total surface area of 1.9 cm² of the photoelectrode was illuminated during the measurement. Generally, when an n-type semiconductor is exposed to irradiation, the photogenerated holes are consumed by the surface absorbed water molecules while the photogenerated electrons accumulate in the conduction band, causing the downshift of potential. However, the accumulated electrons are not stable and often decay very quickly once the illumination is stopped.

[157] Figure 4A11 shows an XPS spectra of W 4f measured in (a) the as-prepared (tungstate-PDDA)₁₀ film and (b) the illuminated (tungstate-PDDA)₁₀ multilayer film after being stored in air for 1 week.

[158] Figure 4A12 shows a Cyclic voltammogram of the (tungstate-PDDA)₁₀ multilayer electrode (a) measured immediately after the photoelectrode was illuminated for 20 mins and (b) measured 5 mins after the first cycle was finished. The black arrows showed the scanning direction. Measurement condition: 0.5 M Na₂SO₄ solution (pH=5.7) was used as the electrolyte, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. During the whole measuring process, a total area of 2 cm² of the electrode was illuminated by the Xe lamp.

[159] In the cyclic voltammogram (CV) of (tungstate-PDDA)₁₀ photoelectrode measured immediately after 20 mins of photocharging (Figure 4A11a), an anodic peak at ca. -0.91 V vs. Ag/AgCl associated with the oxidation of W⁵⁺ to W⁶⁺ was observed, which disappeared in the second scan cycle (Figure 4A12b), presumably due to absence of W⁵⁺. It should be noted that the anodic peak at -0.68 V and the cathodic peak at -0.6 V were not assigned to the (tungstate-PDDA)₁₀ multilayer film. As shown in Figure 4A13, in the cyclic voltammogram of a bare FTO substrate, those two peaks also appeared.

[160] Figure 4A13 shows a cyclic voltammogram of a bare FTO substrate. The black arrows showed the scanning direction. Measurement condition: 0.5 M Na₂SO₄ solution (pH=5.7) was used as the electrolyte, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. During the whole measuring process, a total area of 2 cm² of the electrode was illuminated by the Xe lamp.

[161] Figure 4A14 shows TEM images of *E. coli* cells reacted with a) unilluminated and b) pre-illuminated multilayer film for 6 h. The red arrow in b) indicates the cells with destroyed cell structure. For some cells, a remarkable electron-light region occurs on the edge, and in other cells, missing cytoplasm and big gap between the cytoplasm membrane and the cell wall can be clearly seen.

[162] Figure 4A15 shows a Mott-Schottky plot of monolayered tungstate nanodots. The potential was measured against an Ag/AgCl reference electrode in a 0.1 M NaH₂PO₄/Na₂HPO₄ solution (pH=7). The red dash line shows the linear fit of the plot. Mott-Schottky equation is:

$$\frac{1}{C^2} = \frac{2}{e_0 \epsilon \epsilon_0 N_d} \left(V - V_{FB} - \frac{kT}{e_0} \right)$$

Where C is the interfacial capacitance, e₀ is electron charge, ε is the permittivity of vacuum, ε₀ is the dielectric constant, N_d is the dopant density, V is the applied potential, V_{FB} is the flat band potential, k is the Boltzmann's constant and T is the absolute temperature.

[163] The flat band potential of monolayered tungstate nanodots can be determined by extrapolating the linear fit of the Mott-Schottky plot to the horizontal axis intercept. The flat band potential was calculated to be -1.12 V vs. Ag/AgCl at pH=7. To convert the obtained flat band potential vs. Ag/AgCl to it vs. RHE (NHE at pH=0), the following equation is used:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}^0 (E_{Ag/AgCl}^0 = +0.199V)$$

[164] The converted NHE flat band potential is -0.51 V vs. NHE, which is more negative than both O_2/O_2^- (-0.284 vs. NHE) and O_2/H_2O_2 (+0.682 V vs. NHE). This indicated the fact that the electrons stored in the monolayered tungstate NDs can reduce O_2 to form both O_2^- and H_2O_2 .

Conclusion

[165] This example demonstrated that a transparent ultrathin film with post-illumination photocatalytic properties can be easily fabricated using monolayered tungstate NDs as building block via layer-by-layer self-assembly. The as-fabricated film exhibited n-type semiconducting photoresponse upon illumination, and also effectively stored the photogenerated electrons at the tungsten sites via reduction of tungsten elements. The stored electrons can reduce oxygen to form superoxide species, which endowed the photocharged multilayer film with catalytic bactericidal reactions after the illumination was ceased. The distinct properties of the tungstate multilayer film including phenomenal transparency, clear photoresponse, post-illumination antibacterial effect, low fabrication cost, etc. make it a promising candidate for full-day-servicing self-cleaning window coatings.

EXAMPLE 2 - Design of 2D nanomaterial for transparent film with light-free sustainable superhydrophilicity

[166] The interaction at the water-solid interface will certainly play a crucial role in the surface wetting properties and fundamentally determines the hydrophilicity/hydrophobicity. Surface hydrophilicity/hydrophobicity is a very important factor for many applications, and superhydrophilicity with contact angle of below 10° is often desirable. Although wetting properties of a surface is fundamentally determined by surface chemistry (surface energy) and geometric microstructure, traditional techniques to obtain superhydrophilic surfaces mainly focused on creating

micro-patterns to introduce roughness. Alternatively, plasma treatment has been used to alter the surface energy by grafting hydrophilic functional groups such as hydroxyl groups, but the superhydrophilicity of plasma-treated surfaces generally is not long-lasting. In addition, the surfaces of some semiconductors such as TiO_2 , ZnO can be endowed with superhydrophilicity after light irradiation as the photoexcitation creates surface oxygen vacancies, but the semiconductor surfaces will gradually become less hydrophilic in air. Therefore, to obtain sustainable superhydrophilic surfaces, a material with highly intrinsic hydrophilicity is required.

[167] This example reports the fabrication of a transparent film with long-term superhydrophilicity using extremely hydrophilic 2D tungstate nanodots. The ultrathin tungstate film not only possesses extraordinary optical transparency, but more importantly, shows long-term superhydrophilicity without any UV irradiation or other external stimuli.

Experimental

[168] *Synthesis of exfoliated cesium tungstate (CsWO) nanodots:* 400 mL of HCl solution (0.1 M) was slowly poured into 400 mL solution of Na_2WO_4 (20 mM) and Cs_2CO_3 (10 mM). After 2 days, the product were collected via centrifuge and dried at room temperature. The dried cesium tungstate nanocrystals were then ground to fine powders, dispersed in HCl solution (1 M) and stirred for 3 continuous days. The protonized cesium tungstate was subsequently collected and washed with copious deionised water before being stirred in tetrabutylammonium hydroxide (TBAOH) solution for 10 days. The ratio of TBA^+ to H^+ was set to be 0.075. The as-obtained exfoliated cesium tungstate nanodots were then centrifuged at 10,000 rpm to remove most of the unexfoliated tungstate.

[169] *Synthesis of exfoliated rubidium tungstate (RbWO) nanodots:* The exfoliated rubidium tungstate nanodots were synthesized in a similar way to the synthesis of exfoliated cesium tungstate nanodots except that the starting materials was Rb_2CO_3 instead of Cs_2CO_3 .

[170] *Synthesis of exfoliated titanium oxide nanodots:* Exfoliated titanium oxide nanodots were synthesized via a modified method. A mixture of Cs_2CO_3 (7.694 g)

and TiO_2 (10 g) powders were calcined at 760°C for 12 h to obtain the layered titanate precursor $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$. $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ powders were then proton-exchanged in hydrochloric acid (1 M) for 3 days, washed with copious deionised (DI) water and dried at 50°C . The protonated titanate $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4 \cdot \text{H}_2\text{O}$ was stirred in TBAOH solution for 7 days and subsequently sonicated with a sonication probe for 12 h in an ice bath. The ratio of TBA^+ to H^+ was set to be 1. The obtained *cesium tungstate* nanodots suspension was then centrifuged at 10000 rpm to remove unexfoliated titanate.

[171] *Synthesis of exfoliated manganese oxide nanodots*: 200 mL solution containing 0.6 M NaOH and 2 M H_2O_2 was slowly transferred to 100 mL $\text{Mn}(\text{NO}_3)_2$ solution (0.3 M) under vigorous stirring. After stirring for 30 mins, the sodium manganate was collected via filtration, washed with copious DI water and dried at room temperature. 1.65 g of sodium manganate was stirring in 330 mL HCl solution (0.1 M) for 5 continuous days and the HCl solution were refreshed every 24 hrs. Protonated manganate was collected via centrifugation, washed with copious DI water and dried at room temperature. 1.15 g of protonated manganate was subsequently dispersed in 400 mL TBAOH solution and stirred for 5 days. The ratio of TBA^+ to H^+ was set to be 5. After stirring, the suspension was sonicated with a sonication probe for 12 h in an ice bath. The obtained nanodots suspension was then centrifuged at 10000 rpm to remove unexfoliated manganate.

[172] *Fabrication of multilayer ultrathin films*: Glass substrates (50 mm*50 mm) were first cleaned via being sonicated in HCl (0.1 M), acetone, ethanol and DI water for 10 mins each. The clean glass substrates were then alternately immersed in PDPA solution (0.8 g/L) and nanodots suspension. The glass substrates were cleaned by DI water and dried by an air gun after each deposition cycle.

Results Discussion

[173] The ultrathin superhydrophilic film is fabricated from monolayer cesium tungstate (CsWO) nanodots (NDs), as shown in Figure 5. To synthesize the CsWO NDs, a layered precursor of cesium tungstate nanocrystals with a hexagonal tungsten bronze (HTB) $\text{Cs}_4\text{W}_{11}\text{O}_{35}$ structure (Figure 8A1) were first protonated. Individual slabs of the layered $\text{Cs}_4\text{W}_{11}\text{O}_{35}$ -phase precursor are composed of corner-sharing WO_6

octahedra, which form hexagonal channels filled by 75% of all Cs^+ ions. The remaining 25% of Cs^+ ions occupy the interlayer spaces, which were replaced with H^+ in the protonation process. The protonated precursor was subsequently exfoliated into individual layers (CsWO NDs) via soft chemistry method, and so a portion of the H^+ will be bound to the surface of CsWO NDs. The surface H^+ at the surface of CsWO NDs will act as hydrophilic sites, and thus the CsWO NDs became extremely hydrophilic. The highly hydrophilic CsWO NDs were used as the building unit to fabricate an ultrathin film with a multilayer structure on glass substrates via a simple layer-by-layer (LBL) method using polydiallyldimethylammonium chloride (PDDA) as the binding agent. Due to the hydrophilic nature of CsWO NDs, the multilayer film showed impressively long-term superhydrophilicity even without being exposed to UV irradiation.

[174] The CsWO NDs possess lateral sizes of 5-20 nm, as can be seen from the transmission electron microscopy (TEM) image (Figure 6a). The clear lattice fringe of 0.34 nm observed in the high-resolution TEM image (inset of Figure 6a) corresponds well to the (460) plane of CsWO slabs. The monolayer nature of CsWO NDs was confirmed by atomic force microscopy (AFM). As shown Figure 8A2, the thickness detected from AFM of CsWO NDs was around 2.8 nm, which is slightly larger than the theoretical thickness of a single tungstate slab (2.5 nm) due to the absorption of PDDA, TBA, H_2O etc. Zeta potential measurement depicted that the CsWO NDs carried a negative surface charge of -45 mV, which is a prerequisite for LBL self-assembly. A multilayer CsWO NDs film $((\text{CsWO-PDDA})_{10})$ is fabricated via the LBL self-assembly method using a positively charged polyelectrolyte PDDA as the binding agent. The $((\text{CsWO-PDDA})_{10})$ film is extremely optically transparent (Figure 6b). As shown in Figure S3, the peak-top absorption peak at 240 nm of $((\text{CsWO-PDDA})_n)$ ($n=1-10$) film showed a nearly linear increment with the increase of $((\text{CsWO-PDDA})_n)$ bilayers in the UV-Visible absorption spectra, indicating the successful formation of multilayer structure. XPS analysis was also implemented to confirm the existence of Cs, W and O elements and consequently the successful deposition of CsWO NDs, as shown in Figure 8A4. AFM revealed that the $((\text{CsWO-PDDA})_{10})$ multilayer film possess a rather rough surface (surface roughness $R_{\text{RMS}}= 5.3$ nm) with large amount of nanosized vertical channels between CsWO NDs (Figure 6c). In the multilayer film, CsWO NDs stacked upon each other, forming numerous tiny "islands", and the inter-island spaces

are essentially 3-dimensional channels. Top-view SEM image of the (CsWO-PDDA)₁₀ film also verified its structure (Figure 8A5). To demonstrate the superhydrophilicity of the as-prepared (CsWO-PDDA)₁₀ film, water contact angle was tested. As shown in Figure 6d, after the water droplet was applied to the surface of a freshly prepared (CsWO-PDDA)₁₀ film, the water contact angle quickly dropped below 10 degree (within <0.5 s). More importantly, the superhydrophilicity was still maintained even after the freshly prepared film was stored under dark condition for 28 day (Figure 6d, Figure 8A6), proving the light-free long-term superhydrophilicity of (CsWO-PDDA)₁₀ film.

[175] Even though some works have been reported to modify graphene to obtain surfaces with superhydrophilicity/superhydrophobicity, there is barely any study of transition metal oxide semiconductor NSs for superwetting purposes, not to mention light-free superhydrophilicity for extended time. The (CsWO-PDDA)₁₀ film reported in this work exhibited phenomenal sustainable superhydrophilicity without any irradiation owing to the highly hydrophilic nature of CsWO NDs. However, since the (CsWO-PDDA)₁₀ film also contains PDDA, which is a hydrophilic polymer, comparison experiments were carried out. As shown Figure 7a, pure PDDA film does not possess superhydrophilicity. Moreover, when the as-prepared (CsWO-PDDA)₁₀ film were irradiated by UV light for over 3 days to remove PDDA, the superhydrophilicity was not only retained but also further improved (Figure 7b). It has to be noted that the UV-irradiated (CsWO-PDDA)₁₀ film was kept in air under dark conditions for 1 month before being tested for water contact angle to rule out the possibility of photocatalysis induced superhydrophilicity. Therefore, the superhydrophilicity originates from the hydrophilic nature of CsWO NDs. We have carried out calculations to illustrate the interfacial interaction at the surface of NDs in contact with water.

[176] Theoretical calculations have shown that the surface chemistry of CsWO NDs plays a major role in determining the superhydrophilicity of the (CsWO-PDDA)₁₀ film. To further demonstrate the importance of the CsWO NDs molecular structure, we fabricated a multilayer film with monolayer rubidium tungstate (RbWO) NDs. The RbWO NDs were synthesized using rubidium tungstate precursors with HTB structure (Figure 8A7), and therefore RbWO NDs have very similar molecular structure to that of the CsWO NDs except that the hexagonal channels are filled with Rb⁺ ions. The

RbWO NDs have lateral sizes of 5-30 nm as shown in the TEM image (Figure 8A8). The thickness of RbWO NDs determined by AFM was around 2.88 nm (Figure 8A9), verifying the monolayer nature as the crystallographic thickness of the tungstate host layer is 2.5 nm. The (RbWO-PDDA)₁₀ film was successfully prepared via LBL method, as confirmed by UV-Vis absorption spectrum and XPS (Figure 8A10, Figure 8A11). The as-prepared (RbWO-PDDA)₁₀ film not only possessed a similar rough structure ($R_{\text{RMS}} = 6.89$ nm) with numerous “islands” as confirmed by SEM and AFM (Figure 8A12, Figure 8A13), but more importantly, also exhibited superhydrophilicity, as shown in Figure 7c. Besides RbWO NDs, titanium oxide ($\text{Ti}_{0.91}\text{O}_2$) NDs and manganese oxide (MnO_2) NDs with entirely different surface chemistry were also used to construct multilayer films. $\text{Ti}_{0.91}\text{O}_2$ NDs were synthesized via exfoliating a lepidocrocite-type parental titanate (Figure 8A14), $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$. The lateral sizes of $\text{Ti}_{0.91}\text{O}_2$ NDs are 10-40 nm, as shown in the TEM image (Figure 8A15). The theoretical thickness of monolayer $\text{Ti}_{0.91}\text{O}_2$ NDs is 0.77 nm despite the thickness obtained in AFM (Figure 8A16) was larger (around 1.7 nm) because of absorption of PDDA, TBA, H_2O , etc. In the monolayer $\text{Ti}_{0.91}\text{O}_2$ NDs, edge-sharing TiO_6 octahedra at two different heights along y axis form a corrugated 2D structure, as shown in the inset of Figure 7d. ($\text{Ti}_{0.91}\text{O}_2$ -PDDA)₁₀ film was also successfully prepared (Figure 8A17, Figure 8A18), which exhibited a rough surface ($R_{\text{RMS}} = 2$ nm) with the same “multi-island” structure, as shown in its AFM and SEM image (Figure 8A19, Figure 8A20). Similar to $\text{Ti}_{0.91}\text{O}_2$ NDs, MnO_2 NDs were prepared starting from a birnessite-type manganate precursor NaMnO_2 (Figure 8A21). MnO_2 NDs possess small sizes of 5-40 nm as shown in the TEM (Figure 8A22), and the AFM image confirmed the monolayer nature (Figure 8A23). The thickness of MnO_2 NDs detected by AFM is ca. 1.7 nm, slightly larger than the previously reported value presumable due to the absorption of PDDA. After the fabrication of (MnO_2 -PDDA)₁₀ film via LBL method (Figure 8A24, Figure 8A25), its “multi-island” structure was also revealed by SEM and AFM (Figure 8A26, Figure 8A27). As shown in Figure 8e to 8f, neither ($\text{Ti}_{0.91}\text{O}_2$ -PDDA)₁₀ nor (MnO_2 -PDDA)₁₀ films was conferred with superhydrophilicity (Figure 7d and e).

[177] Besides the significant importance of the surface chemistry of CsWO NDs, it is also noted that the formation of multilayer film structure facilitates the superhydrophilicity of (CsWO-PDDA)₁₀ film. As shown in Figure 9a, with increasing

number of CsWO NDs layers, the hydrophilicity of the multilayer film was gradually improved. When the number of (CsWO-PDDA) bilayers goes above 3, a superhydrophilic surface can be achieved. As discussed above, the (CsWO-PDDA)₁₀ film has a rough surface with numerous “islands” and vertical channels between individual “islands”. The inter-island channels are essentially water pathway, providing more contact area between water molecules and CsWO NDs surface. As shown in Figure 8A28 and Figure 8A29, with the increase of deposition layers, the surface became more rough (R_{RMS} increased from 1.07 nm of 1 layer to 2.93 nm of 5 layers) and the vertical channels between CsWO NDs became longer (The AFM image of (CsWO-PDDA)₁ film was shown in Figure 8A2). The increased surface roughness and water pathway will inevitably promote the hydrophilicity. However, a possible 3D capillary effect of the vertical channels is very minor since merely three layers of CsWO NDs can create a superhydrophilic surface.

[178] Owing to the superhydrophilicity of (CsWO-PDDA)₁₀ film, the film showed antifogging properties. As shown in Figure 8c, the two halves of a piece of glass half-coated with (CsWO-PDDA)₁₀ film on the right side exhibited distinctly different fogging properties when exposed to water vapour. In addition, due to the extremely small lateral sizes and thicknesses of CsWO NDs, the (CsWO-PDDA)₁₀ film is nearly 100% optically transparent in the visible range (Figure 8b).

Conclusion

[179] This example demonstrates that through careful design of the structure of 2D tungstate nanomaterials, an ultrathin transparent film with long-term superhydrophilicity can be easily fabricated using 2D monolayer CsWO and RbWO NDs. The ultrathin film is extremely transparent in the visible range due to the small lateral size and thickness of CsWO and RbWO NDs. More importantly, the unique molecular structure associated with the CsWO and RbWO NDs results in the impressively sustainable superhydrophilicity without the need of UV irradiation.

EXAMPLE 3 – Other Fabrication Methods

[180] The fabrication of a highly transparent (>95% transparency over the visible light range) and superhydrophilic (water contact angle low than 10°) tungstate nanodot (TND) multifunctional coating on glass can be achieved by various methods,

including layer-by-layer deposition, spin-coating, spray coating, electrophoretic deposition, chemical vapour deposition, plasma deposition etc. The following provides examples of different methods of obtaining this product:

3.1 Layer-by-layer deposition

[181] Layer-by-layer deposition is used to deposit TNDs on glass with a precisely controlled layer number. By sequentially dipping a clean glass (washed by 0.1 M HCl, acetone, ethanol and water) into 20 g/L PDDA solution for 20 mins and then 0.1 g/L TND suspension for 20 mins, a layer of TND is coated on glass. The desired number of TND layers is achieved by repeating the dipping process. After coating of more than 3 TND layers, the water contact angle of the glass decreases to less than 10°, indicating that the TNDs layers are successfully coated on glass substrate.

[182] Table 1: Water contact angle for each layer in layer-by-layer deposition

Layer number	1	2	3	4	5	6	7	8	9	10
Water contact angle (degree)	18	12	9	8	8	7	7	6	6	6

3.2 Spin coating

[183] TND layers can be deposited on glass by spin coating. 20 g/L PDDA solution was first spin coated on the clean glass at 3000 rpm for 90s, followed by 0.1 g/L TND suspension at 1000 rpm for 90s. Repeating the steps for more than 3 times produce superhydrophilic TND coated glass with its contact angle lower than 7° indicating that the TNDs layers are successfully coated on glass substrate by the spin coating method. A SEM image of the deposited layers is provided in Figure 9.

3.3 Spray coating

[184] Spray coating is a rapid method to prepare large-area TND-coated glass. A 5 g/L PDDA dispersion is first spray coated on a clean glass substrate with 30 cm distance away. After drying, TND dispersion with a concentration of 0.05 g/L is sprayed on the glass forming a TND film. The thickness of the TND film can be tuned by controlling the time of spraying time. A superhydrophilic multi-layered TND coating with its water contact angle lower than 10° on the glass can be obtained when the spraying time is around 1 second.

3.4 Electrophoretic deposition

[185] TNDs can also be coated on electrically conductive glasses by electrophoretic deposition. When an electric field with a voltage of 3V is applied to the dispersion of TND, the negatively charged TNDs migrate to the anode and self-assemble into a film within 20 minutes. The thickness of the film or the transparency of the glass can be simply adjusted by changing the applied voltage and the deposition time.

3.5 Chemical vapour deposition

[186] Tungsten oxide layer can be deposited on glass by chemical vapour deposition using volatile precursors ($W(CO)_6$, WF_6 , $W(OEt)_x$, etc.). The precursor powder is placed in a sublimator which is heated up to 150 to 450 °C to produce tungsten oxide vapour. After growth, the glass substrate remains highly transparent (>95% transparency) but with multi-layered tungsten oxide deposited on its surface.

3.6 Plasma deposition

[187] TNDs can be firmly coated on glass and other substrates by plasma deposition. The substrates are first treated by oxygen plasma (radio frequency power of 100 W) for 100s – 500s to produce oxygen vacancies on the surface. Immediately after the plasma treatment, the glass substrate is immersed in 0.1 g/L TND solution, and 3-10 cycles of PDDA/TND adsorption are performed. The resultant glass deposited with multi-layered TNDs via plasma deposition has a water contact angle lower than 10°.

EXAMPLE 4 - Stabilizing TND coatings on glass by heat treatment.

[188] The TND coatings deposited by chemical vapour deposition, electrophoretic deposition and plasma deposition are stable on substrates under intensive mechanical friction. For the TND coatings by layer-by-layer deposition, spin coating and spray coating, they require a heat post-treatment if they are used under harsh conditions to enhance the mechanical stability of the TND coatings. After the heat treatment at 350-550 °C (according to softening points of the glass substrates) for 3h, the TND coating can firmly anchor on the glass substrate and becomes very stable even under intensive mechanical friction. In addition, after the heat treatment, the

water contact angle of the TND-coated glass decreases to less than 5° in 1s as shown in Figure 10.

EXAMPLE 5 - Stability of TND coatings on glass

5.1 Temperature

[189] The TND coating from Example 3.1 shows an excellent stability in a broad temperature range from 4 °C up to 550° C. After treatments under such extreme temperature conditions (550 °C) for more than 24h, the glass coated with TNDs can still retain its superhydrophilicity with the water contact angles in the range of 5-8°.

5.2 Mechanical stirring in water

[190] The TND-coated glass (without heat treatment) from Example 3.1 can retain its superhydrophilicity even under an intensive stirring in water (850 rpm) for more than two days (water contact angle = 7° after stirring), indicative of a firm mechanical combination between the glass and the TNDs as shown in Figure 11. The TND coated glass (with heat treatment) retains its water contact angle under the same intensive stirring as shown in Figure 11.

5.3 Long-term stability

[191] The TND coating from Example 3.1 has shown a great long-term stability in a more than 1-year time period. The water contact angles for TND-coated glass have been experimentally found to remain in the range of 6-8° even after 18 months as demonstrated by the results provided in Table 2.

[192] Table 2 – Aged water contact angle of TND-coated glass

Time	Fresh	1 week	1 month	3 months	6 months	12 months	18 months
Water contact angle (degree)	6-8	6-8	6-8	6-8	6-8	6-8	6-8

[193] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the present invention.

[194] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding the presence of one or more other feature, integer, step, component or group thereof.

CLAIMS

1. A functional coating for a substrate comprising at least one functional layer formed from a plurality of tungstate nanodots.
2. A functional coating according to claim 1, wherein each functional layer comprises a monolayer formed from a plurality of tungstate nanodots.
3. A functional coating according to claim 1 or 2, wherein the tungstate nanodots are arranged in a substantially spaced apart relation to each other within each layer.
4. A functional coating according to any preceding claim, wherein the nanodots comprise small lateral sizes of from 1 to 50 nm, preferably from 5 to 20 nm and thickness of between 1 and 3 nm, preferably about 2.5 to 2.8 nm.
5. A functional coating according to any preceding claim, wherein the nanodots are characterised by an absorption edge at 300 to 400 nm and a band gap of 3.2 to 4.0 eV, preferably 335 nm and band gap of 3.42 eV.
6. A functional coating according to any preceding claim, wherein the tungstate nanodots have a negative charge of between -30 and -70 mV, preferably -40 and -50 mV, preferably about -45 mV.
7. A functional coating according to any preceding claim, wherein the tungstate nanodots have a flat band potential of -0.51 V vs. NHE.
8. A functional coating according to any preceding claim, wherein the tungstate nanodots are selected from at least one of caesium tungstate or rubidium tungstate.
9. A functional coating according to any preceding claim, wherein each function layer comprises a bilayer comprising a monolayer formed from a plurality of tungstate nanodots and a binding polycation layer preferably selected from polydiallyldimethylammonium chloride (PDDA), diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI).

10. A functional coating according to any preceding claim, having a surface roughness R_{RMS} of from 5 to 6 nm, preferably from 5.2 to 5.7 nm.
11. A functional coating according to any preceding claim, comprising a 10 layer tungstate-polycation multilayer film, and having a thickness of less than 30 nm.
12. A functional coating according to any preceding claim, having a clear n-type photoresponse.
13. A functional coating according to any preceding claim, having an open circuit potential from +0.88 V to +0.25 V.
14. A functional coating according to any preceding claim, having a solar energy storage capacity of at least $1 \times 10^{-4} \text{ C/cm}^2$ after 20 mins of irradiation.
15. A functional coating according to any preceding claim, having a post-illumination "memory" catalytic antibacterial activity.
16. A functional coating according to any preceding claim, wherein having a water contact angle of less than 10 degrees, preferably less than 7 degrees.
17. A functional coating according to any preceding claim, that is at least 90%, preferably at least 95%, more preferably at least 99% optically transparent in the visible light range.
18. A functional coating according to any preceding claim, wherein the substrate comprises a glass substrate.
19. A functional coating according to any preceding claim, that is stable in a broad temperature range from 4 °C up to 550 °C, preferably retaining its superhydrophilicity with the water contact angles in the range of 5 to 8° in these temperature ranges.
20. A method of forming a functional coating for a substrate, comprising:
providing a substrate, preferably a glass substrate;

depositing at least one functional layer on the surface of the substrate, each functional layer formed from a plurality of tungstate nanodots;
thereby forming a functional coating of tungstate nanodots on the substrate.

21. A method according to claim 20, wherein the depositing step comprises at least one of:

- a layer-by-layer (LBL) method, preferably a self-assembly layer-by-layer method;
- spin coating;
- spray coating;
- dip coating
- chemical vapour deposition;
- Plasma deposition or
- electrodeposition process.

22. A method according to claim 20 or 21, wherein the depositing step comprises:
depositing at least two functional layers, preferably at least three functional layers on the surface of the substrate.

23. A method according to claim 20, 21 or 22, wherein in the depositing step, each functional layer comprises a monolayer formed from a plurality of tungstate nanodots.

24. A method according to any one of claims 20 to 23, wherein each functional layer is formed using a binding polycation, preferably selected from polydiallyldimethylammonium chloride (PDDA), diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI).

25. A method according to claim 20 to 24, wherein each function layer comprises a bilayer comprising a monolayer formed from a plurality of tungstate nanodots and a binding polycation layer preferably selected from polydiallyldimethylammonium chloride (PDDA), diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI).

26. A method according to any one of claims 20 to 25, wherein each functional layer is formed by:

applying a binding polycation solution to the substrate, preferably a polydiallyldimethylammonium chloride (PDMA) solution, diallyldimethylammonium chloride (DADMAC), poly(allylamine hydrochloride)(PAH), polyethylenimine (PEI) or polyaniline (PANI);

drying the binding polycation coated substrate; and

applying a tungstate nanodots suspension to the binding polycation coated substrate.

27. A method according to claim 26, wherein the tungstate nanodots suspension comprises tungstate nanocrystals suspended in a dispersion solution, preferably tetrabutylammonium hydroxide (TBAOH) solution.

28. A method according to claim 27, wherein the tungstate nanodots suspension has a concentration of tungstate nanodots of from 0.01 to 5 g/L, preferably from 0.05 to 1 g/L, more preferably from 0.05 to 0.1 g/L.

29. A method according to any one of claims 24 to 28, wherein the binding polycation comprises polydiallyldimethylammonium chloride (PDMA) solution having a concentration of from 0.1 to 2 g/L, preferably from 0.5 to 1.5 g/L, more preferably about 0.8 g/L.

30. A method according to any one of claims 26 to 29, wherein the substrate is immersed in one or both of the binding polycation solution, or the tungstate nanodots suspension for at least 1 mins, preferably at least 5 mins, more preferably at least 10 mins, more preferably at least 20 mins.

31. A method according to any one of claims 20 to 30, wherein the tungstate nanodots are produced by exfoliation of layered tungstate nanocrystals.

32. A method according to any one of claims 20 to 31, wherein the tungstate nanodots are synthesized by exfoliating nanocrystals (NCs) of a layered precursor

comprising $A_{1.2}Cs_{2.8}W_{11}O_{35} \cdot xH_2O$ ($A = Na^+$ and H^+ , $x < 10.5$) with hexagonal tungsten bronze (HTB) $Cs_4W_{11}O_{35}$ structure.

33. A method according to any one of claims 20 to 32, further including the step of:
heat treatment of the coated substrate at 350 to 550 °C for at least 0.5 h, preferably at least 1 h, more preferably at least 3h.

34. A method according to any one of claims 20 to 33, further including the pretreatment step of:
treating the surface of the substrate with oxygen plasma to produce oxygen vacancies on the surface.

35. A functional coating for a glass substrate according to any one of claims 1 to 19 formed by a method according to any one of claims 20 to 34.

36. A smart window coating according to any one of claims 1 to 19 or formed by a method according to any one of claims 20 to 34.

- 1/30 -

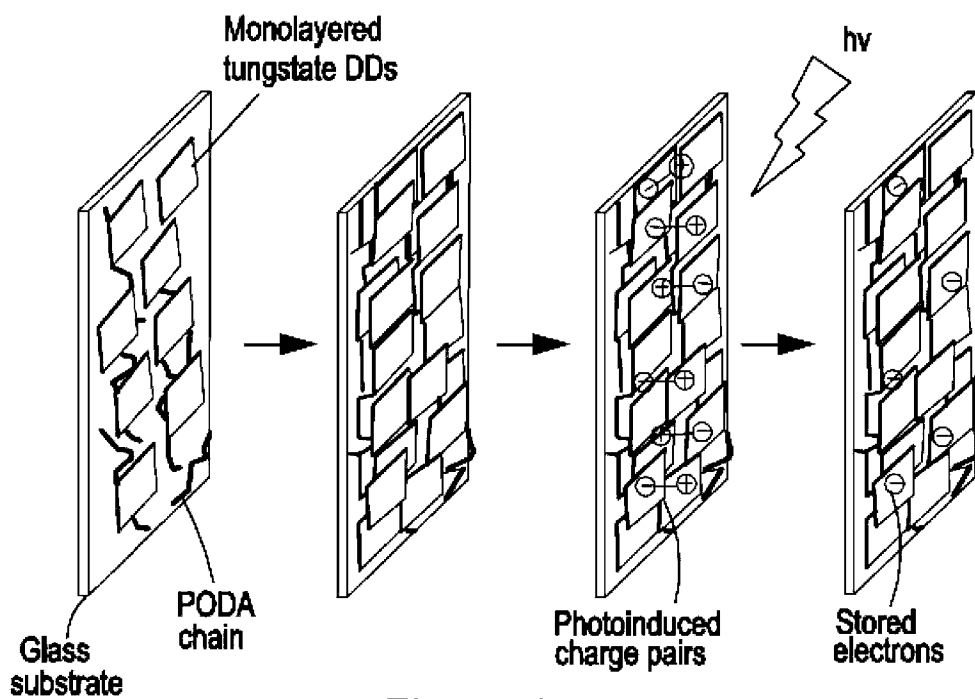


Figure 1

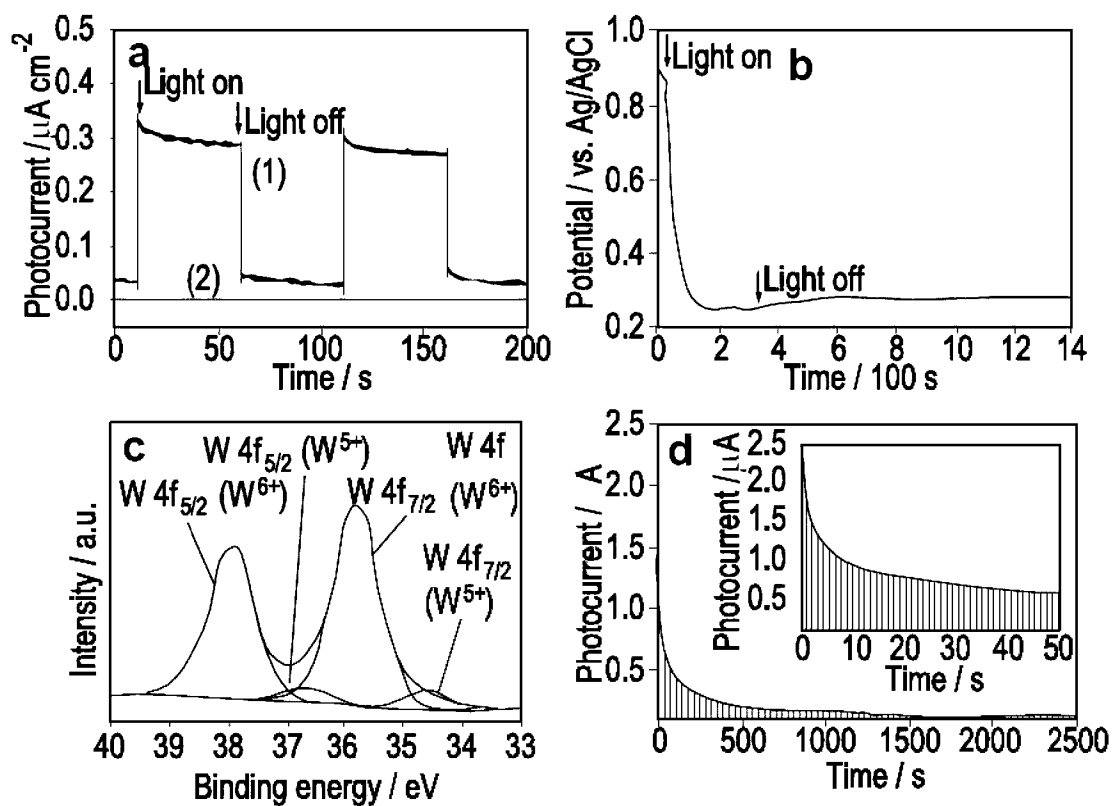


Figure 3

- 2/30 -

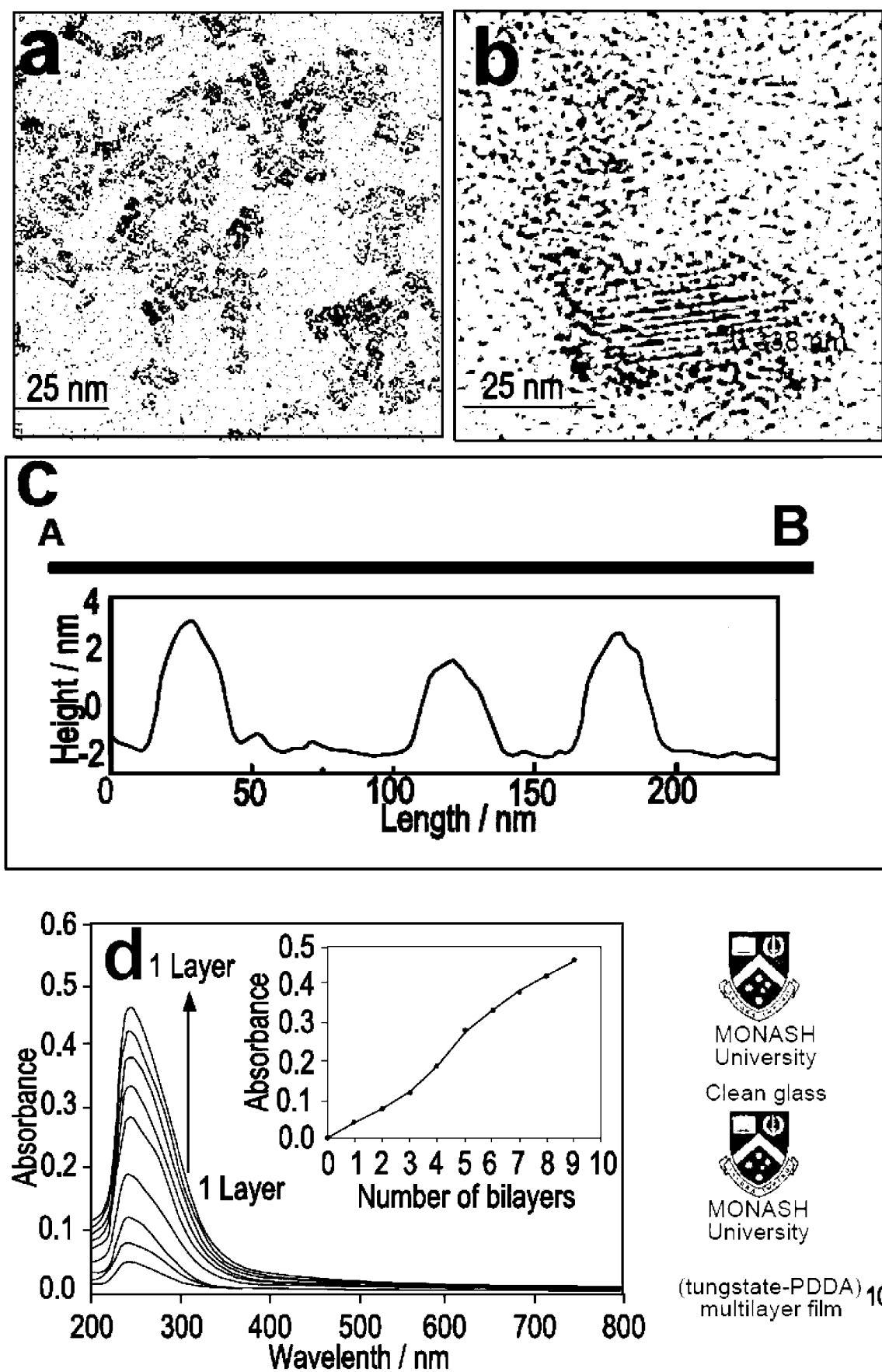


Figure 2

- 3/30 -

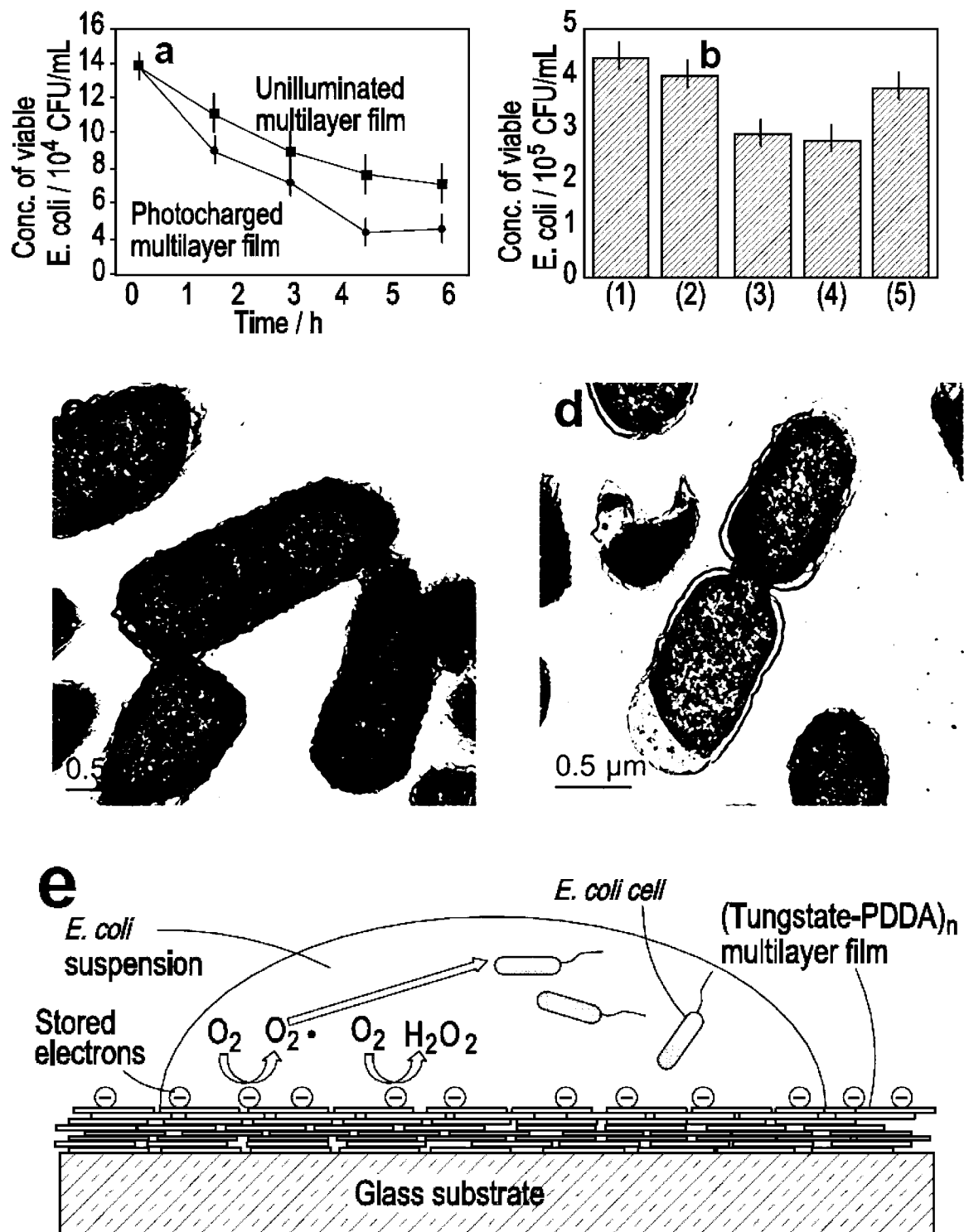


Figure 4

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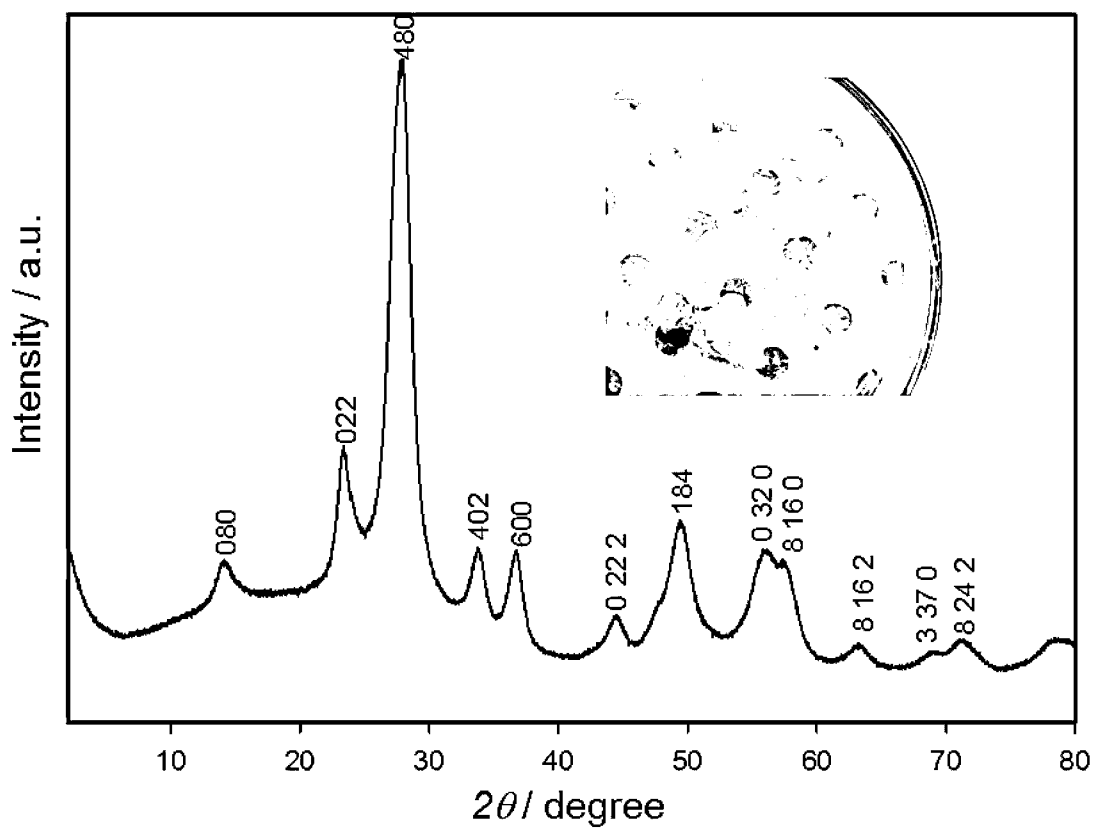


Figure 4A1

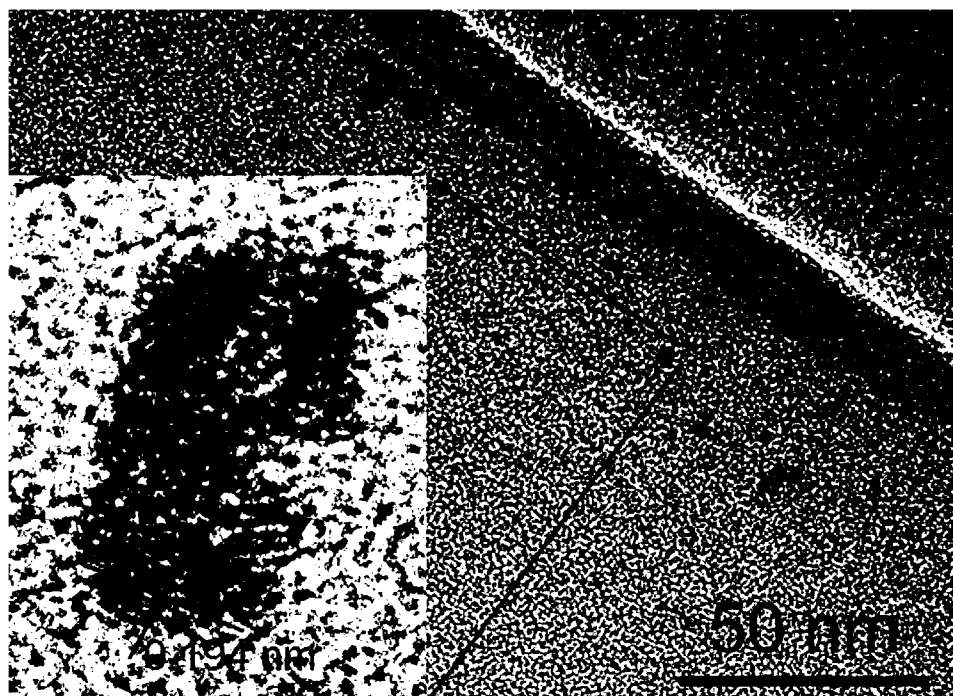


Figure 4A2

- 5/30 -

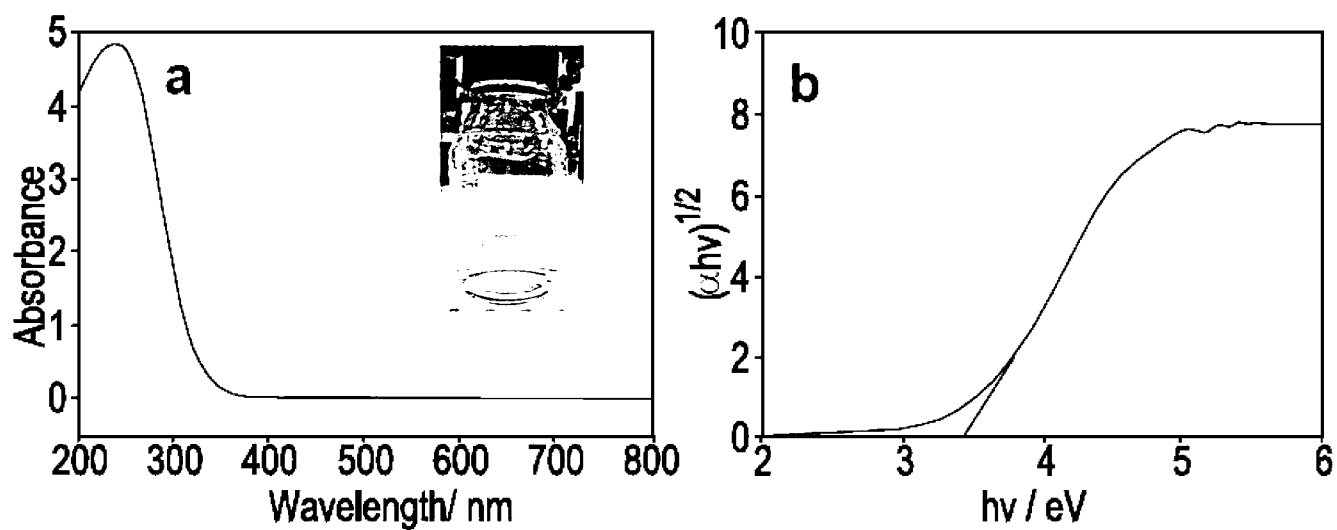


Figure 4A3

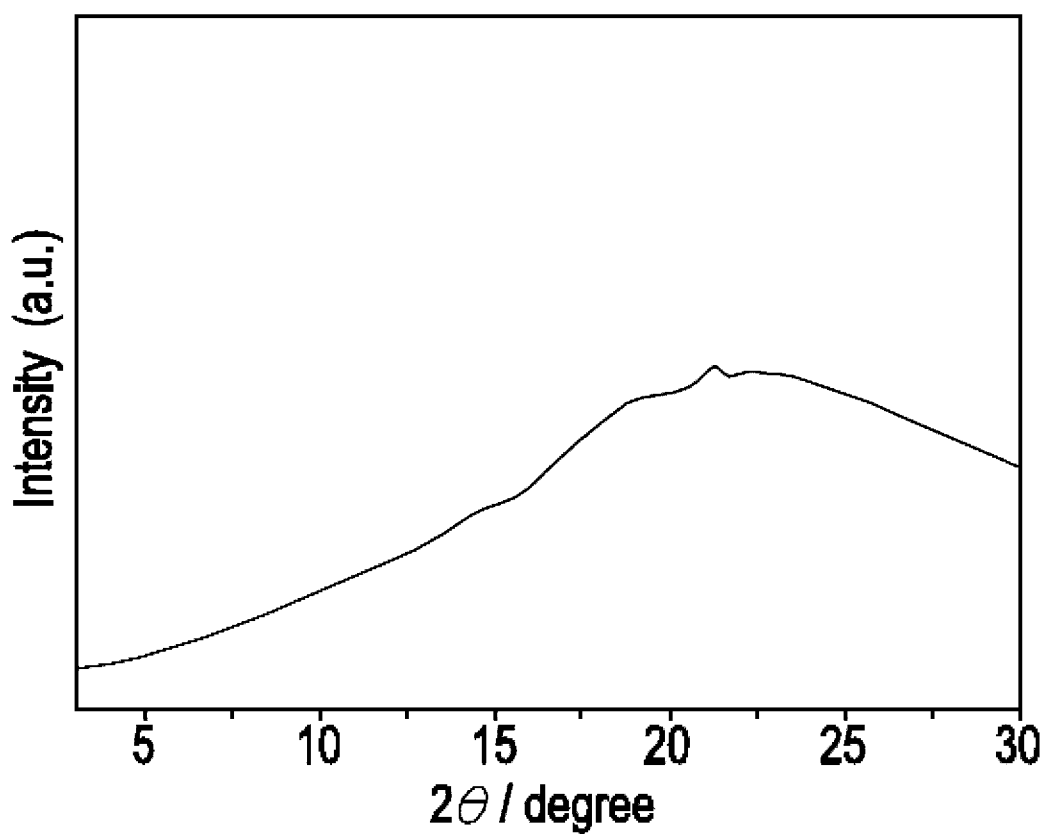


Figure 4A4

- 6/30 -

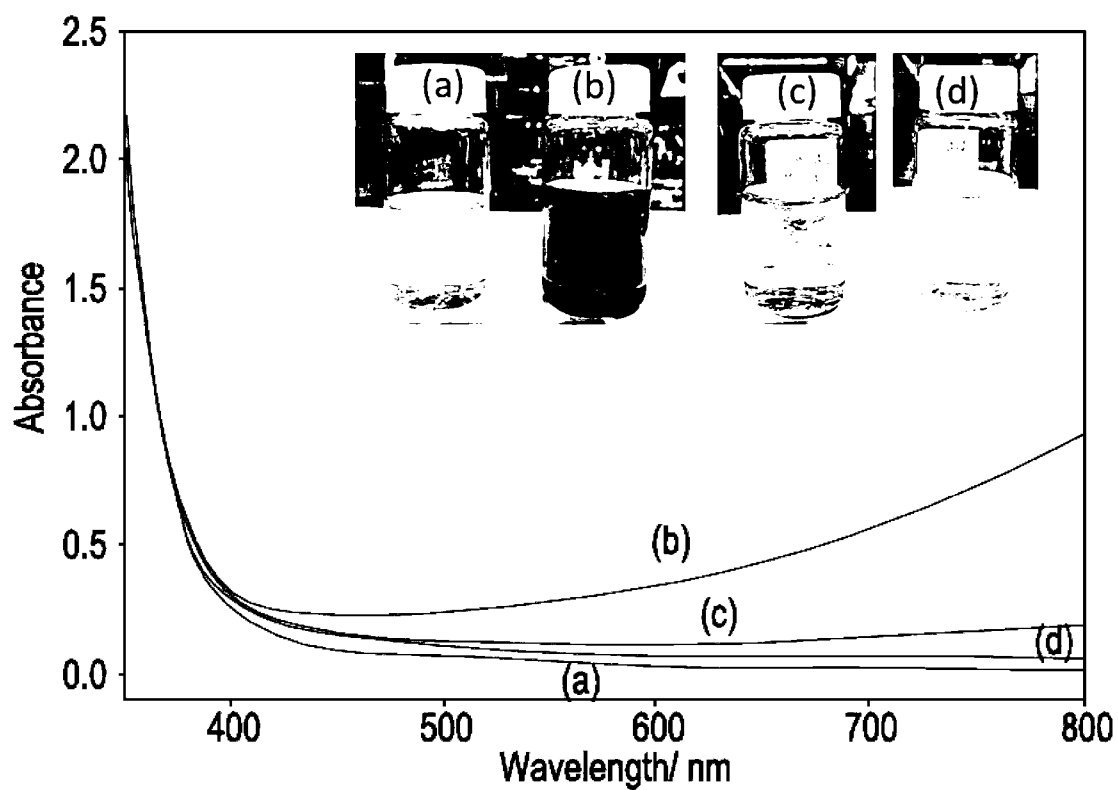


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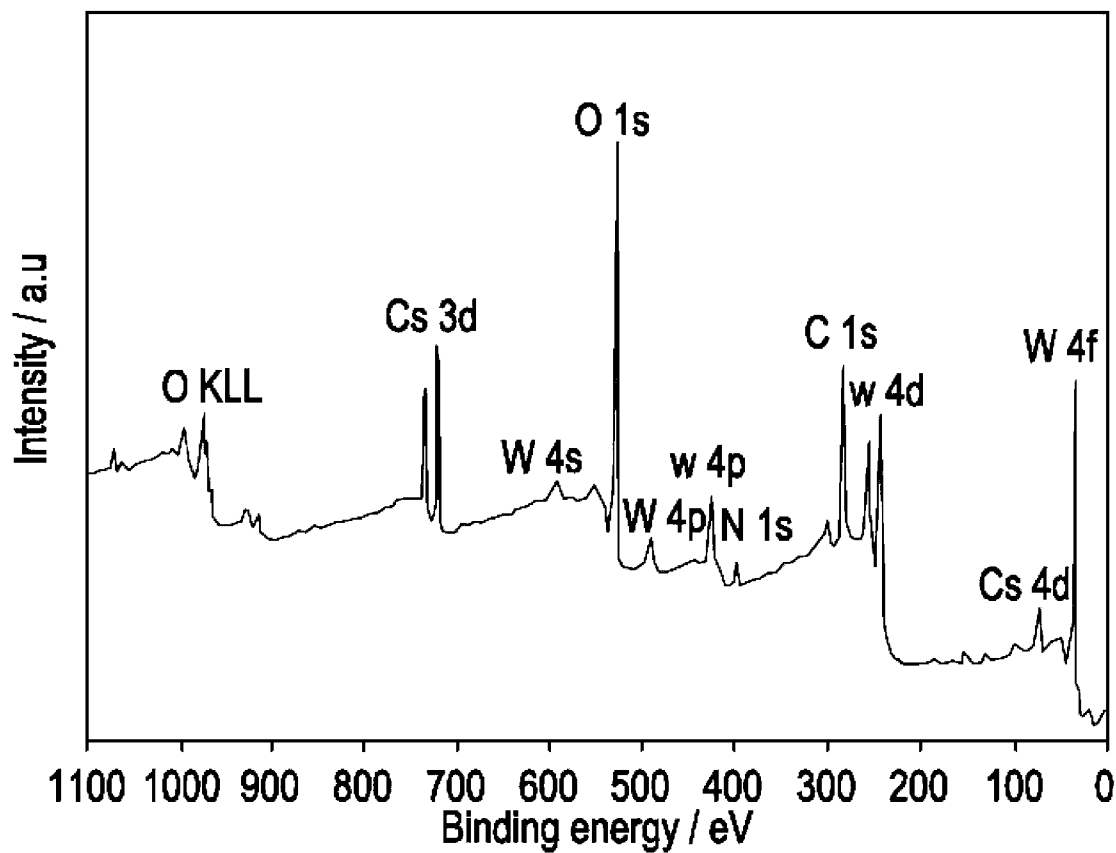


Figure 4A6

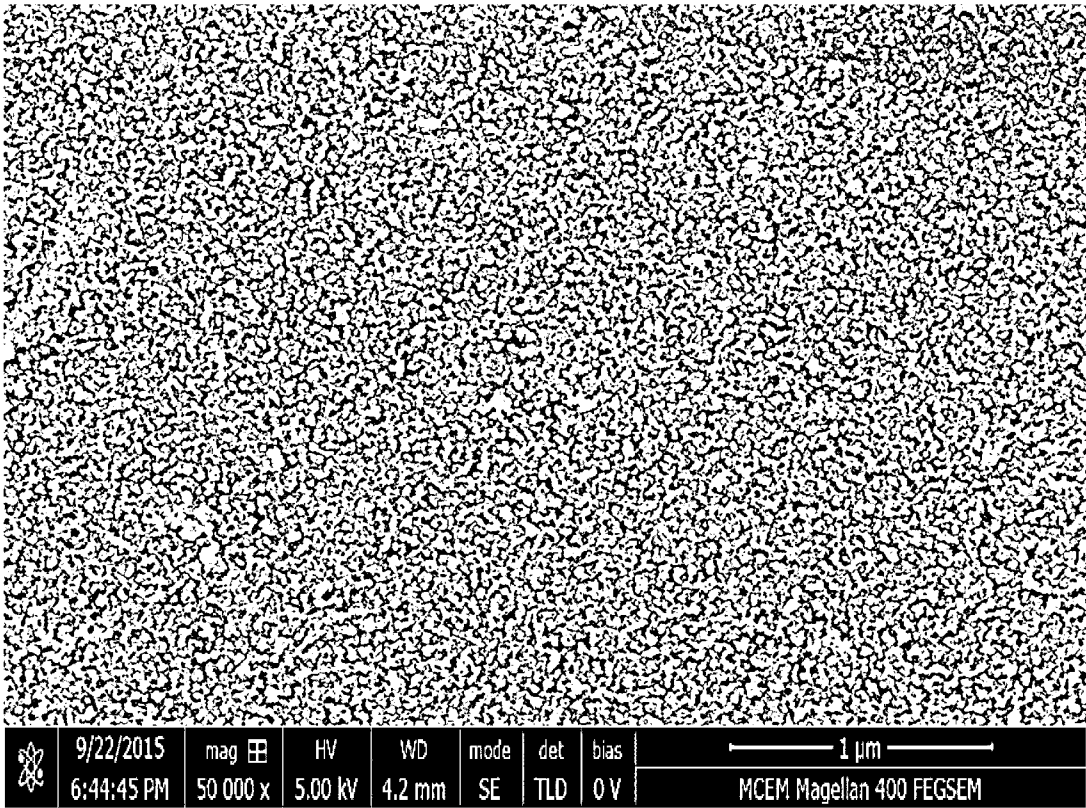


Figure 4A7

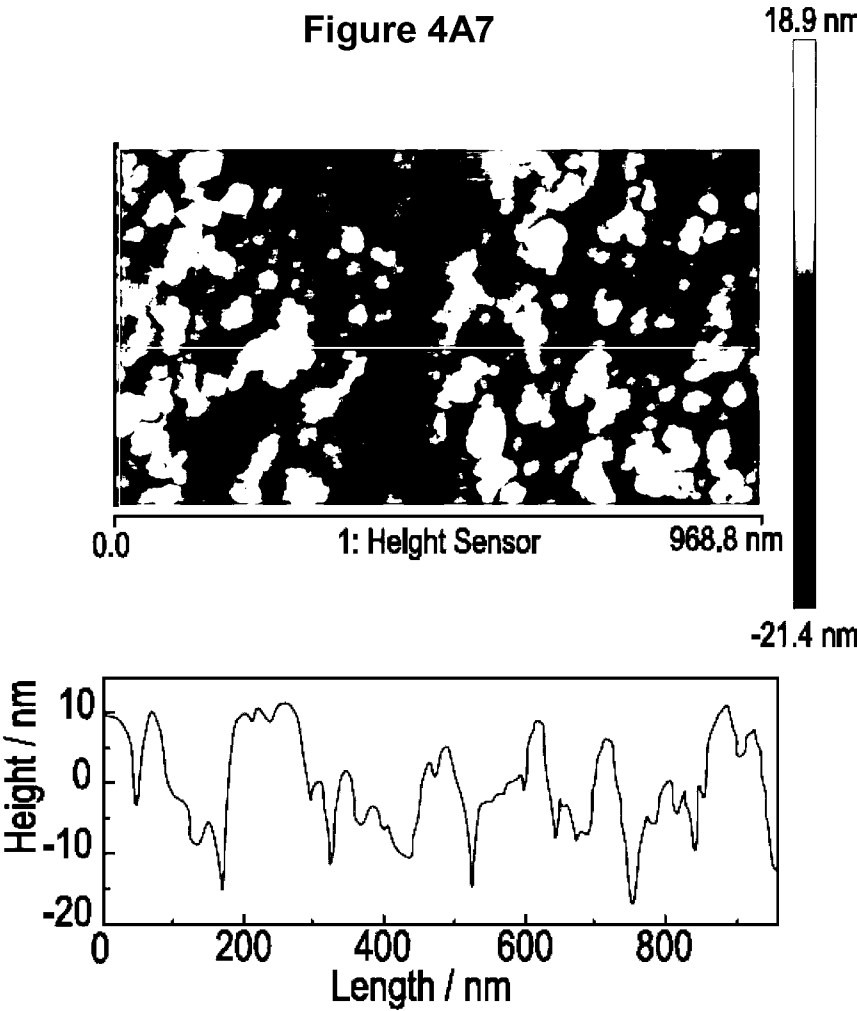


Figure 4A8

- 8/30 -

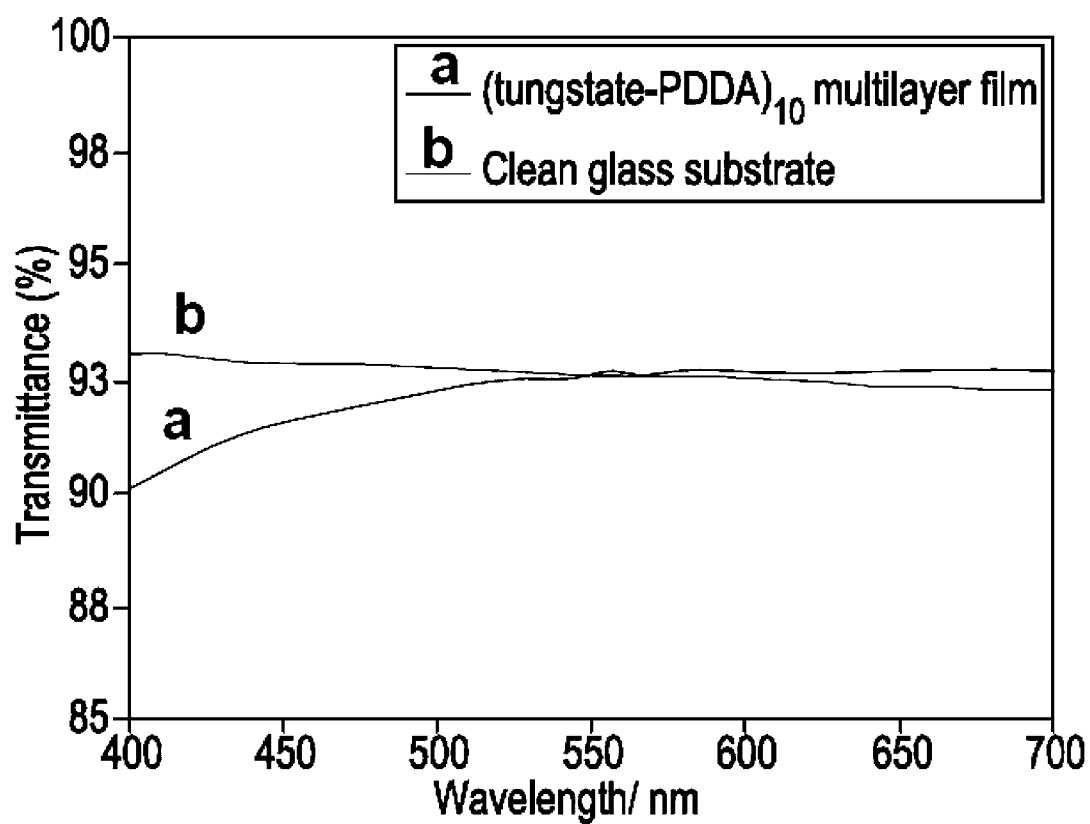


Figure 4A9

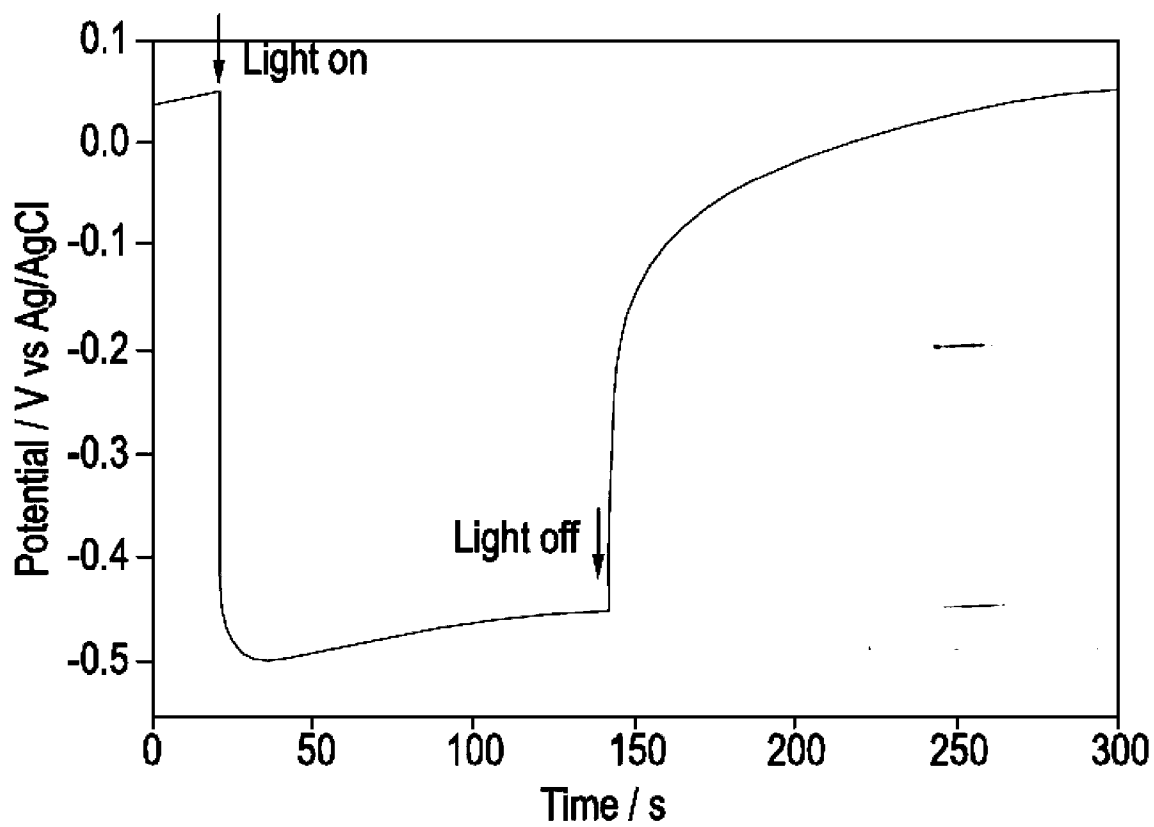


Figure 4A10

- 9/30 -

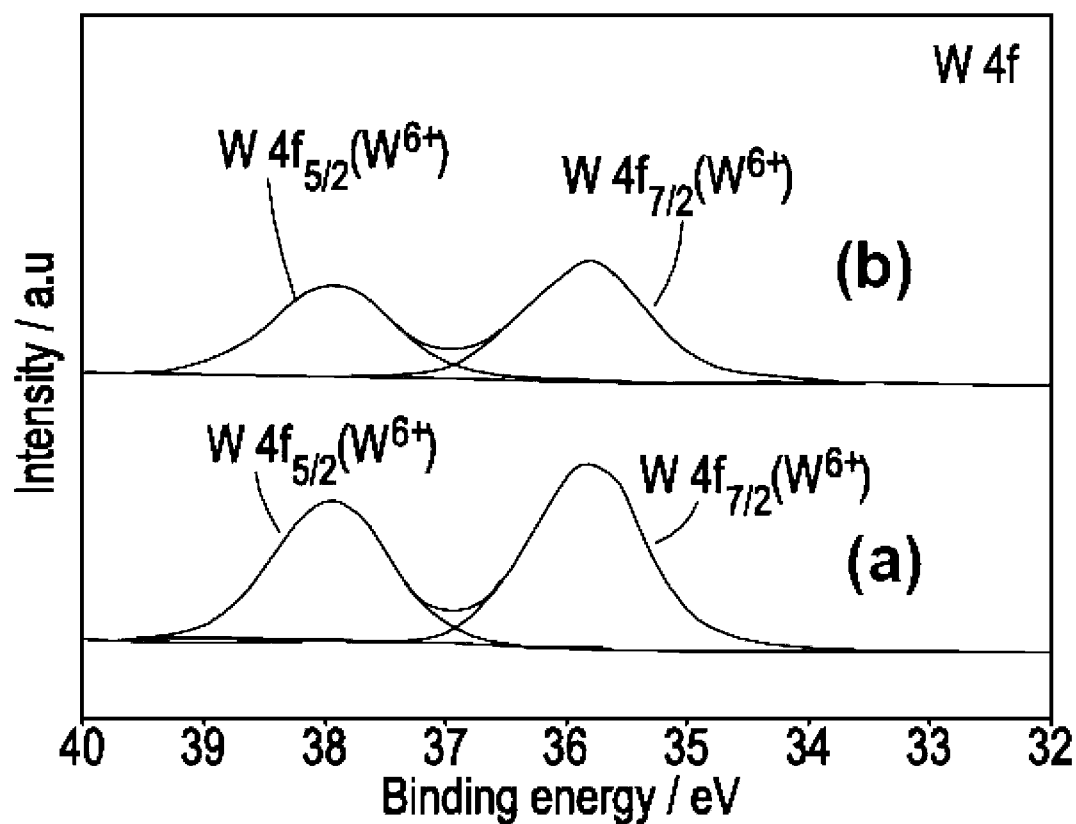


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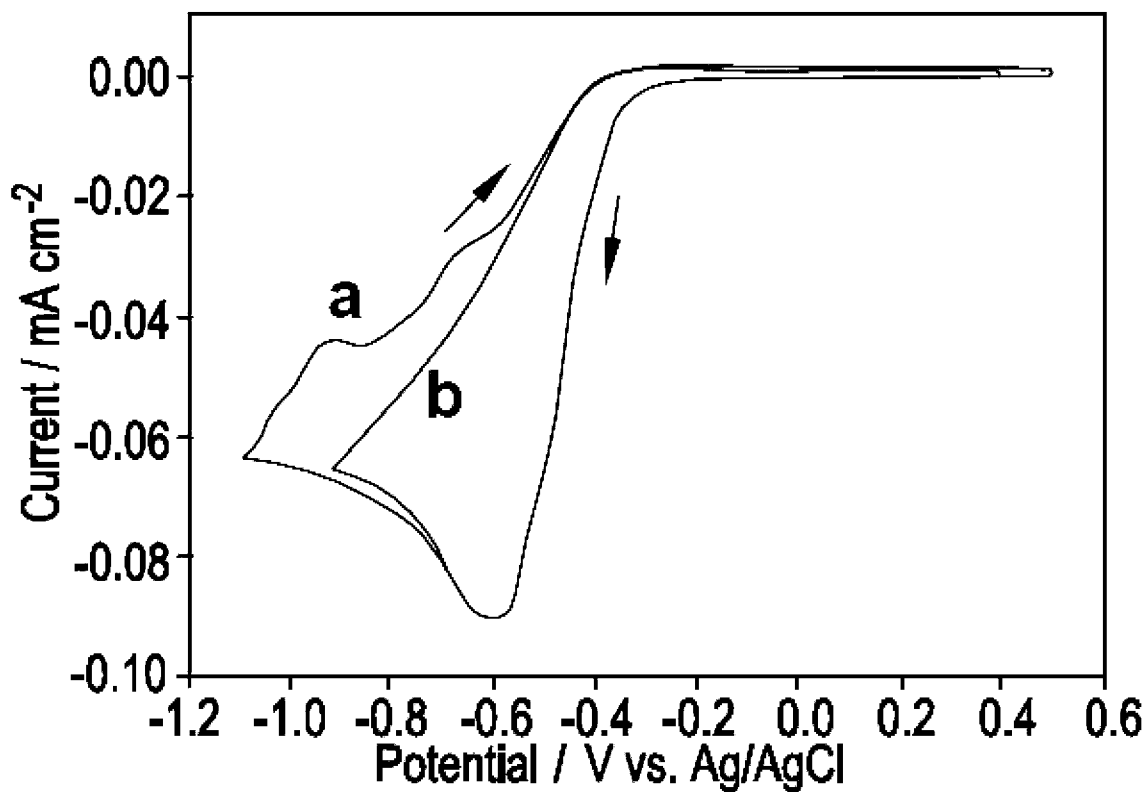


Figure 4A12

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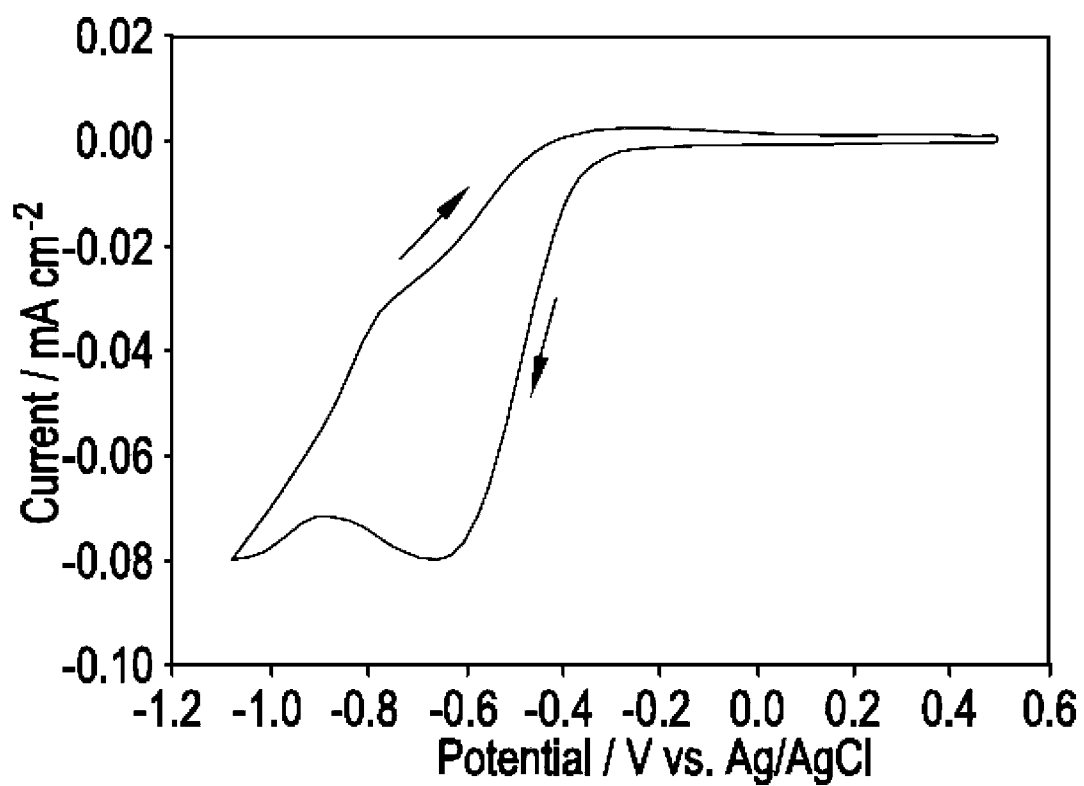


Figure 4A13

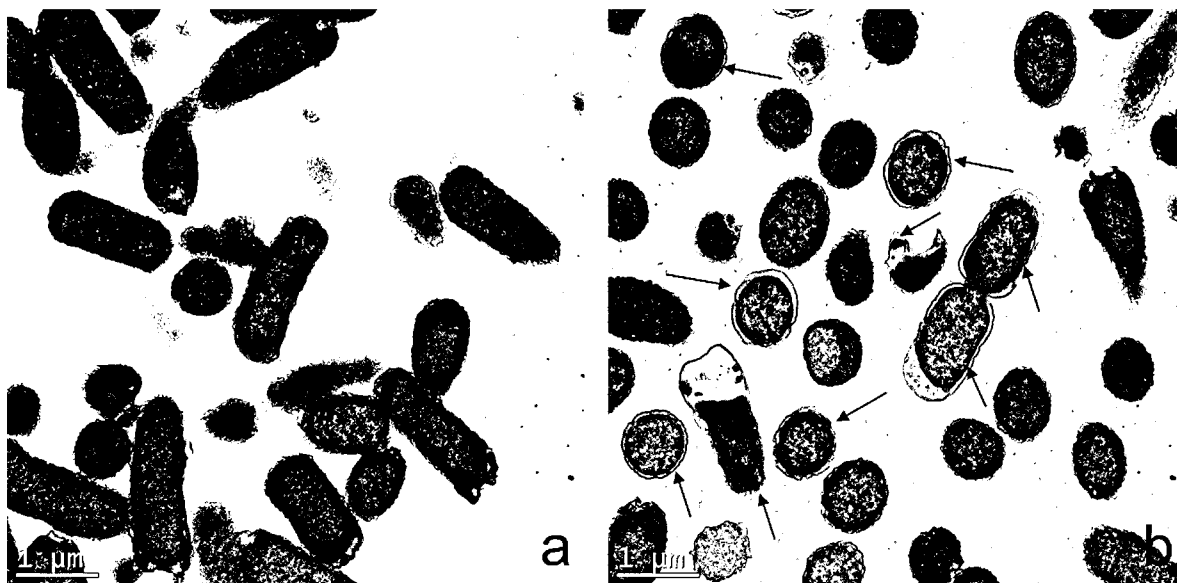


Figure 4A14

- 11/30 -

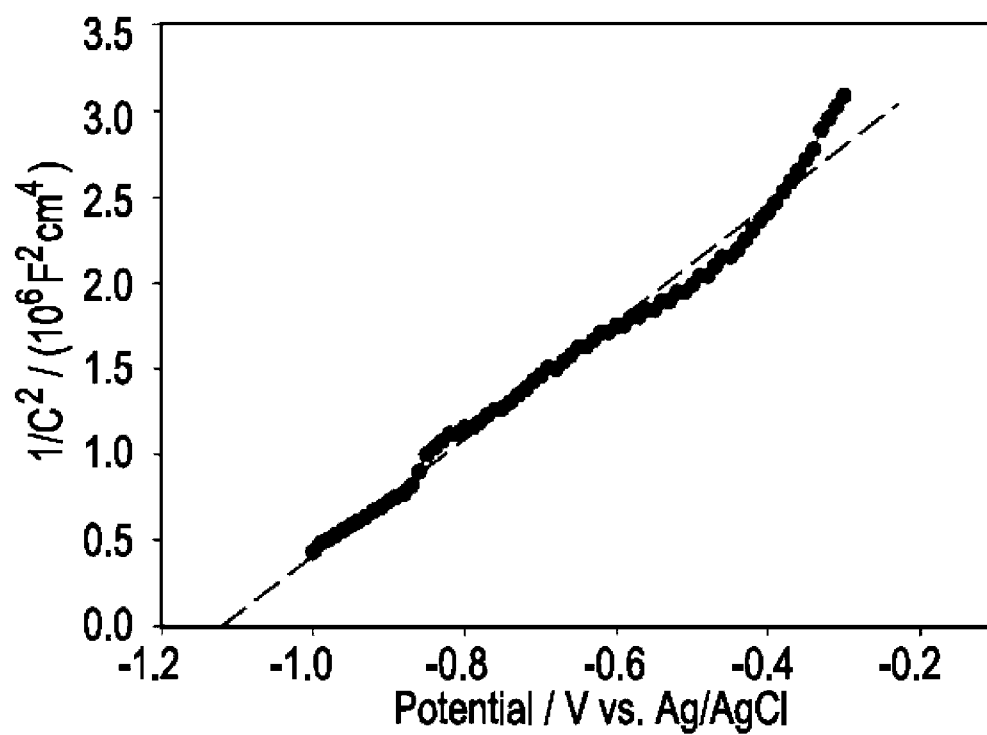


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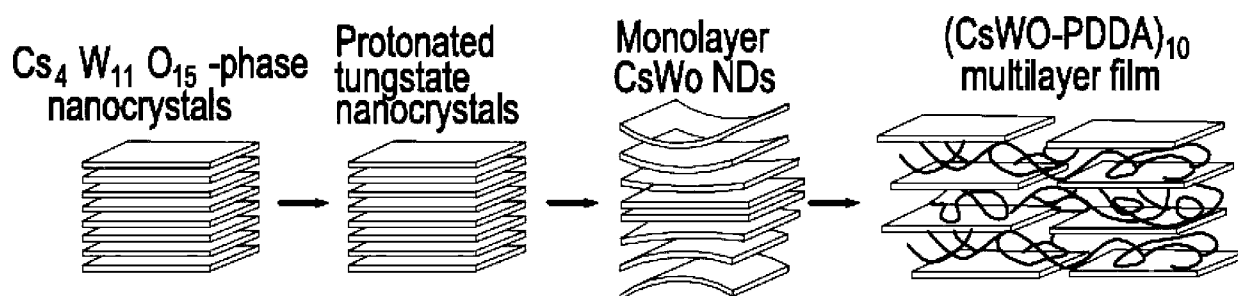


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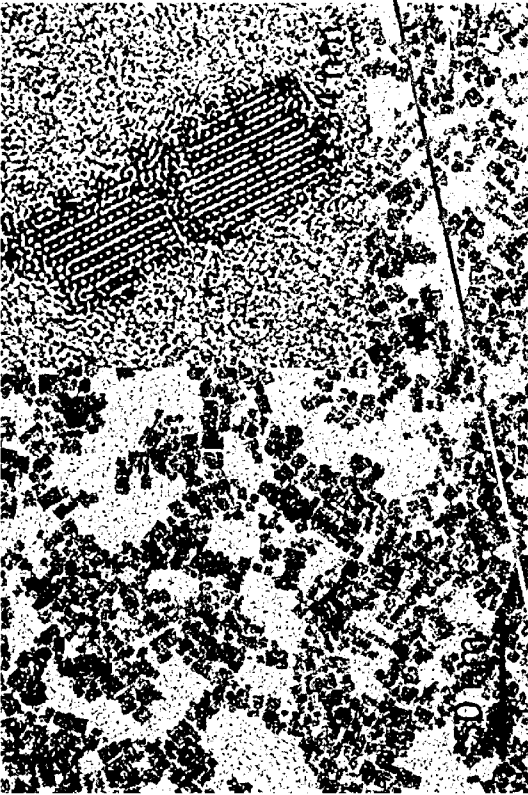
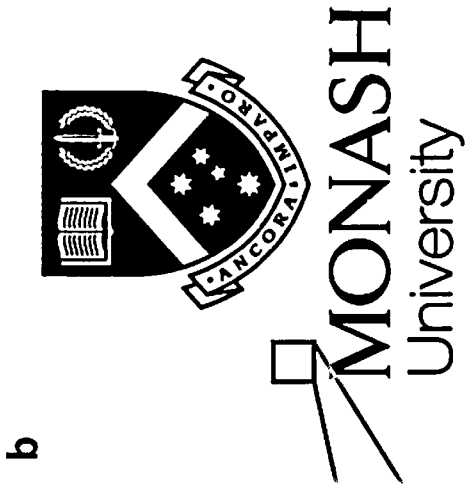
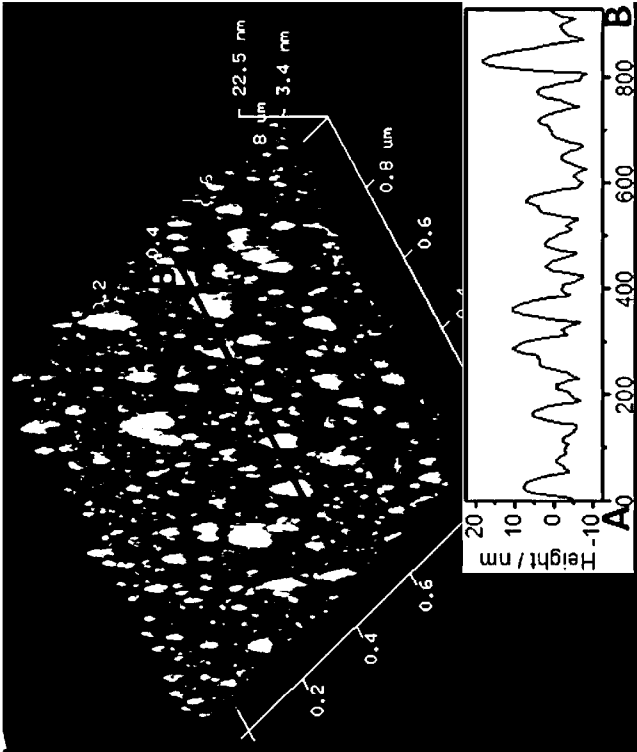
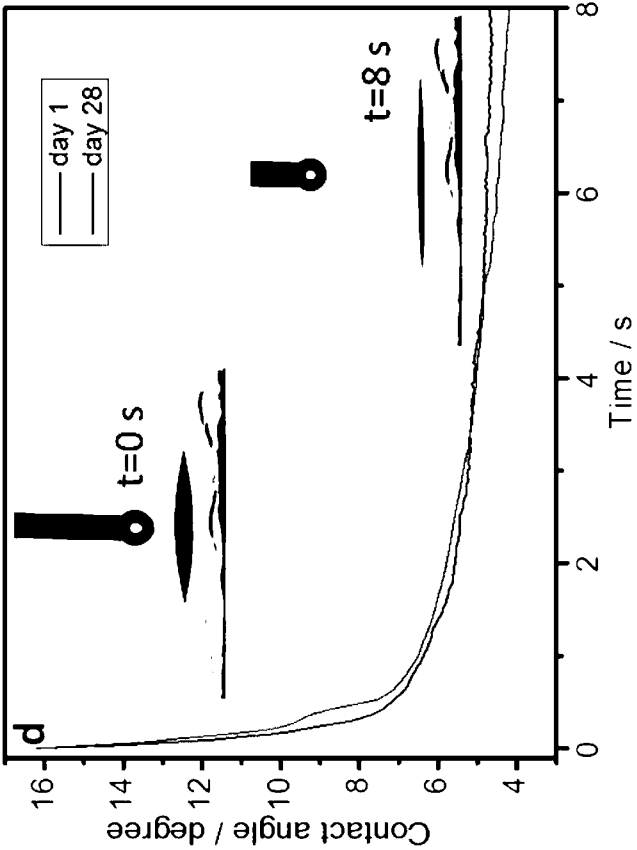


Figure 6

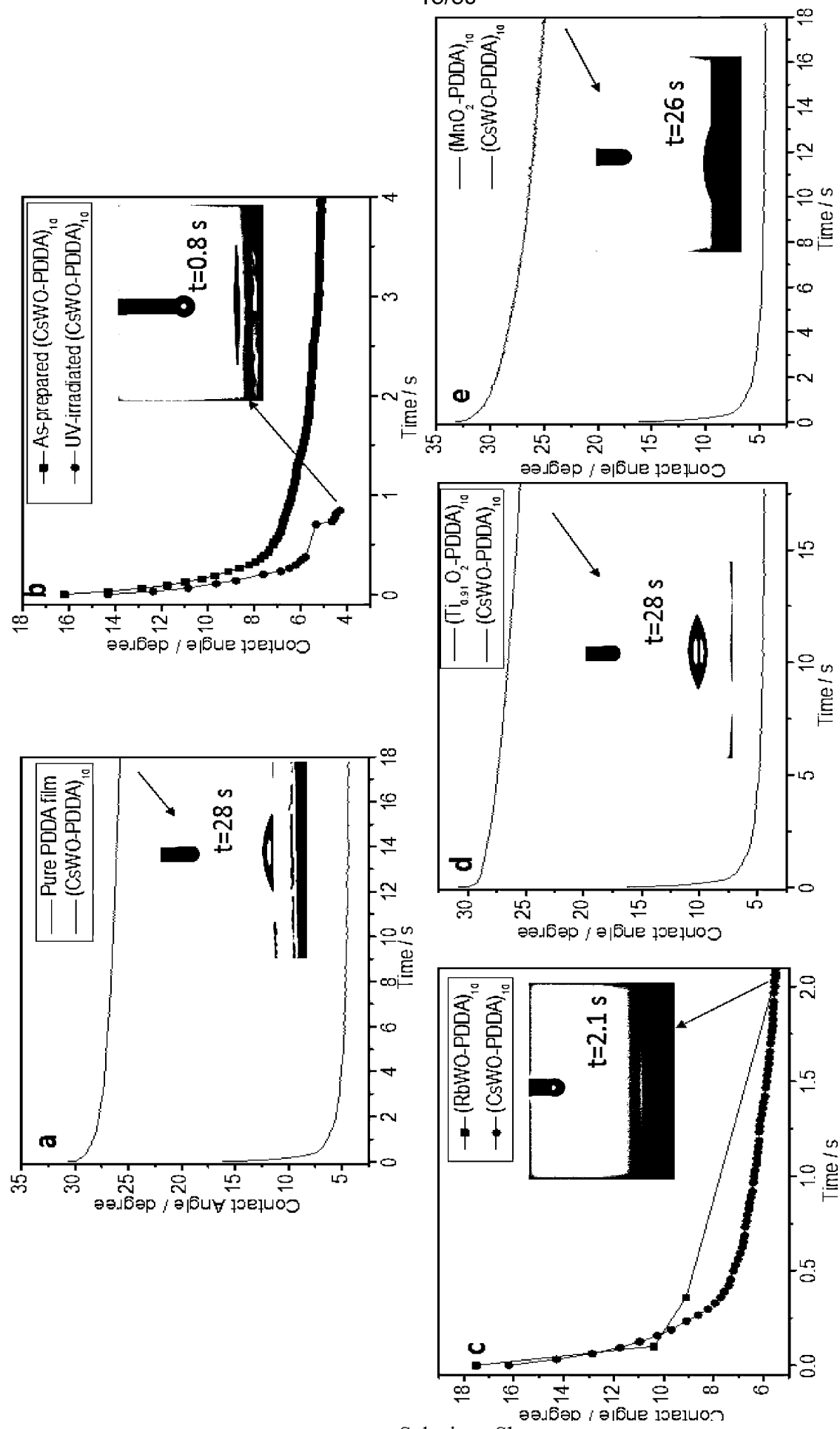


Figure 7

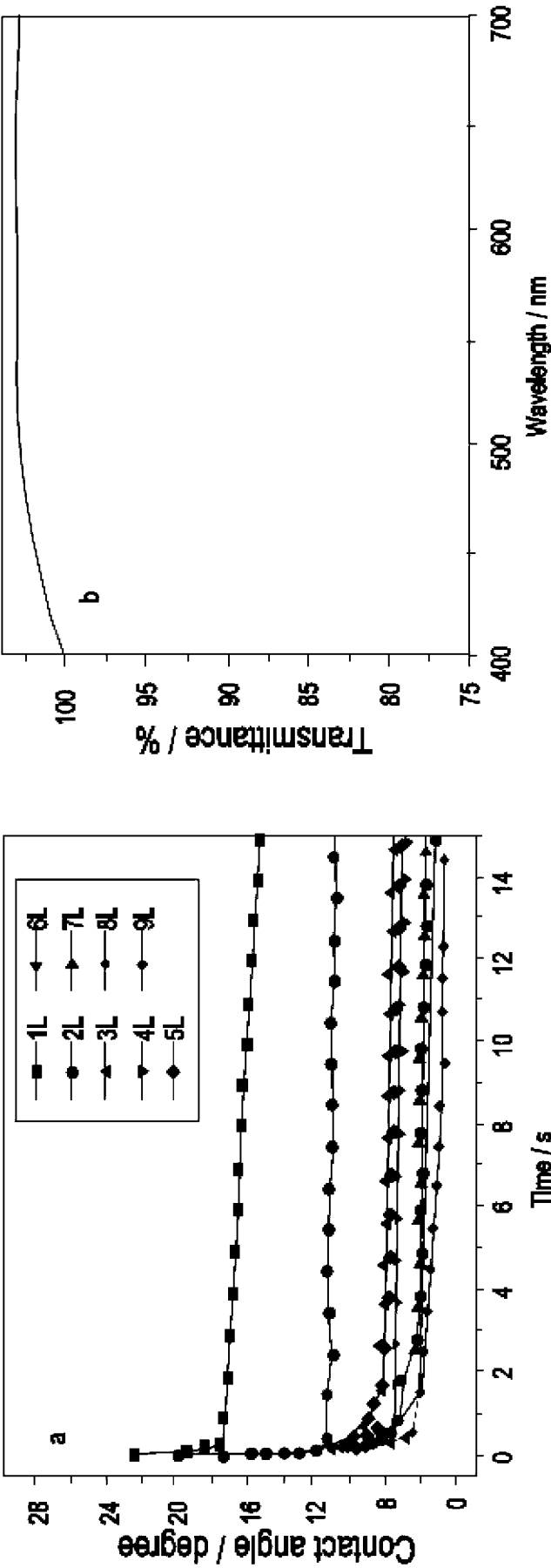
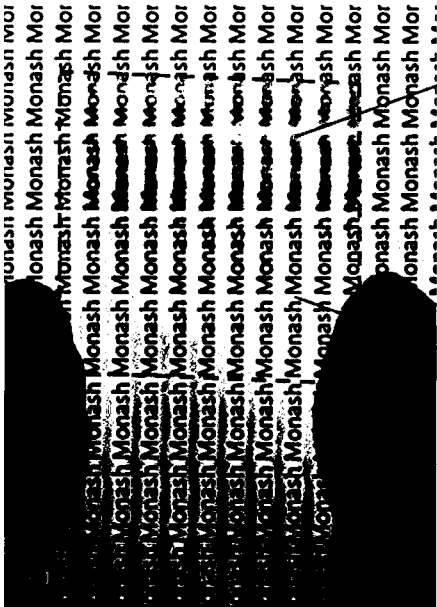


Figure 8



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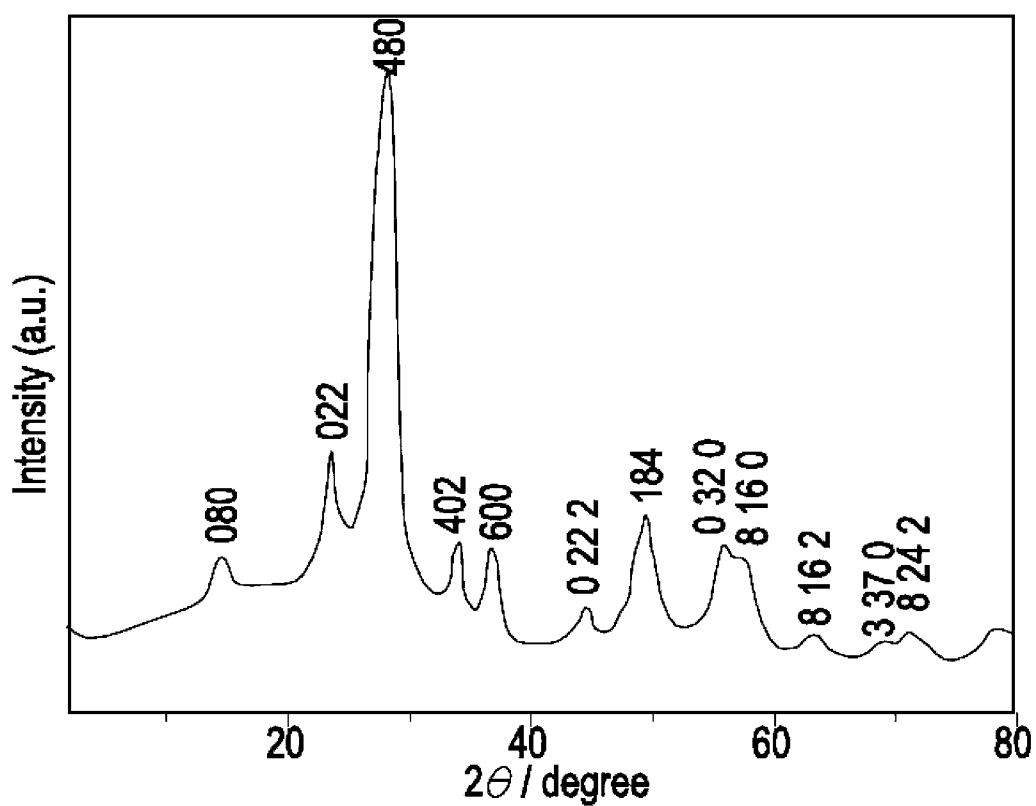


Figure 8A1

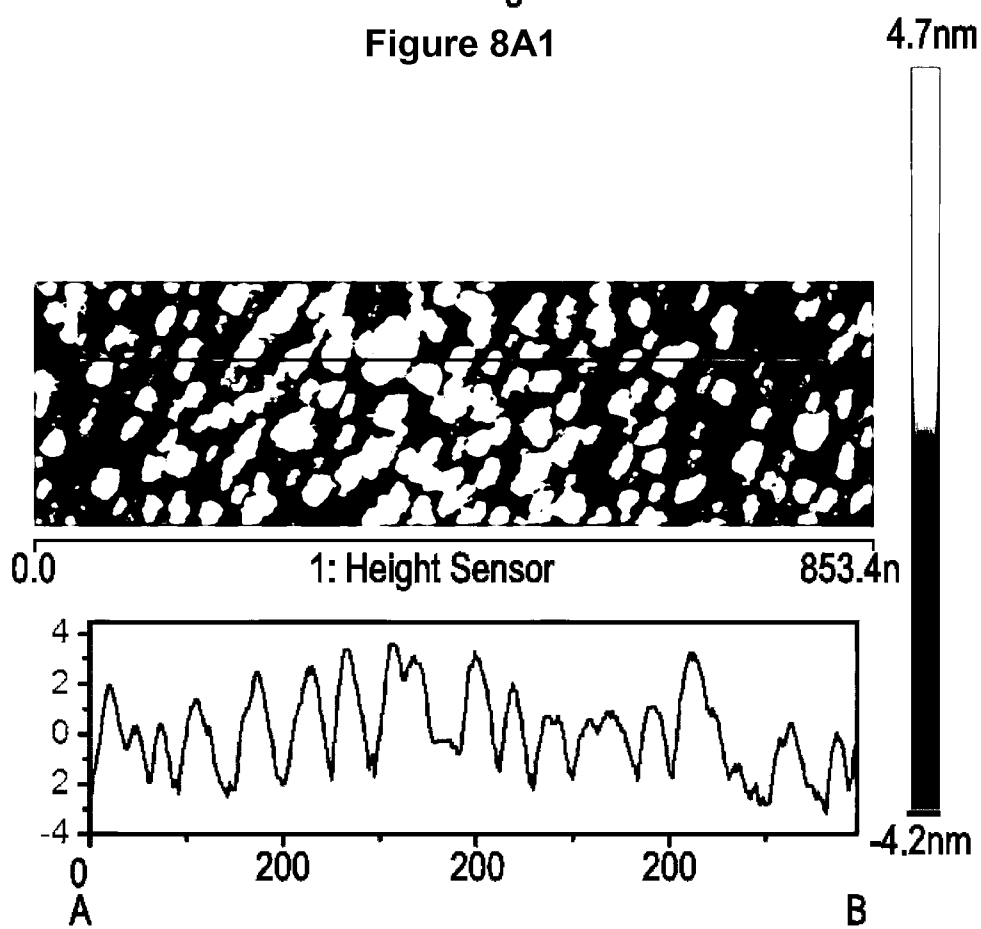


Figure 8A2

- 16/30 -

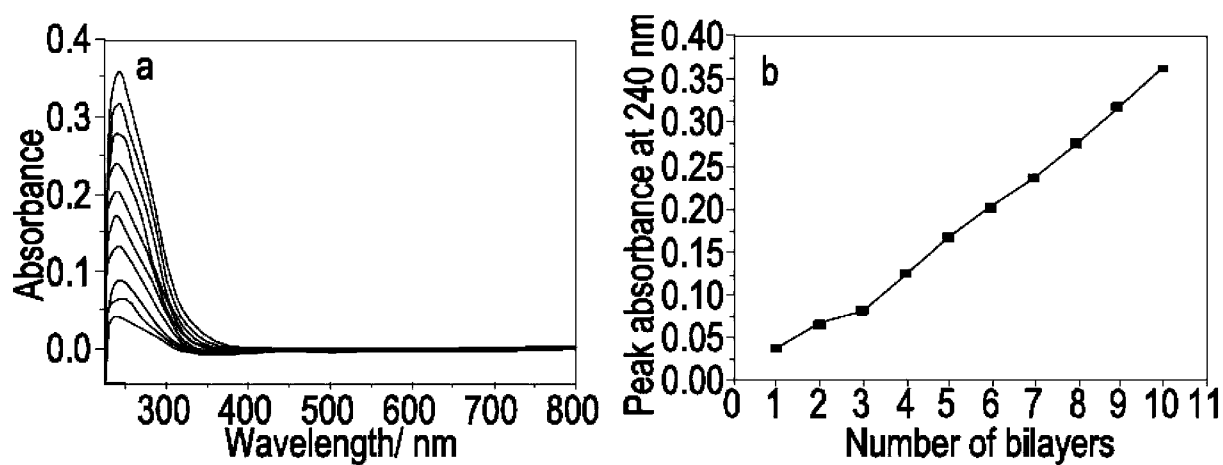


Figure 8A3

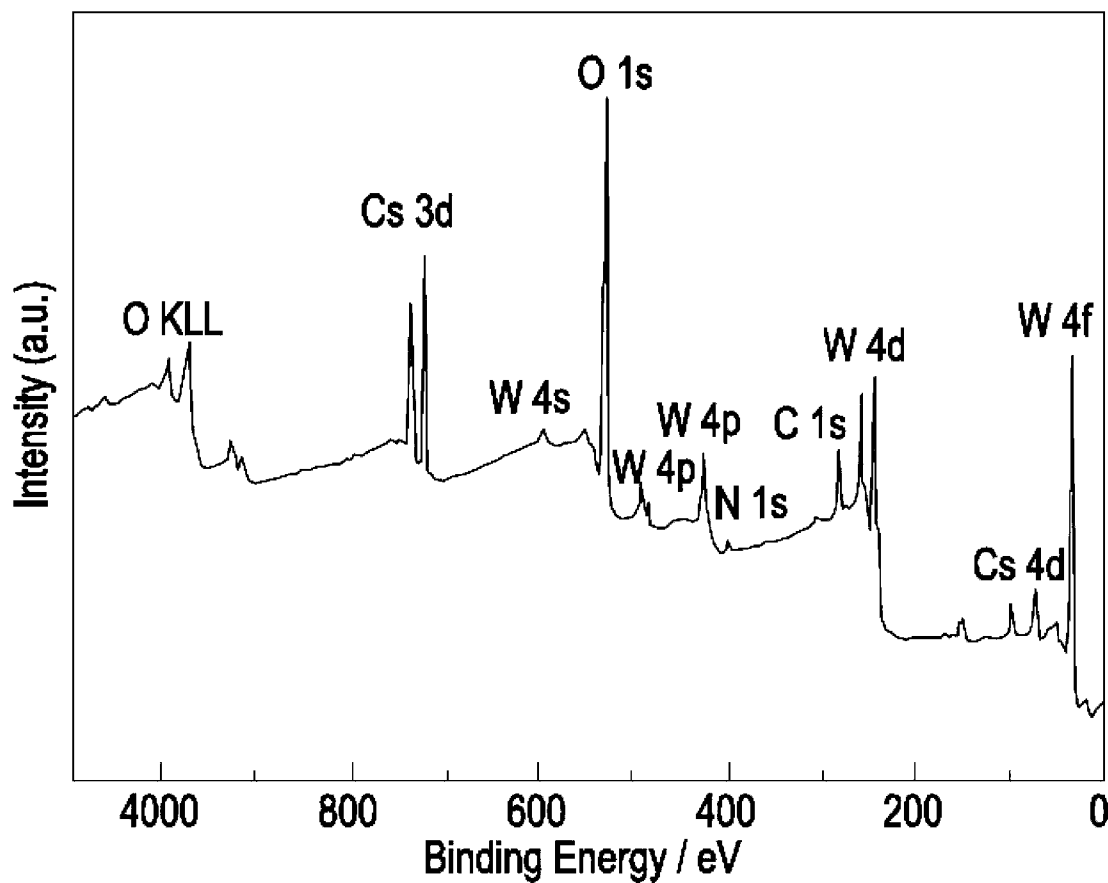


Figure 8A4

- 17/30 -

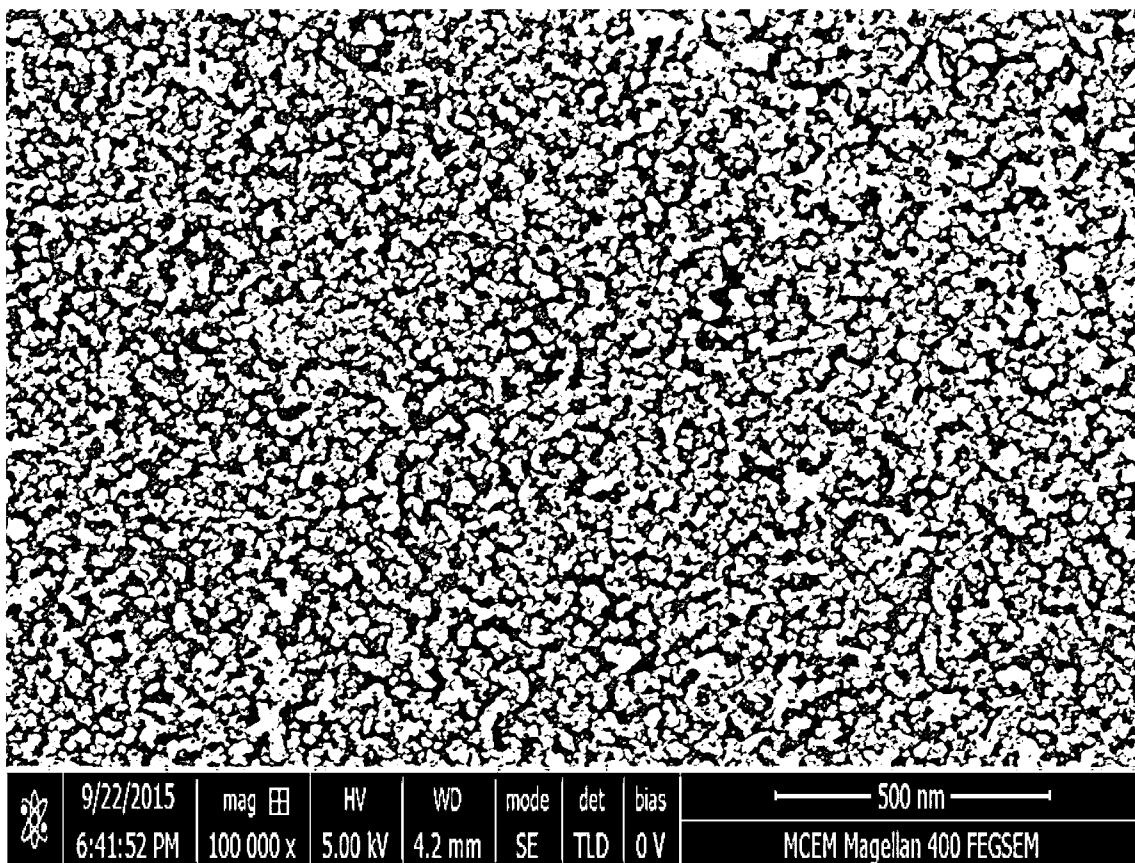


Figure 8A5

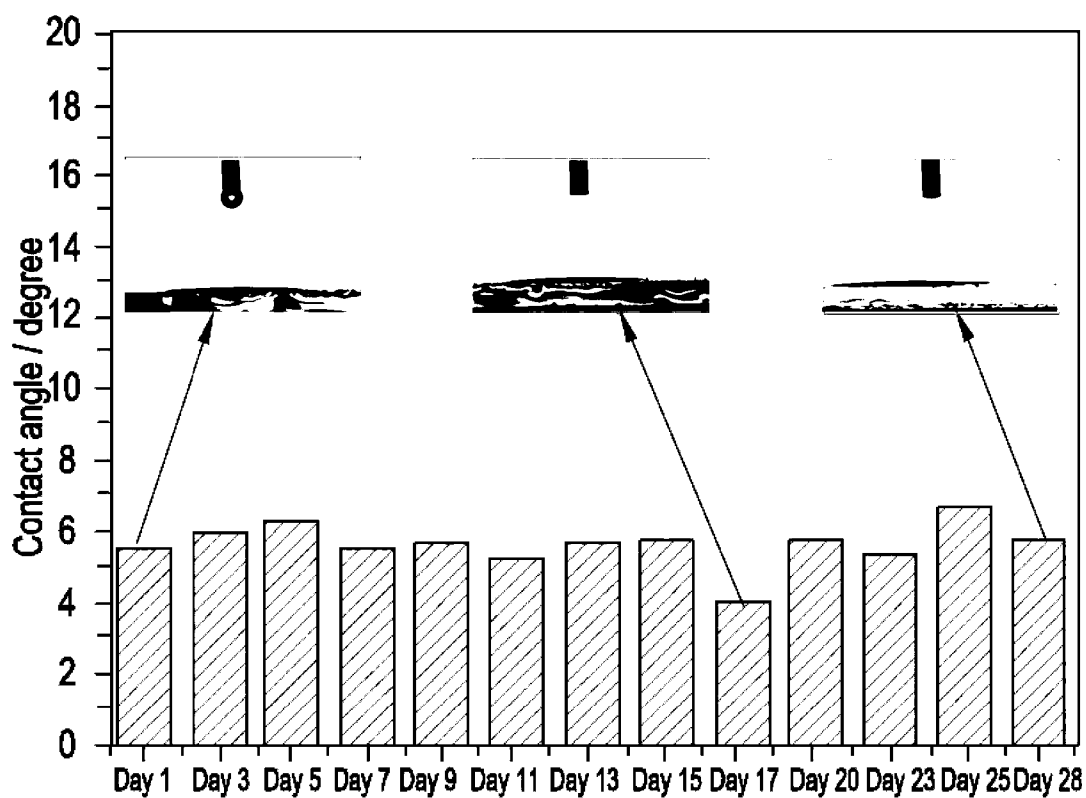


Figure 8A6

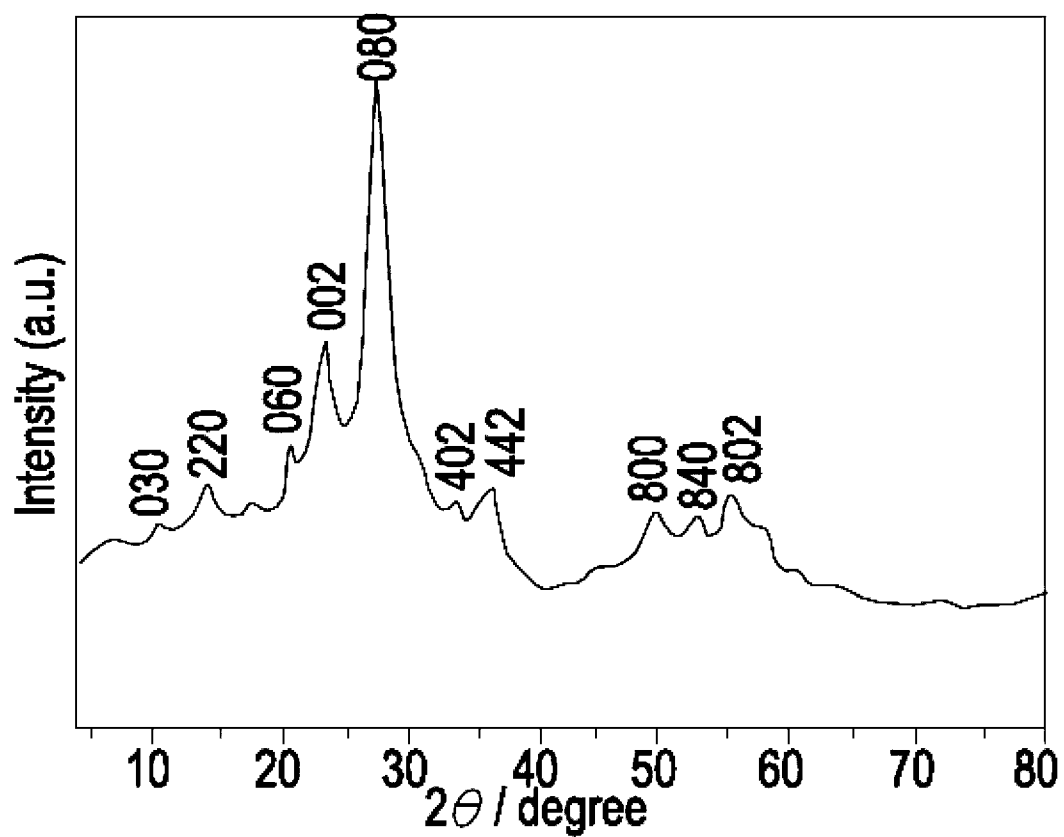


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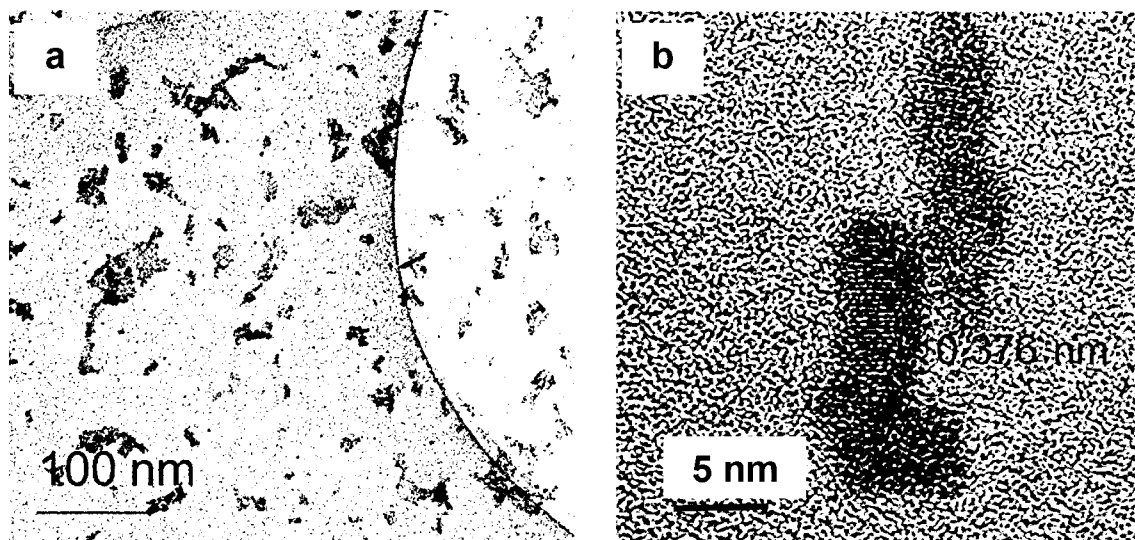


Figure 8A8

- 19/30 -

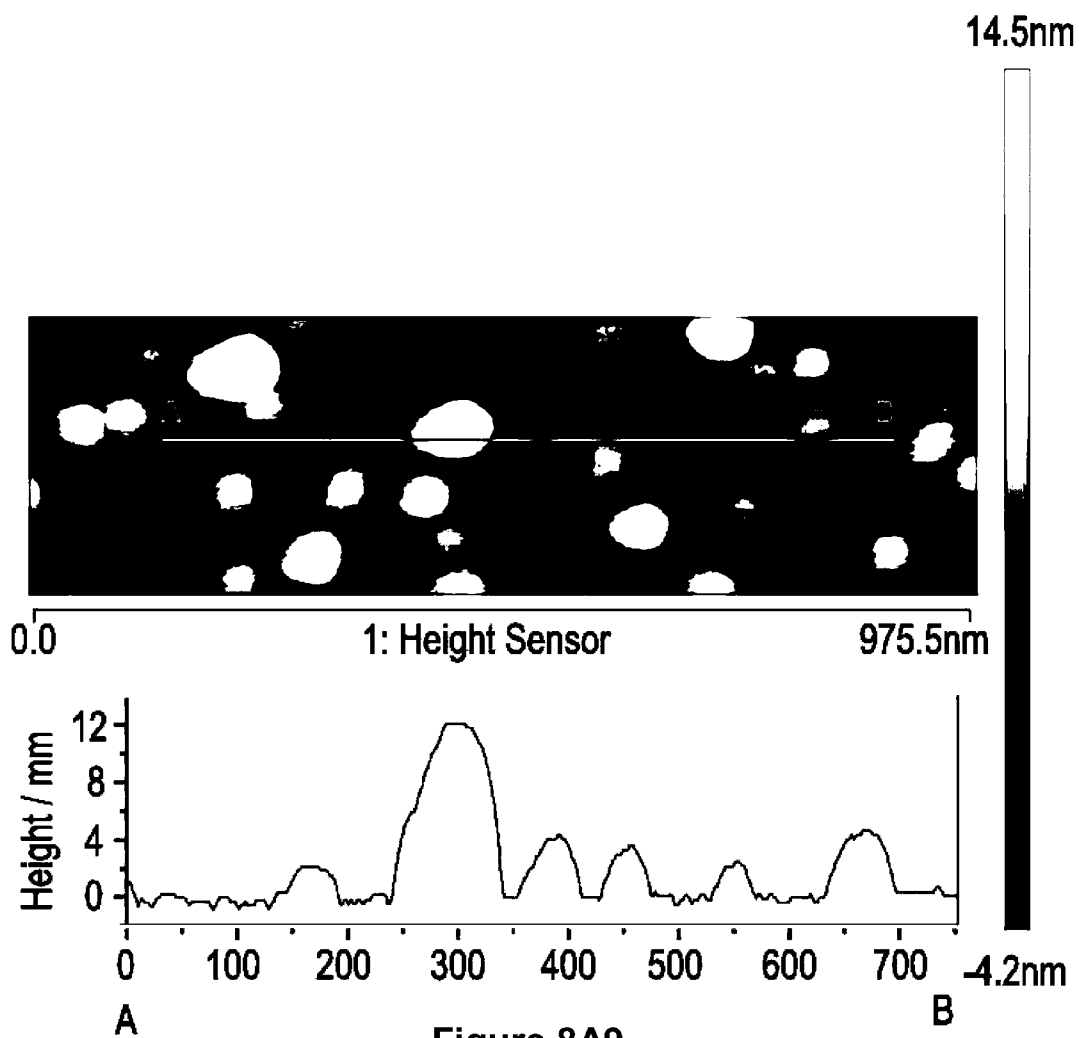


Figure 8A9

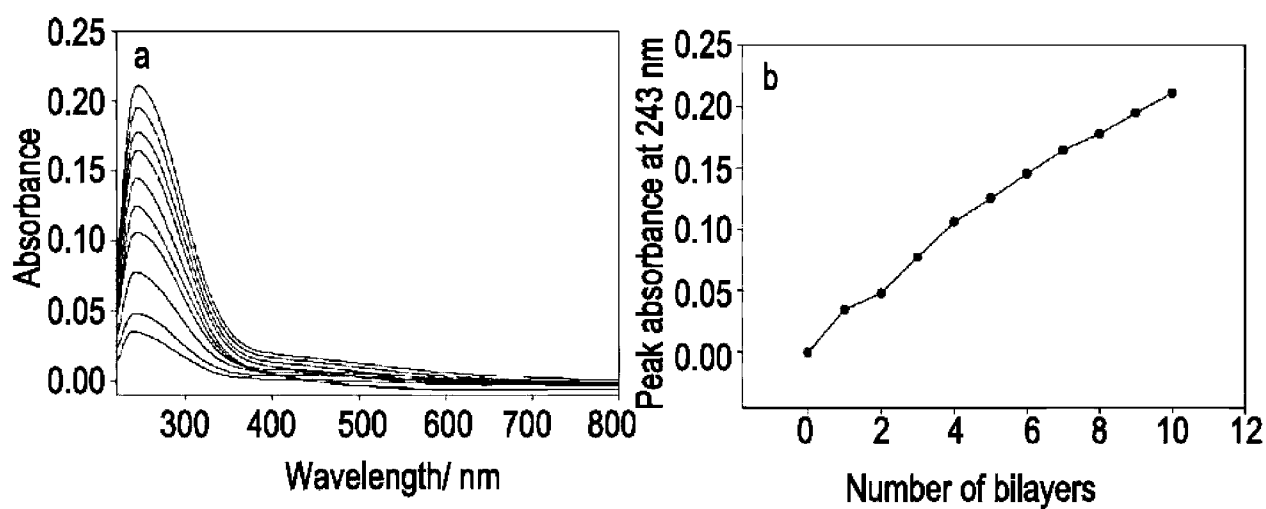


Figure 8A10

- 20/30 -

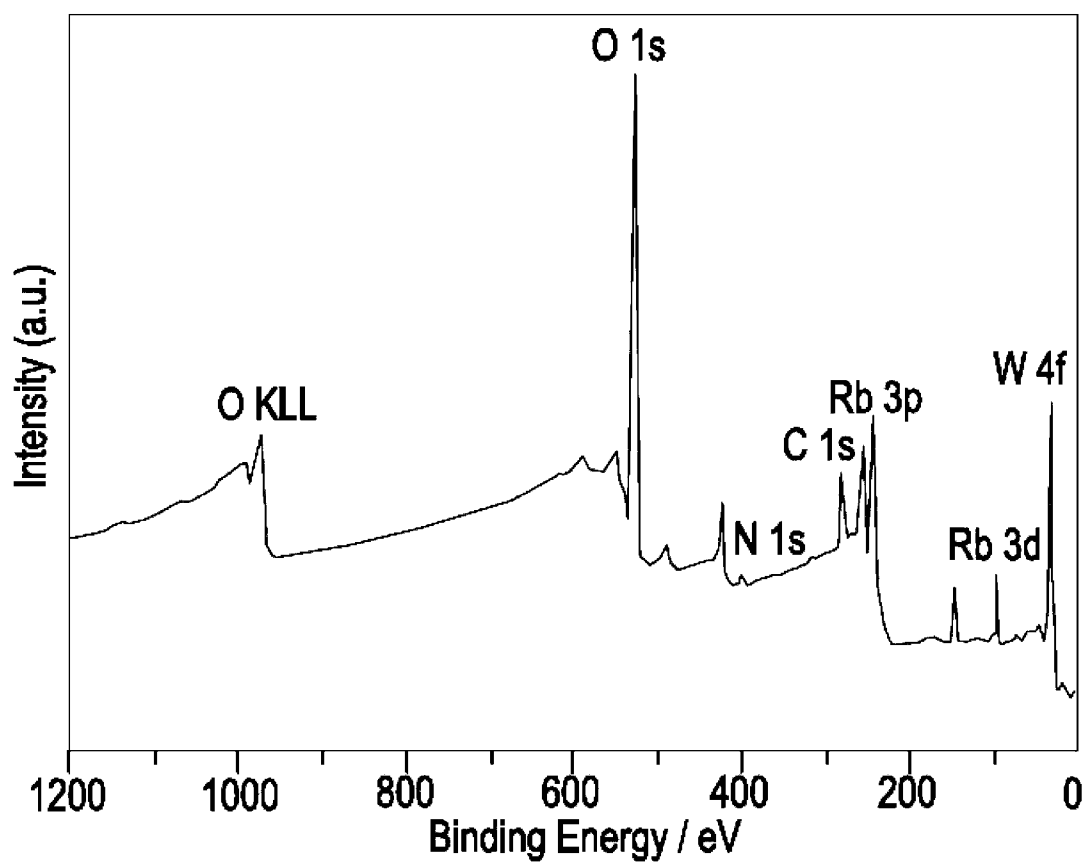


Figure 8A11

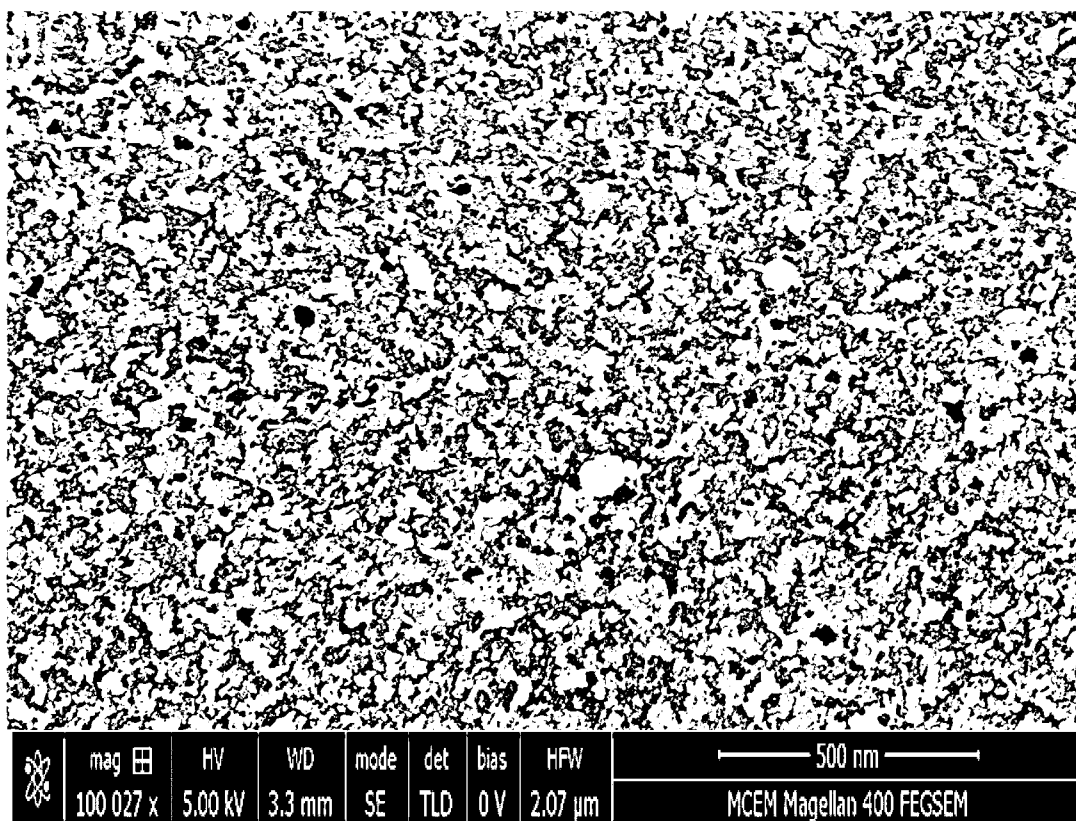


Figure 8A12

- 21/30 -

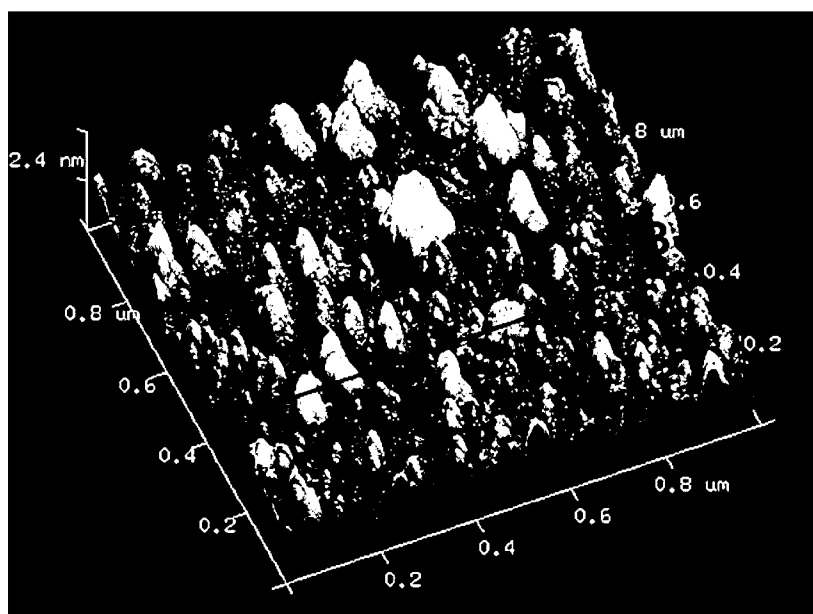
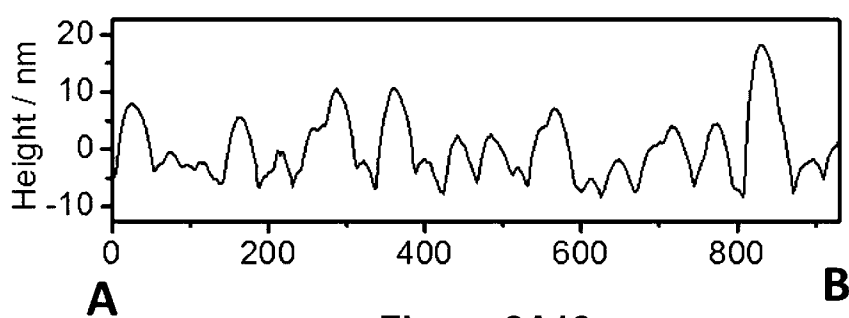


Figure 8A13

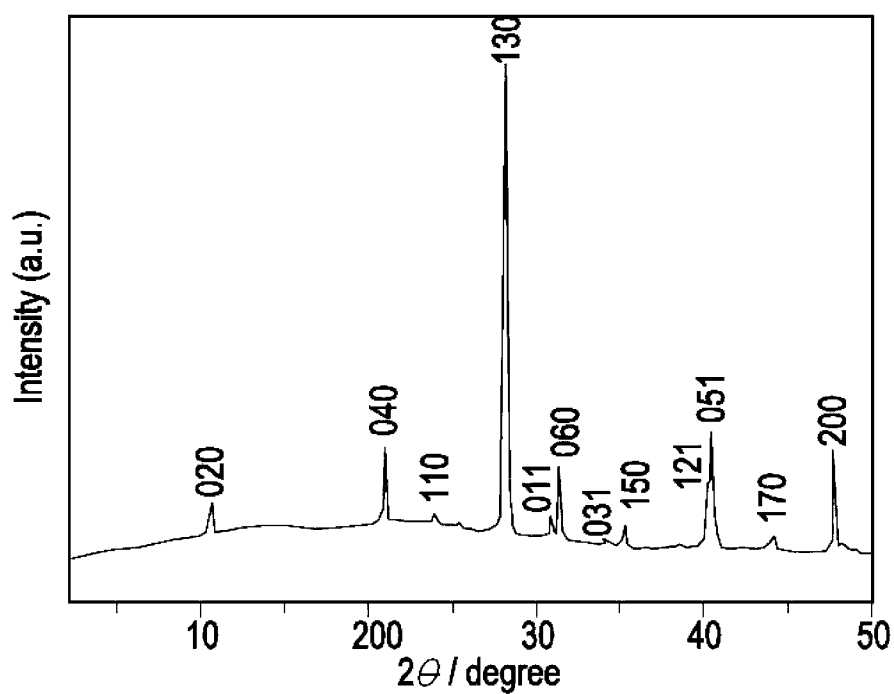


Figure 8A14

- 22/30 -

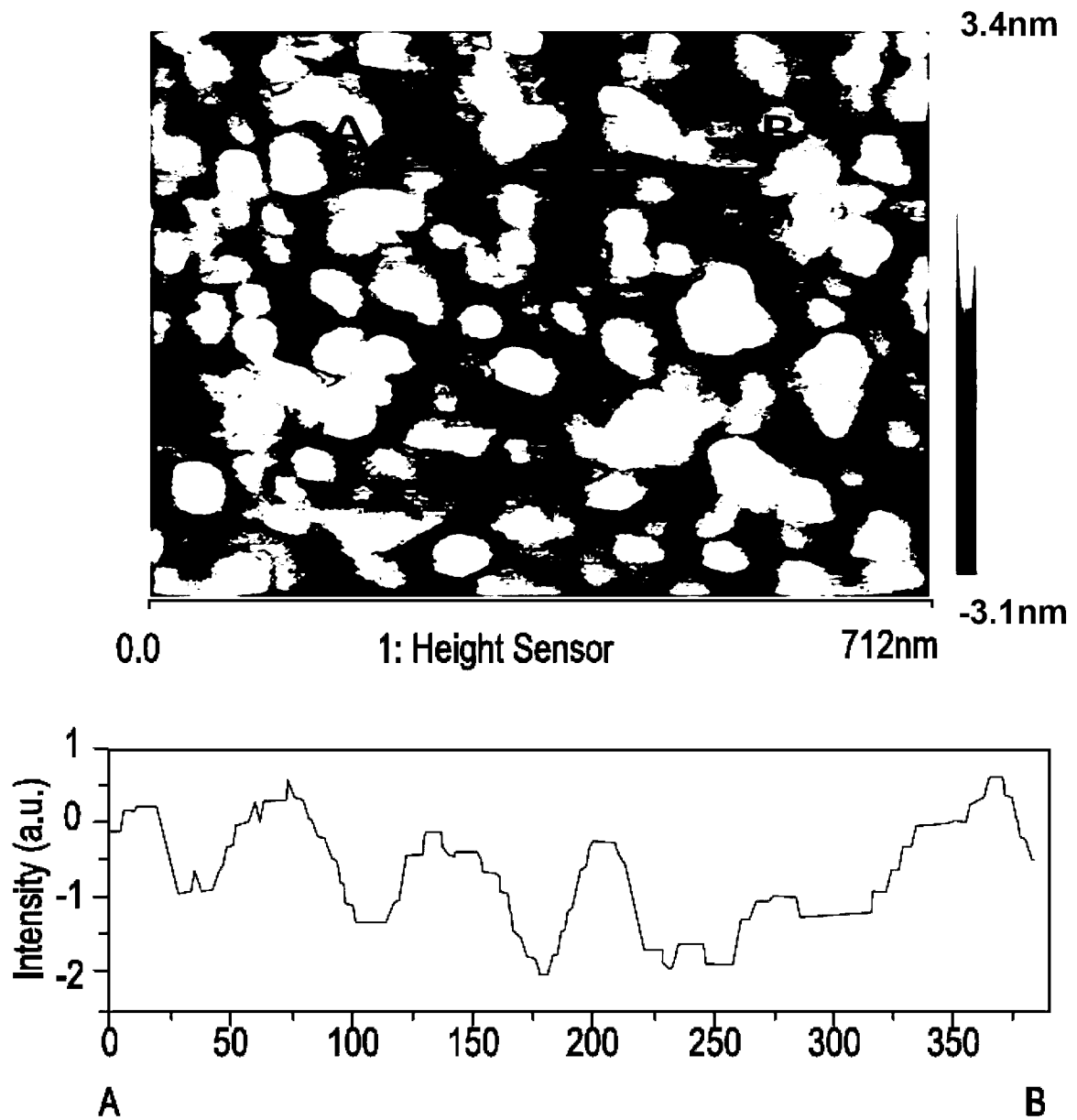


Figure 8A16

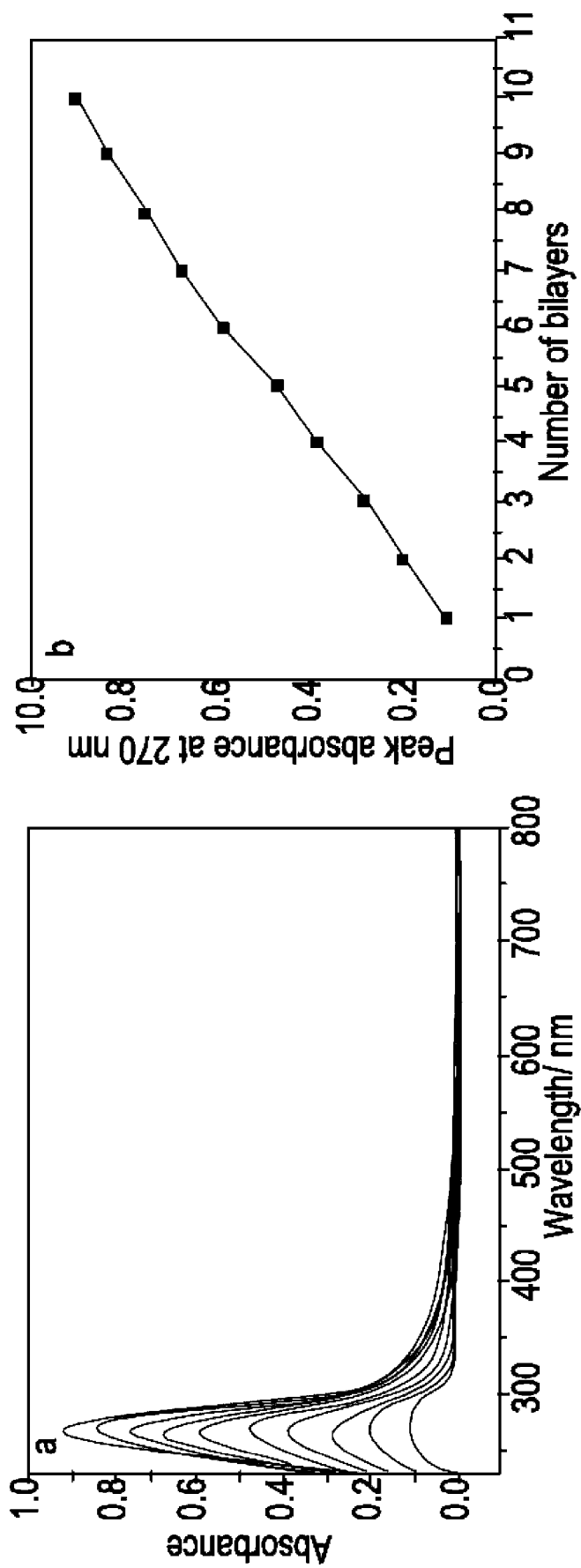


Figure 8A17

- 24/30 -

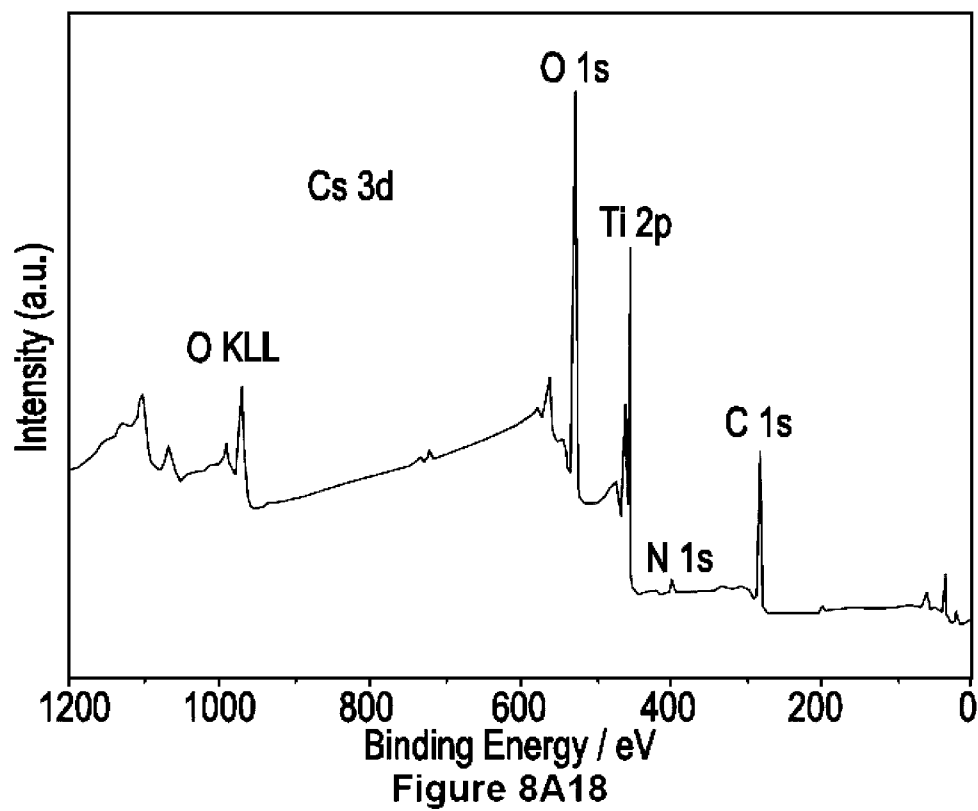
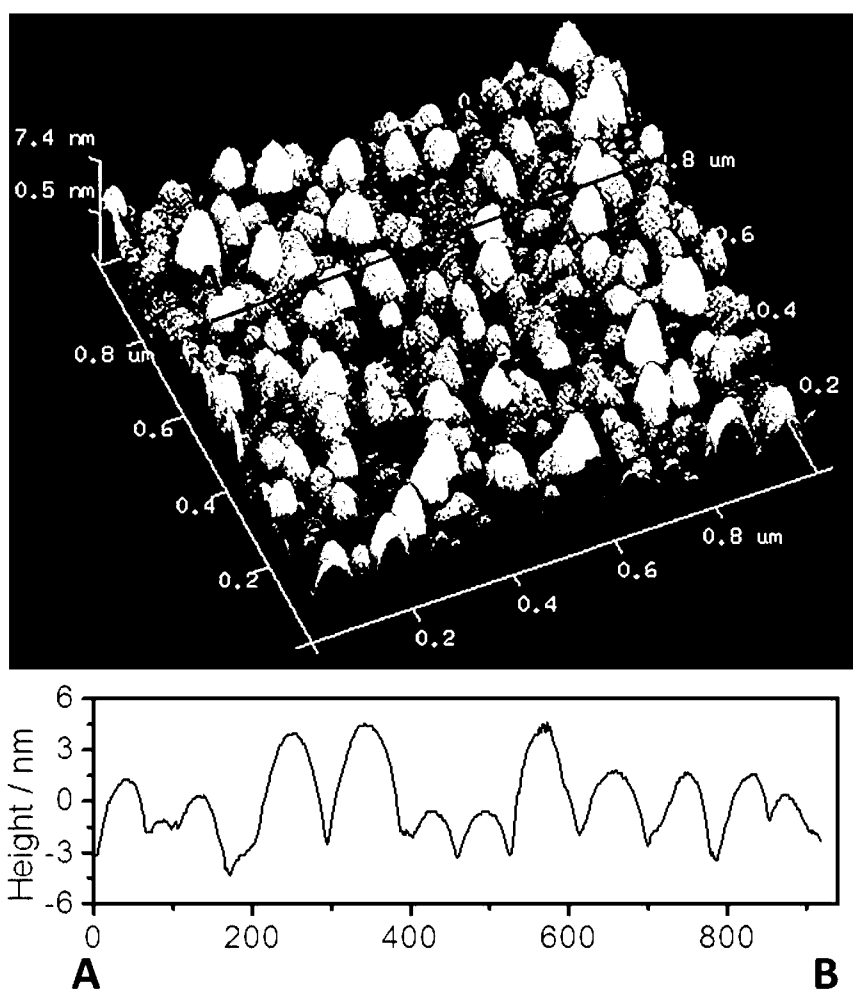
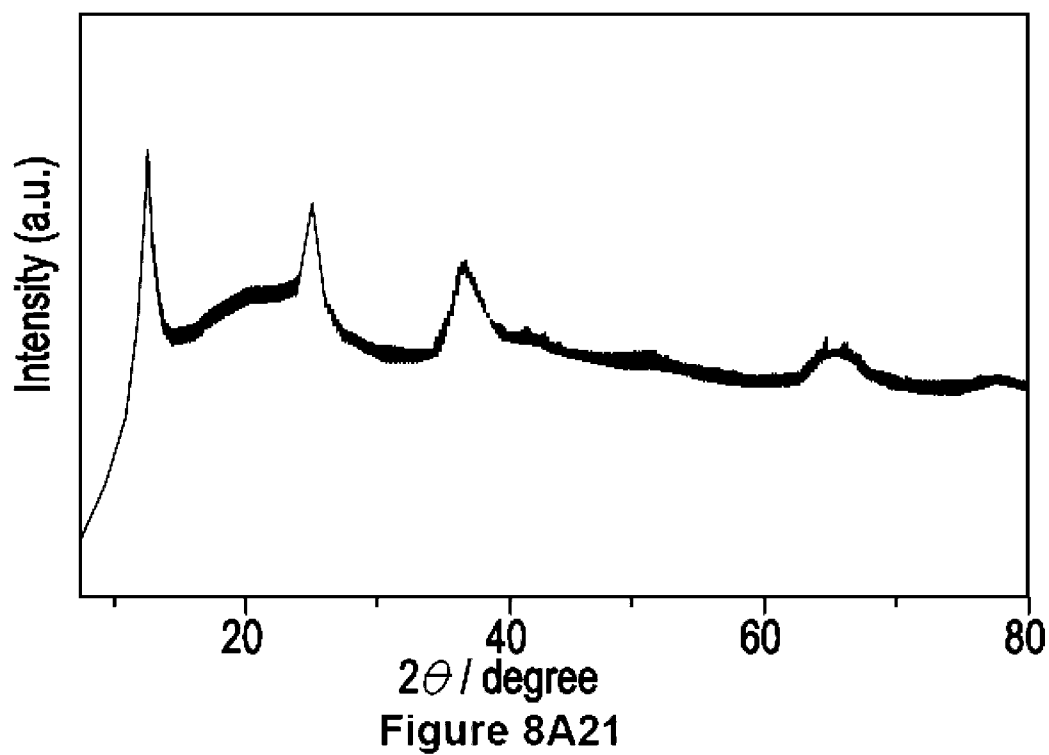
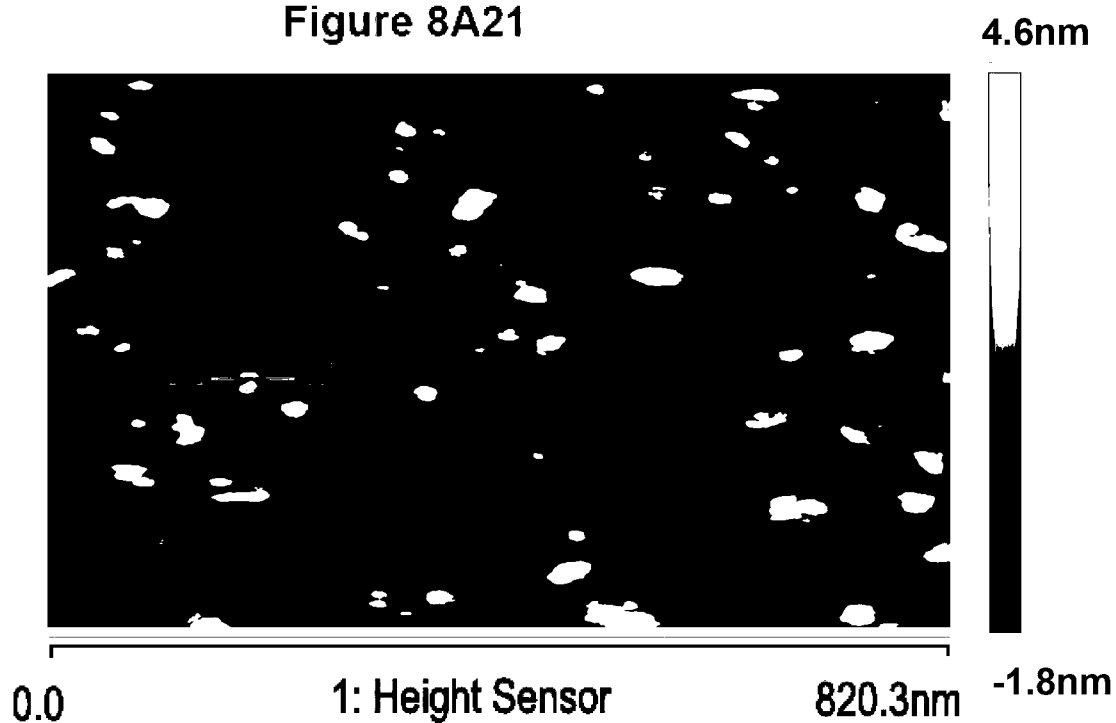
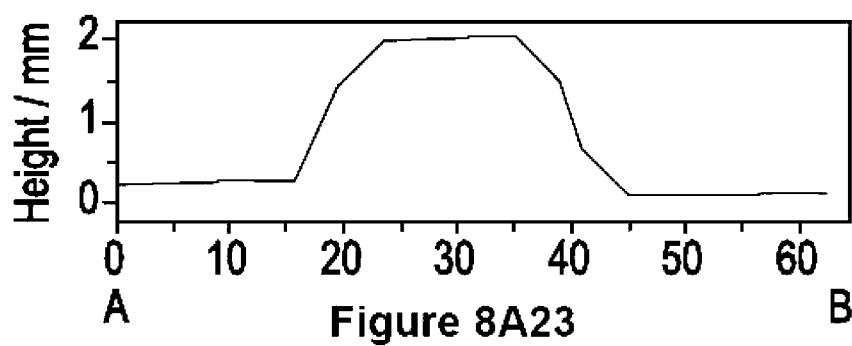


Figure 8A19

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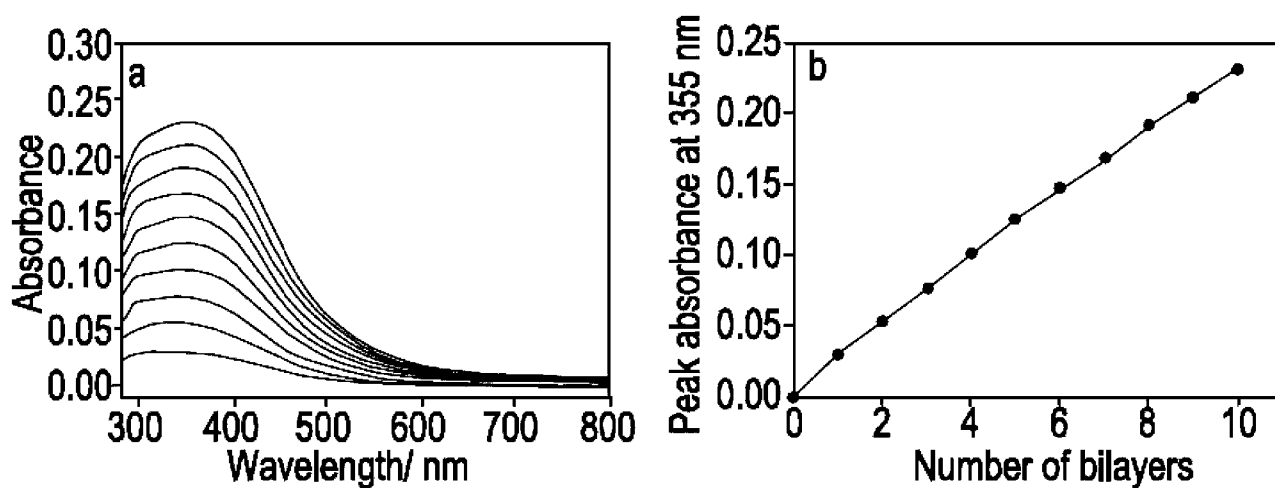


Figure 8A24

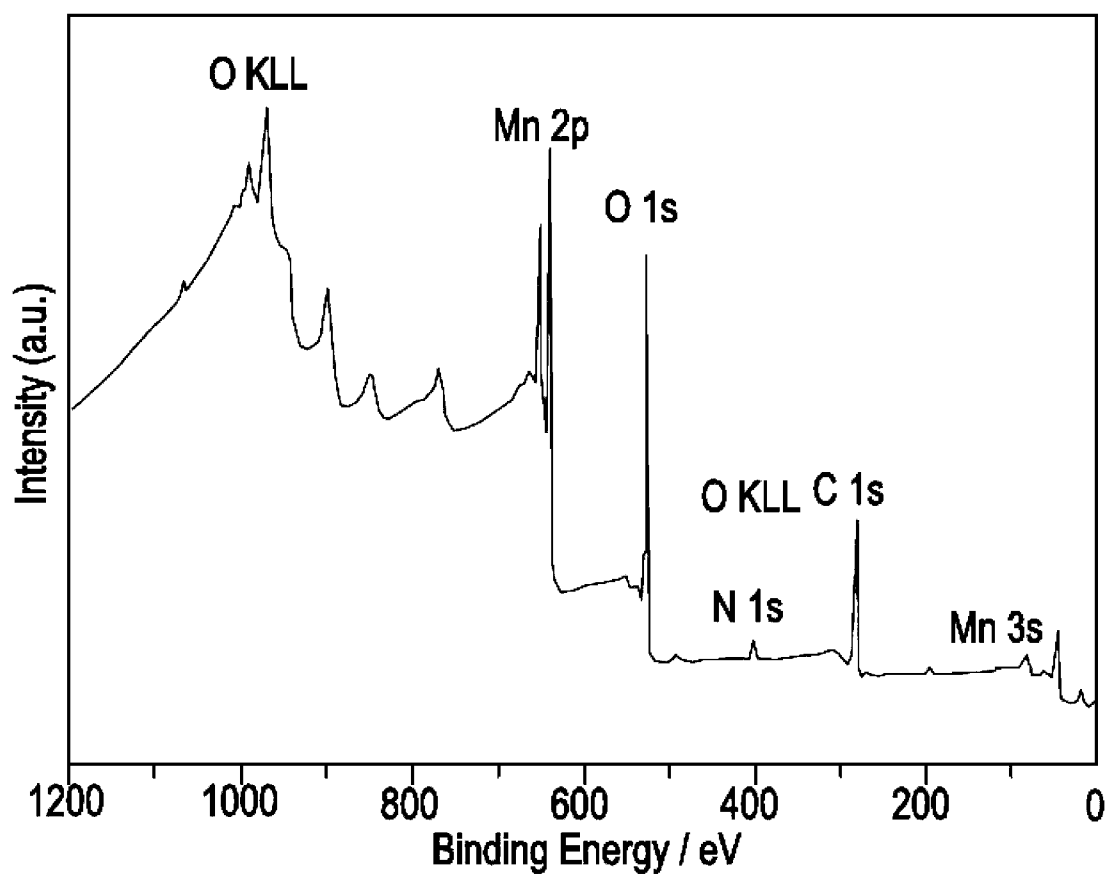


Figure 8A25

- 27/30 -

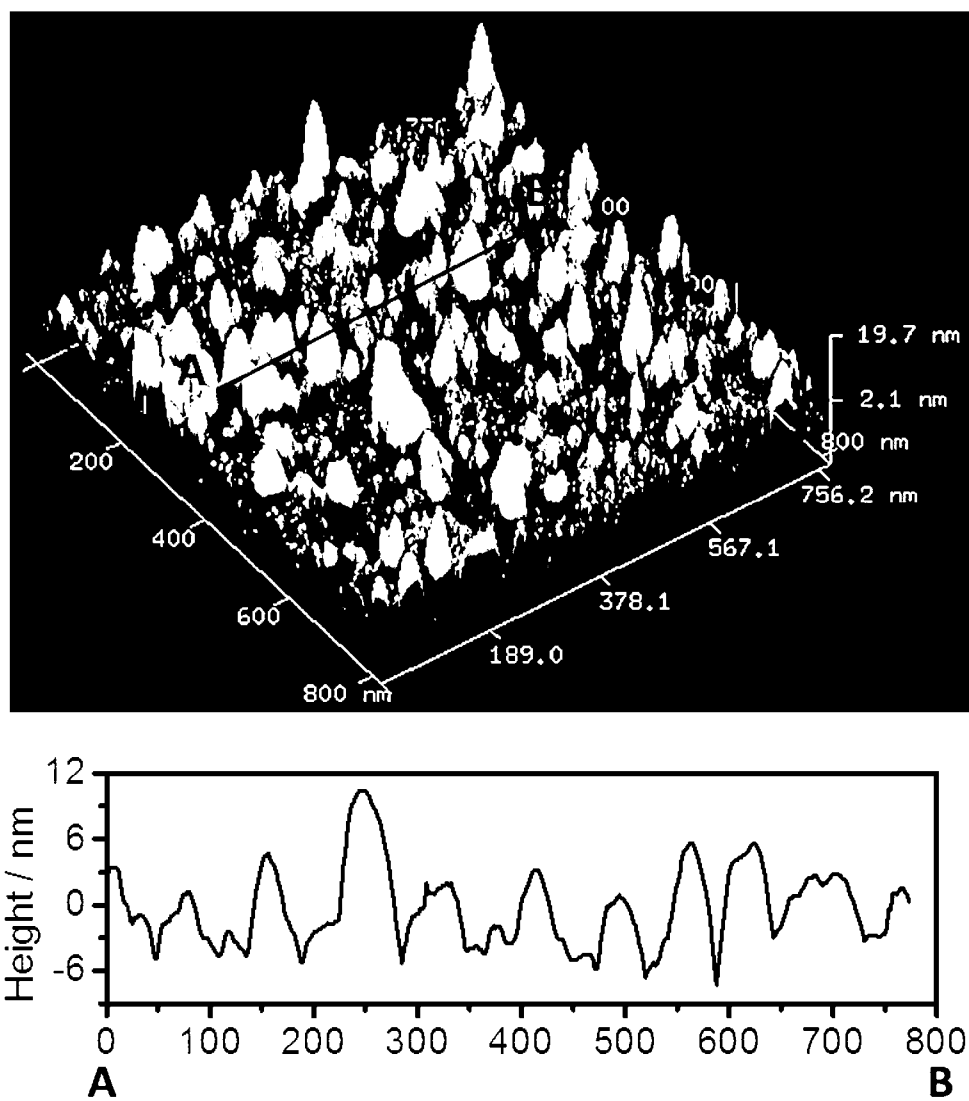


Figure 8A27

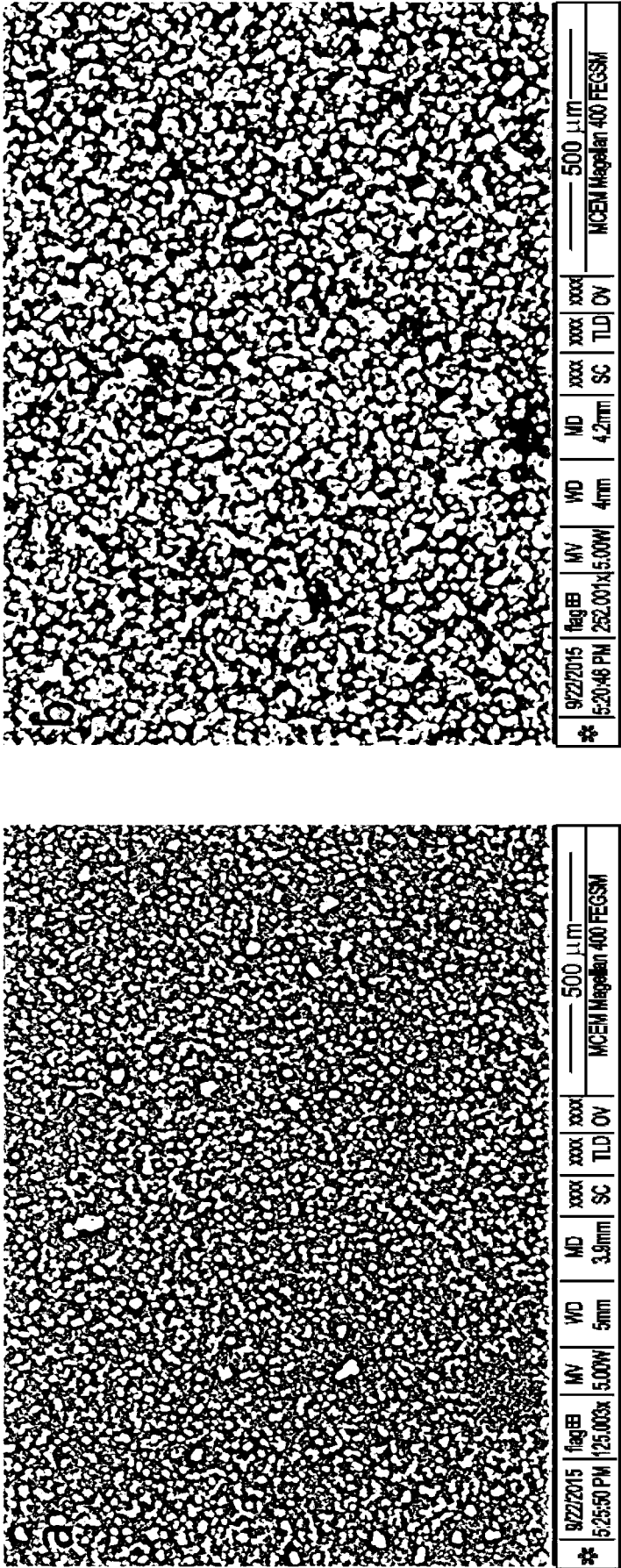


Figure 8A28

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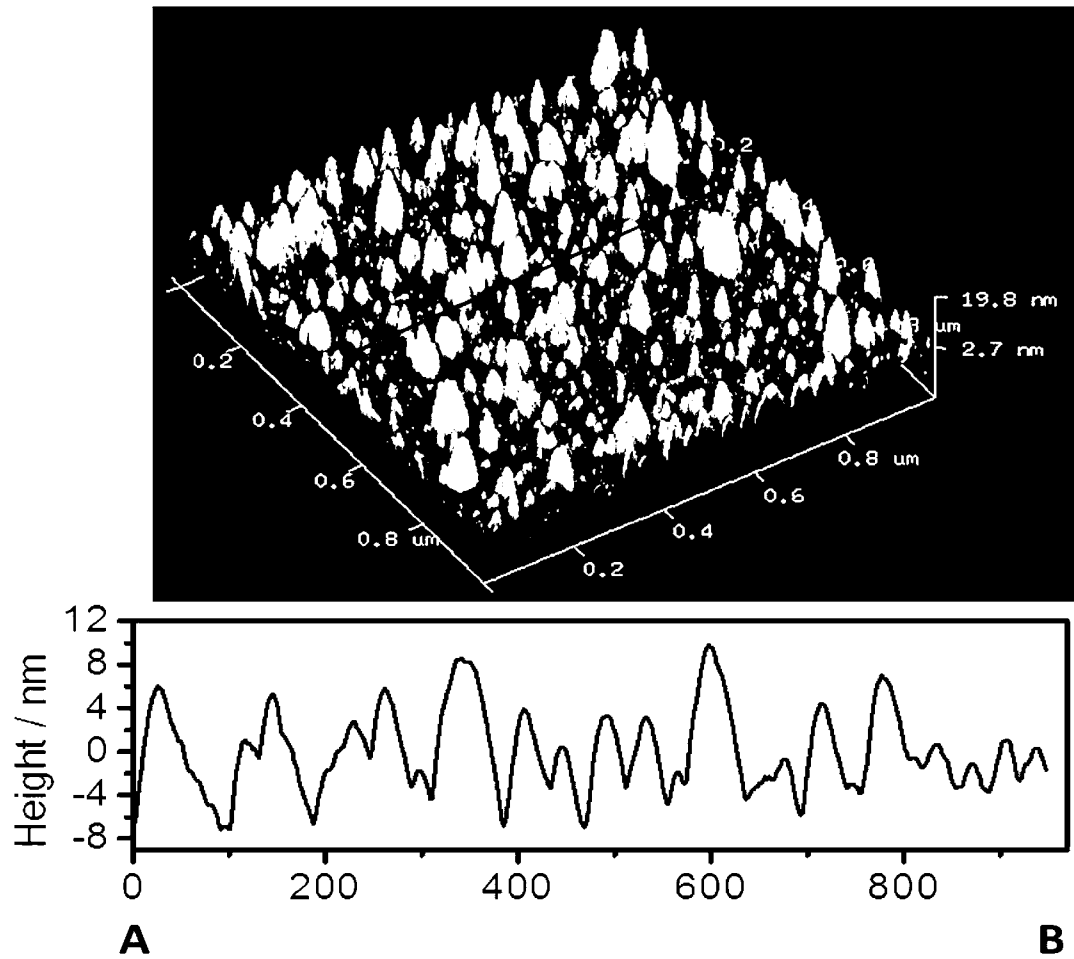


Figure 8A29

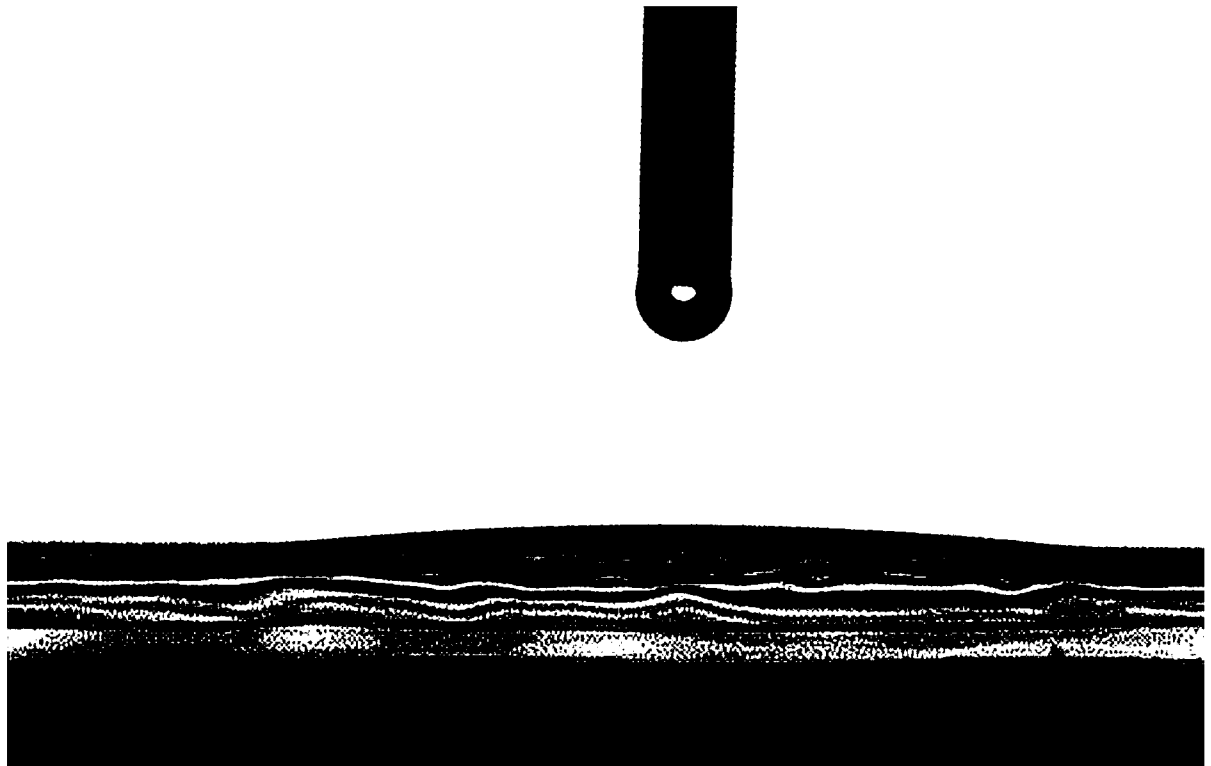


Figure 9

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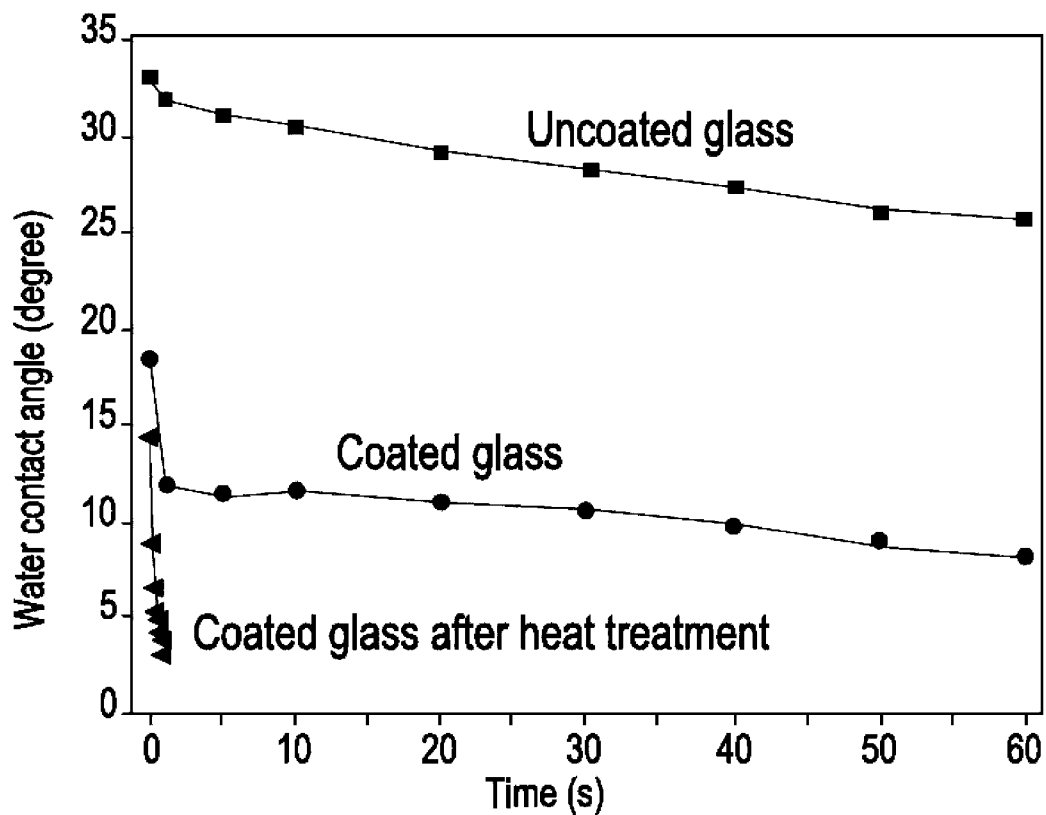


Figure 10

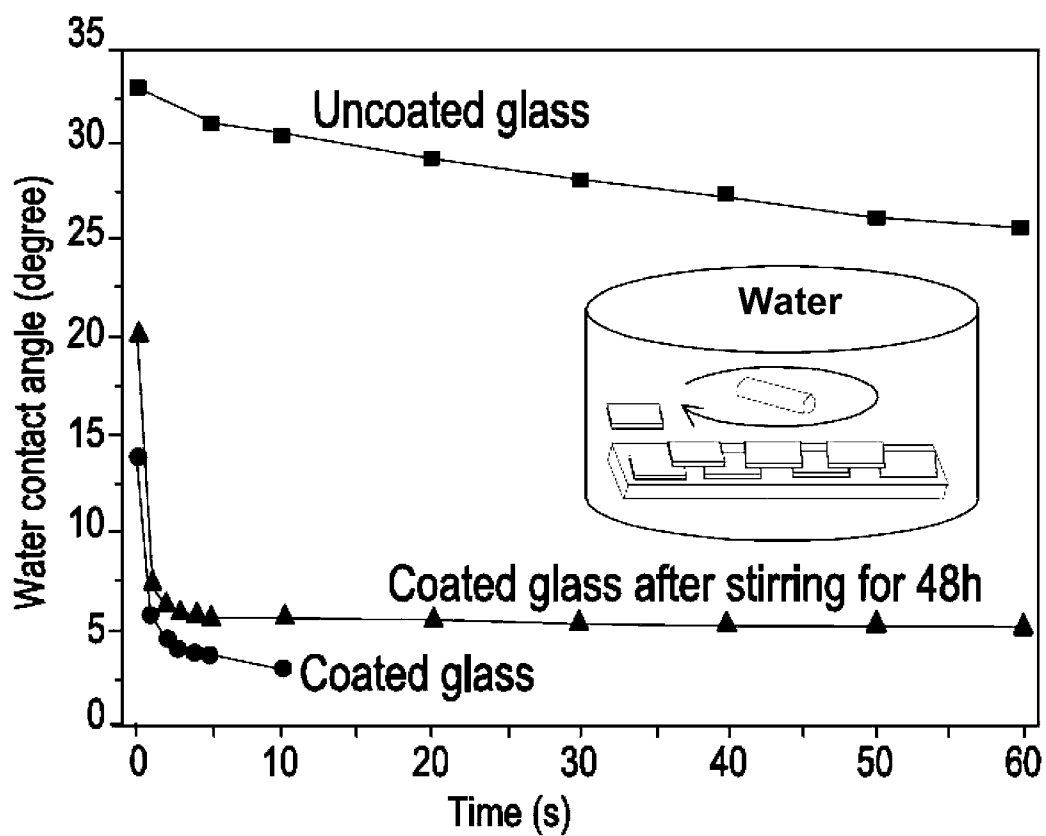


Figure 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2017/050262

A. CLASSIFICATION OF SUBJECT MATTER

C01G 41/02 (2006.01) C03C 17/23 (2006.01) G02B 5/23 (2006.01) B82Y 30/00 (2011.01) B01J 23/30 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, REGISTRY, WPIAP, EPODOC, ESPACENET, GOOGLE PATENTS/SCHOLAR, keywords: nano+, functional, +tungst+, WO3, smart, switchable, intelligent, bronze, plasmon+, electrochromic, thermochromic, self_clean+, superhydrophob+, photocatal+, window?, glass, glazing, insulating, shield+, layer+, monolayer+, bilayer+, film?, self_assembl+, lbl, l-b-l, polycation, positive?? W charge?, tbaoh, exfoliat+, PDDA, DADMAC, PAH, PEI, PANI, cesium, rubidium, Cs, Rb, +diallyldimethylammonium+, +allylamine W hydrochloride, polyethyleneimine, nano_layer+, array, nanodot?, light, irradiat+, solar, sunlight, absorption edge, bandgap, photoelectron, antibacterial, ((OR C01G41/LOW, C03C17/23/LOW, G02B5/208/LOW, G02B5/23, B01J23/30) AND (OR B82Y30/00, C01P2004/64, C01P2004/24, B32B17/LOW, B32B2307/206, B32B2307/212, B32B2307/412, B32B2307/754))/CN, (((Cs or Bi or Li or Rb)/els) and W/els and O/els) and TIS/Cl, ("Films, ultrathin" OR "Monolayers" OR "Nanofilms" OR "Ultrathin films")/CT, (U) ("NANO")/rl, Applicant/Inventor search in CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 22 May 2017		Date of mailing of the international search report 22 May 2017	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Giuseppe Zagari AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262833130	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/050262
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Jung Kyu Kim, et al: "Fabrication of photocatalytic effects of tungsten trioxide nano-pattern arrays" <i>Mater. Express</i> , Vol. 1, No. 3, (2011) 245-251 abstract; chapter 2.4; chapter 4 conclusions; Figures 1-3	1-3, 16-21, 23, 33-36
X	Park Y.T., Grunlan J.C.: "Fast switching electrochromism from colloidal indium tin oxide in tungstate-based thin film assemblies" <i>Electrochimica Acta</i> 55 (2010) 3257-3267 abstract; Introduction, Experimental; Figures 1, 7, see also Figure 2, 8a and Chapter 3.2, chapter 2.2 and 2.3	1-4, 9-12, 16-26, 28-30, 34-36
X	Patrocino, Antonio Otavio T. et al: "Layer-by-layer TiO ₂ /WO ₃ thin films as efficient photocatalytic self cleaning surfaces" <i>ACS Appl. Mater. Interfaces</i> 2014, 6 16859-16866 abstract; Experimental section beginning on p16860 lhc; Table 1; Figures 4, 7, 8; Conclusions p16864, lhc	1-4, 12, 16-23, 28-30, 33, 35, 36
X	Katsutoshi Fukuda, et al: "Photochromogenic nanosheet crystallites of tungstate with a 2D bronze structure" <i>Inorganic Chemistry</i> 2012, 51, 1540-1543 Experimental section p1540, rhc, 1st full paragraph onwards	1-3, 5, 8-9, 12, 16-21, 23-32, 35, 36
X	Keisuke N. et al.: "Monolayered nanodots of transition metal oxides" <i>J. Am. Chem. Soc.</i> 2013, 135, 4501-4508 abstract; Results and Discussion, pg 4502, rhc onwards; p4506, rhc 1st and 2nd full paragraphs; Figures 3-5; conclusions	1-28, 30-32, 35-36
X	Xiaoyong Wu, et al: "A Cs _x WO ₃ /ZnO nanocomposite as a smart coating for photocatalytic environmental cleanup and heat insulation" <i>Nanoscale</i> , 2015, 7, 17048-17054 abstract; p17048, lhc, first full paragraph; Experimental, p 17049, lhc onwards; Figures 2, 4-9	1-3, 8, 12-16, 18-21, 23, 35-36
X	US 2015/0153478 A1 (Sumitomo Metal Mining Co., Ltd.) 04 June 2015 abstract; para 1-10, 51-55, 63, 78, 94, 100, 153 259-261, 280; Examples 3, 5, 6, 8-13, comparative example 1; claims	1-3, 8, 12, 16-18, 20-21, 35, 36
X	US 2014/0127522 A1 (Fujita et al.) 08 May 2014 abstract; para 24-26, 29, 40-43, 46, 49, 77onwards; Examples	1-4, 8, 12, 16-18, 20-21, 35, 36
X	US 2011/0052662 A1 (Nakano et al.) 03 March 2011 abstract; para 4-7, 17, 26-27, 37, 39, 40, 42, 47, 53, 57, 66-67, 71, 107; Examples 2-3, 6-13 of Table 1; claims	1-4, 15-21, 33, 35, 36
Form PCT/ISA/210 (fifth sheet) (July 2009)		

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2017/050262	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2015/0153478 A1	04 June 2015	US 2015153478 A1	04 Jun 2015
US 2014/0127522 A1	08 May 2014	US 2014127522 A1	08 May 2014
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