(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 December 2012 (06.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/165753 A1

(51) International Patent Classification:
*C01B 31/02* (2006.01) *B82B 3/00* (2006.01)
*C01G 9/02* (2006.01)

(21) International Application Number:
PCT/KR2012/001433

(22) International Filing Date:
24 February 2012 (24.02.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2011-0051557 30 May 2011 (30.05.2011) KR

(71) Applicant *(for all designated States except US)*: **KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY** [KR/KR]; 39-1 Hawolgok-dong, Seongbuk-gu, Seoul 136-791 (KR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CHOI, Won-Kook** [KR/KR]; 303-1202, Mokdong Apt., Mok 5-dong, Yangcheon-gu, Seoul 158-753 (KR). **PARK, Dong Hee** [KR/KR]; 202, 167-18, Nonhyeon-dong, Gangnam-gu, Seoul 135-010 (KR). **KWON, Byoung Wook** [KR/KR]; 101-2205, Doosan Apt., Haengdang 1-dong, Seong-dong-gu, Seoul 133-731 (KR). **SON, Dong Ick** [KR/KR]; 102-805, Samsung Apt., Yeomni-dong, Mapo-gu, Seoul 121-776 (KR).

(74) Agent: **HALLA PATENT&LAW FIRM**; 9F KAMCO Yangjae Tower, 949-3 Dogok-dong, Gangnam-gu, Seoul 135-270 (KR).

(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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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.

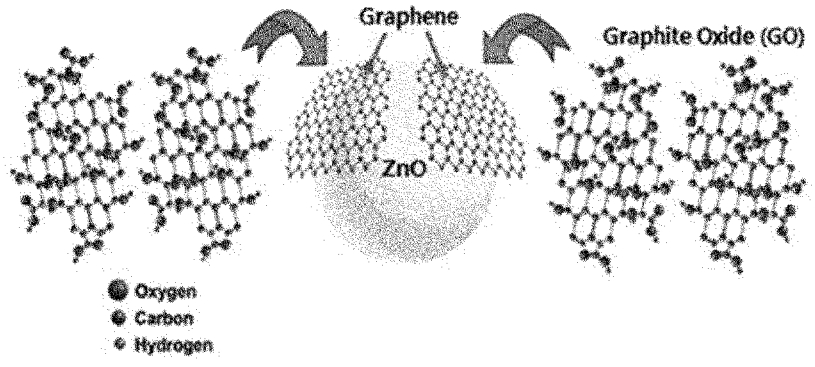
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, 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, ML, MR, NE, SN, TD, TG).

**Published**:

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

(54) **Title**: THE METHOD FOR PRODUCING GRAPHENE BY CHEMICAL EXFOLIATION

[Fig. 1]




(57) **Abstract**: Disclosed are a method for preparing pure graphene using chemical bonding between graphite oxide and a metal oxide nanoparticle, graphene prepared thereby, and a nanoparticle having a quasi metal oxide-graphene core-shell structure. The disclosed method for preparing graphene is advantageous in that the source materials are inexpensive, chemical bonding and separation can be achieved through the simple acid treatment process, and the processing facility does not require high cost since the reaction can be performed at low temperature. Furthermore, pure graphene with less defect can be produced quickly in large quantities because the processing time is short.

WO 2012/165753 A1

# Description

## Title of Invention: THE METHOD FOR PRODUCING GRAPHENE BY CHEMICAL EXFOLIATION

### Technical Field

[0001] The present invention relates to a method for preparing pure graphene using chemical bonding between graphite oxide and a metal oxide nanoparticle, graphene prepared thereby, and a nanoparticle having a quasi metal oxide-graphene core-shell structure.

[0002]

### Background Art

[0003] Graphene, which has a single-atom-thick planar sheet structure and is called the next-generation dream material, is highly esteemed for its characteristic advantages, including excellent thermal conductivity, electron mobility and flexibility in spite of shorter research period than other nanocarbon materials such as carbon nanotube (CNT), fullerene, graphite, etc. The representative potential applications of graphene include the followings.

[0004] I) Graphene can replace the ITO oxide used in the transparent electrode of LEDs, solar cells, etc. With superior flexibility, it can be used in flexible electronic devices to provide flexibility and greatly improve the lifetime and durability of the devices without significantly affecting their performance. Also, graphene can be used as an electrode material of secondary batteries, supercapacitors, or the like.

[0005] II) With high thermal conductivity, graphene is also seen as a new heat-sink material capable of solving the heating problem in the manufacture of high-efficiency, high-luminance III-V GaN LEDs.

[0006] III) With better dispersibility than CNT and high strength in the 2-dimensional planar structure, it can be used as a new material for high-strength carbon composite materials.

[0007] IV) Since the energy of electrons in graphene show a linear relationship with respect to wavenumber in the energy-wavenumber (E-k) curve, the electrons behave with zero (0) effective mass ($m_e^* = \frac{\partial^2 E}{\partial^2 k}$). That is to say, since they move at fast speed like massless photons, graphene allows the fabrication of ultrahigh-fast electronic devices and is highly valued as the next-generation transistor material.

[0008] V) Besides, with very low water vapor transmission rate, graphene can be used as a barrier film material for flexible electronic devices and packaging and medical applications.

[0009] Researches are continuously carried out for methods of preparing pure graphene. The

existing methods of preparing graphene include, in addition to preparation of graphene by physical exfoliation of graphite using Scotch tape, preparation of graphene using CNTs [M. Terrones, Materials science: Nanotubes unzipped, *Nature* 458, 845 (2009)], growth of graphene by chemical vapor deposition (CVD) [K. S. Kim et al, Large-scale pattern growth of graphene films for stretchable transparent electrodes, *Nature* 457, 706 (2009); D.H. Lee et al, Versatile carbon hybrid films composed of vertical carbon nanotubes grown on mechanically compliant graphene films, *Adv. Mater.* 22, 1247 (2010)], chemical exfoliation in liquid phase [A. A. Green et al, Solution phase production of graphene with controlled thickness via density differentiation, *Nano Letters* 9, 4031 (2009)], or the like.

[0010] However, since the known methods are expensive or have difficulty in producing pure graphene, a simple process allowing the production of pure graphene is required.

## Summary of Invention

## Technical Problem

[0011] The inventors of the present invention have studied for a method for easily preparing pure graphene. As a result, they have found out that when graphite oxide is mixed with a metal oxide nanoparticle and treated with an acid, graphene is exfoliated from the surface of a particle having a quasi metal oxide-graphene core-shell structure and is obtained as a sheet.

[0012] The present invention is directed to providing a method for preparing graphene, including mixing graphite oxide with a metal oxide nanoparticle and then treating with an acid.

[0013] The present invention is also directed to providing a nanoparticle having a metal oxide-graphene core-shell structure, with a metal oxide nanoparticle enclosed by graphene, which is obtained by mixing graphite oxide with a metal oxide nanoparticle.

[0014]

## Solution to Problem

[0015] In one general aspect, the present invention provides a method for preparing graphene using a metal oxide, including: 1) treating the surface of graphite with an acid to prepare graphite oxide; 2) mixing the graphite oxide with a metal oxide nanoparticle to prepare a particle in which carbon is bound to the metal oxide; and 3) separating graphene from the prepared particle by treating with an acid.

[0016] In another general aspect, the present invention provides graphene prepared by the preparation method.

[0017] In another general aspect, the present invention provides a nanoparticle having a metal oxide-graphene core-shell structure prepared from a reaction of graphite oxide with a metal oxide nanoparticle, wherein graphene encloses the metal oxide

nanoparticle.

[0018]

## Advantageous Effects of Invention

[0019] The method for preparing graphene according to the present invention is advantageous in that the source materials are inexpensive, chemical bonding and separation can be achieved through the simple acid treatment process, and the processing facility does not require high cost since the reaction can be performed at low temperature. Furthermore, pure graphene with less defect can be produced quickly in large quantities because the processing time is short.

[0020] In addition, since the particle having a quasi metal oxide-graphene core-shell structure obtained as an intermediate is enclosed by graphene with a very high electron mobility, it exhibits very fast electron transfer rate and response speed as well as superior optical characteristics. Accordingly, it can replace $TiO_2$ in the electron transport layer of metal oxide quantum dot-based UV sensors, LEDs and dye-sensitized solar cells (DSSC).

[0021]

## Brief Description of Drawings

[0022] FIG. 1 schematically shows exfoliation of the surface of a graphite oxide layer from a zinc oxide nanoparticle.

[0023] FIG. 2 schematically shows chemical bonding between the functional groups (carboxyl, hydroxy and epoxy groups) of an exfoliated carbon single layer and zinc oxide nanoparticles.

[0024] FIG. 3 schematically shows a particle having a quasi metal oxide-graphene core-shell structure wherein graphene encloses a zinc oxide nanoparticle.

[0025] FIG. 4 schematically shows graphene prepared by removing zinc oxide from a particle having a quasi zinc oxide-graphene core-shell structure.

[0026] FIG. 5 shows transmission electron microscopic images of a particle having a quasi zinc oxide-graphene core-shell structure prepared in Example 1.

[0027] FIG. 6 shows a transmission electron microscopic image and scanning electron microscopic images (top left and right) of graphene prepared in Example 1.

[0028] FIG. 7 shows X-ray diffraction patterns of a particle having a quasi zinc oxide-graphene core-shell structure and graphene (top right) prepared in Example 1.

[0029] FIG. 8 shows a Raman spectrum of a particle having a quasi zinc oxide-graphene core-shell structure prepared in Example 1.

[0030] FIG. 9 shows a Raman spectrum of graphene prepared in Example 1.

[0031] FIG. 10 shows an analysis result of graphene prepared in Example 1 by electron energy loss spectroscopy (EELS).

[0032] FIG. 11 shows an analysis result of graphene prepared in Example 1 by energy-dispersive X-ray spectroscopy (EDX).

[0033] FIG. 12 shows an analysis result of graphene prepared in Example 1 by X-ray photo-electron spectroscopy (XPS).

[0034] FIG. 13 shows a transmission electron microscopic image of a particle having a quasi copper oxide-graphene core-shell structure prepared in Example 2.

[0035] FIG. 14 shows an X-ray diffraction pattern of a particle having a quasi copper oxide-graphene core-shell structure prepared in Example 2.

[0036]

## Best Mode for Carrying out the Invention

[0037] Hereinafter, the embodiments of the present invention will be described in detail with reference to accompanying drawings.

[0038] The present invention provides a method for preparing pure graphene using chemical bonding between graphite oxide and a metal oxide nanoparticle.

[0039] The method for preparing graphene according to the present invention comprises: 1) treating the surface of graphite with an acid to prepare graphite oxide; 2) mixing the graphite oxide with a metal oxide nanoparticle to prepare a particle in which carbon is bound to the metal oxide; and 3) separating graphene from the prepared particle by treating with an acid.

[0040] First, the surface of graphite is treated with an acid to form graphite oxide having a functional group on the graphite surface. The acid treatment can be performed by adding graphite in powder form to an acid and carrying out reaction. As a result, functional groups such as carboxyl (-COOH), hydroxy (-OH) or epoxy groups may be formed on the graphite surface. The acid may be one or more selected from sulfuric acid, nitric acid and hydrochloric acid. Specifically, a mixture of sulfuric acid and nitric acid may be used.

[0041] The acid-treated graphite turns dark gray, which is washed and dried to obtain graphite oxide.

[0042] Then, the prepared graphite oxide is mixed with a metal oxide nanoparticle to prepare a particle wherein carbon is bound to the metal oxide. When the graphite oxide is mixed with the metal oxide nanoparticle, a solid component is formed in solution, which is dried to obtain the particle wherein carbon is bound to the metal oxide.

[0043] Although the metal oxide is not particularly limited, it may be selected from, specifically, ZnO, CuO, $BaCO_3$, $Bi_2O_3$, $B_2O_3$, $CaCO_3$, $CeO_2$, $CrO_2$, $Cr_2O_3$, FeO, CoO, NiO, GeO, $Y_2O_3$, $ZrO_2$, MoO, $RuO_2$, PdO, AgO, CdO, SnO, $HfO_2$, $Ta_2O_5$, $Fe_2O_3$, $Ga_2O_3$, $In_2O_3$, $Li_2CO_3$, $LiCoO_2$, MgO, $IrO_2$, $Al_2O_3$, $SiO_2$, $P_2O_5$, $PO_2$, CaO, $Sc_2O_3$, $Mn_2O_3$, $MnCO_3$, $MnO_2$, $Mn_3O_4$, $Nb_2O_5$, PbO, $Sb_2O_3$, $SnO_2$, $SrCO_3$, $Ta_2O_5$, $TiO_2$, $BaTiO_3$, $VO_2$,

$V_2O_5$, $WO_3$, $Bi_2O_3$ and $ZrO_2$. More specifically, ZnO or CuO may be used.

[0044] The metal oxide nanoparticle may be prepared by dissolving a precursor of the metal oxide in a solvent. The metal oxide precursor is not particularly limited. Any compound that can be dissolved in a reaction solvent to give the metal oxide nanoparticle can be used, such as acetate, acetate monohydrate, acetate dihydrate, nitrate tetrahydrate or nitrate hexahydrate of the metal.

[0045] Specifically, the graphite oxide and the metal oxide nanoparticle may be mixed in a reaction solvent. The reaction solvent may be N,N-dimethylformamide or N,N-diethylformamide, specifically N,N-dimethylformamide.

[0046] Specifically, the precursor of the metal oxide may be dissolved in the solvent at a concentration of 0.0001-0.1 M. A uniform distribution of the metal oxide nanoparticle may be attained with the aforesaid range.

[0047] Although the mixing of the graphite oxide with the metal oxide nanoparticle may be achieved in a single reaction solution, they may also be dispersed in different solvents to prepare a graphite oxide solution and a metal oxide solution and then mixed. In this case the mixing ration of the two solutions may be from 1 : 1 to 1 : 10 based on volume.

[0048] As the graphite oxide is mixed with the metal oxide nanoparticle, through chemical bonding between the functional groups (carboxyl, hydroxy and epoxy groups) formed on the surface of graphite consisting of multiple layers of carbon and the metal oxide nanoparticle, the carbon layer is exfoliated and encloses the circumference of the metal oxide nanoparticle as it bends to form a particle having a quasi metal oxide-graphene core-shell structure.

[0049] Then, acid treatment is carried out to dissolve the metal oxide located at the core portion of the particle having a quasi metal oxide-graphene core-shell structure. As the metal oxide is dissolved by the acid, the bent graphene is spread to give a single-layer sheet.

[0050] Specifically, the acid used for the acid treatment may be a strong acid of pH 5 or lower. More specifically, one or more selected from hydrochloric acid, nitric acid and sulfuric acid may be used to dissolve the metal oxide.

[0051] The process by which the particle having a quasi metal oxide-graphene core-shell structure is prepared is schematically shown in FIGS. 1 to 4.

[0052] The present invention also provides graphene prepared by the above-described process. The graphene may have a multi-layer structure of 1-10 layers, specifically 1-5 layers, of carbon atoms and may have a thickness of 0.34-3.4 nm.

[0053] The present invention further provides a nanoparticle having a metal oxide-graphene core-shell structure prepared from a reaction of graphite oxide with a metal oxide nanoparticle, wherein graphene encloses the metal oxide nanoparticle. The

nanoparticle has a structure consisting of a metal oxide core and a single-layer graphene shell exfoliated from graphite oxide and bent to enclose the core.

[0054]

## Mode for the Invention

[0055] The examples and experiments will now be described.

[0056] The following examples and experiments are for illustrative purposes only and not intended to limit the scope of the present invention.

[0057] **Preparation Example: Preparation of graphite oxide**

[0058] First, 30 mg of graphite powder (Alfa Aesar) was added to a 3 : 1 (v/v) mixture of 18 M sulfuric acid ($H_2SO_4$) and 17 M nitric acid ($HNO_3$) and sonicated for 2 hours at 45 ℃, at 200 W.

[0059] The sonicated dispersion was kept at room temperature for about 4 days until the color of the dispersion turned dark gray. The dispersion was centrifuged and gradient separated repeatedly, washed with ethanol and dried in an oven of 55 ℃ for 12 hours to obtain gray graphite oxide.

[0060] **Example 1: Preparation of ZnO-graphene nanoparticle**

[0061] 40 mg of graphite oxide obtained in Preparation Example was added to 40 mL of N,N-dimethylformamide and sonicated for 10 minutes to obtain a graphite oxide dispersion.

[0062] Meanwhile, 0.93 g of zinc acetate dehydrate ($[Zn(CH_3COO)_2 \cdot H_2O]$) was added to 200 mL of N,N-dimethylformamide to obtain a zinc precursor solution.

[0063] The zinc acetate dehydrate can be converted to zinc oxide in N,N-dimethylformamide according to Scheme 1.

[0064] [Scheme 1]

[0065] $Zn(CH_3COO)_2 \cdot H_2O + (CH_3)2NC(O)H \rightarrow ZnO + (CH_3COO)_2CHN(CH_3)_2 + H_2O$

[0066] Then, the graphite oxide dispersion was added to the zinc precursor solution and stirred at 95 ℃ at a speed of 150 rpm. The mixture solution, which was initially black, turned transparent 30 minutes later. After 1 hour, the solution became hazy and turned white gradually. After 5 hours, gray solid was formed out of the transparent solution.

[0067] The solid was separated, washed with ethanol and distilled water and dried in an oven at 55 ℃ for 12 hours to obtain nanoparticles having a quasi zinc oxide-graphene core-shell structure as powder.

[0068] The powder was added to 100 mL of 0.1 M nitric acid and sonicated for 20 minutes. The resulting dispersion was diluted by continuously adding water.

[0069] Lastly, the diluted solution was filtered to separate the product. After washing with ethanol and distilled water, followed by vacuum concentration, graphene was obtained as the final product.

[0070] High-resolution transmission electron microscopic (TEM) images of the nanoparticle powders having a quasi zinc oxide-graphene core-shell structure are shown in FIG. 5.

[0071] Also, a high-resolution TEM image and scanning electron microscopic images (SEM) of the finally produced graphene are shown in FIG. 6. As seen from the TEM image, graphene was formed up to five layers. And, the SEM images showed that the graphene was thinly dispersed on the whole.

[0072] X-ray diffraction patterns (Rigaku ATX-G, Cu $K_\alpha$ = 0.154 nm) of the nanoparticle powders having a quasi zinc oxide-graphene core-shell structure and the finally produced graphene are shown in FIG. 7. As seen from FIG. 7, zinc oxide nuclei grown in the (100), (002) and (101) directions and the graphene shell formed along the (002) and (100) directions were observed for the nanoparticle powder. Also, the X-ray diffraction pattern of the graphene shows that graphene was grown only in the (002) and (100) directions.

[0073] Raman spectra of the nanoparticle powders having a quasi zinc oxide-graphene core-shell structure and the finally produced graphene are shown in FIGS. 8 and 9.

[0074] As seen from FIG. 8, it was confirmed that single-layer graphene encloses the particle via chemical bonding as a shell.

[0075] Also, as seen from FIG. 9, the $I_D/I_G$ ratio of D band and G band was very small as 0.05, suggesting low defect rate of the prepared graphene.

[0076] An electron energy loss spectroscopy (EELS) spectrum of the prepared graphene is shown in FIG. 10. As seen from FIG. 10, the π- and σ-bonding peaks confirmed that the graphene was prepared. The intensity of the σ-bonding peak was considerably lower than that of the graphene prepared according to the existing methods, suggesting that the graphene produced according to the present invention has very high purity.

[0077] Analysis results of the prepared graphene by energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) are shown in FIGS. 11 and 12. It was confirmed that the graphene consist only of carbon, without any impurities.

[0078] **Example 2: Preparation of CuO-graphene nanoparticle**

[0079] 40 mg of graphite oxide obtained in Preparation Example was added to 40 mL of N,N-dimethylformamide and sonicated for 10 minutes to obtain a graphite oxide dispersion.

[0080] Meanwhile, 0.93 g of copper(II) acetate monohydrate ($[Cu(CH_3COO)_2 \cdot H_2O]$) was added to 200 mL of N,N-dimethylformamide to obtain a copper precursor solution. Then, the graphite oxide dispersion was added to the copper precursor solution and stirred at 95 °C at a speed of 150 rpm. The mixture solution, which was initially black, turned transparent 30 minutes later. After 1 hour, the solution became hazy and turned white gradually. After 5 hours, khaki solid was formed out of the transparent solution.

[0081] The solid was separated, washed with ethanol and distilled water and dried in an

oven at 55 °C for 12 hours to obtain nanoparticles having a quasi copper oxide-graphene core-shell structure as powder.

[0082] The powder was added to 100 mL of 0.1 M hydrochloric acid and sonicated for 20 minutes. The resulting dispersion was diluted by continuously adding water.

[0083] Lastly, the diluted solution was filtered to separate the product. After washing with ethanol and distilled water, followed by vacuum concentration, graphene was obtained as the final product.

[0084] High-resolution TEM images of the nanoparticle powders having a quasi copper oxide-graphene core-shell structure are shown in FIG. 13.

[0085] Also, X-ray diffraction patterns of the nanoparticle powders having a quasi copper oxide-graphene core-shell structure and the finally produced graphene are shown in FIG. 14. As seen from FIG. 14, copper oxide (CuO, $Cu^{2+}$) nuclei grown in the (100), (002), (111) and (210) directions were observed for the nanoparticle powder. $Cu_2O$ ($Cu^{+}$) peak was not observed. Also, the X-ray diffraction pattern of the graphene shows that graphene was grown in the (002) and (100) directions.

[0086] The present application contains subject matter related to Korean Patent Application No. 10-2011-0051557, filed in the Korean Intellectual Property Office on May 30, 2011, the entire contents of which is incorporated herein by reference.

[0087] Those skilled in the art will appreciate that the conceptions and specific embodiments disclosed in the foregoing description may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present invention. Those skilled in the art will also appreciate that such equivalent embodiments do not depart from the spirit and scope of the invention as set forth in the appended claims.

# Claims

[Claim 1] A method for preparing graphene using a metal oxide, comprising:
treating the surface of graphite with an acid to prepare graphite oxide;
mixing the graphite oxide with a metal oxide nanoparticle to prepare a particle in which carbon is bound to the metal oxide; and
separating graphene from the prepared particle by treating with an acid.

[Claim 2] The method for preparing graphene according to Claim 1, wherein the particle in which carbon is bound to the metal oxide has a quasi metal oxide-graphene core-shell structure with the metal oxide nanoparticle enclosed by graphene.

[Claim 3] The method for preparing graphene according to Claim 1, wherein the metal oxide is selected from ZnO, CuO, $BaCO_3$, $Bi_2O_3$, $B_2O_3$, $CaCO_3$, $CeO_2$, $CrO_2$, $Cr_2O_3$, FeO, CoO, NiO, GeO, $Y_2O_3$, $ZrO_2$, MoO, $RuO_2$, PdO, AgO, CdO, SnO, $HfO_2$, $Ta_2O_5$, $Fe_2O_3$, $Ga_2O_3$, $In_2O_3$, $Li_2CO_3$, $LiCoO_2$, MgO, $IrO_2$, $Al_2O_3$, $SiO_2$, $P_2O_5$, $PO_2$, CaO, $Sc_2O_3$, $Mn_2O_3$, $MnCO_3$, $MnO_2$, $Mn_3O_4$, $Nb_2O_5$, PbO, $Sb_2O_3$, $SnO_2$, $SrCO_3$, $Ta_2O_5$, $TiO_2$, $BaTiO_3$, $VO_2$, $V_2O_5$, $WO_3$, $Bi_2O_3$ and $ZrO_2$.

[Claim 4] The method for preparing graphene according to Claim 1, wherein the acid used in said treating of the surface of graphite is one or more selected from sulfuric acid, nitric acid and hydrochloric acid.

[Claim 5] The method for preparing graphene according to Claim 1, wherein the acid used in said treating of the prepared particle is one or more selected from sulfuric acid, nitric acid and hydrochloric acid.

[Claim 6] Graphene prepared by the preparation method according to any one of Claims 1 to 5.

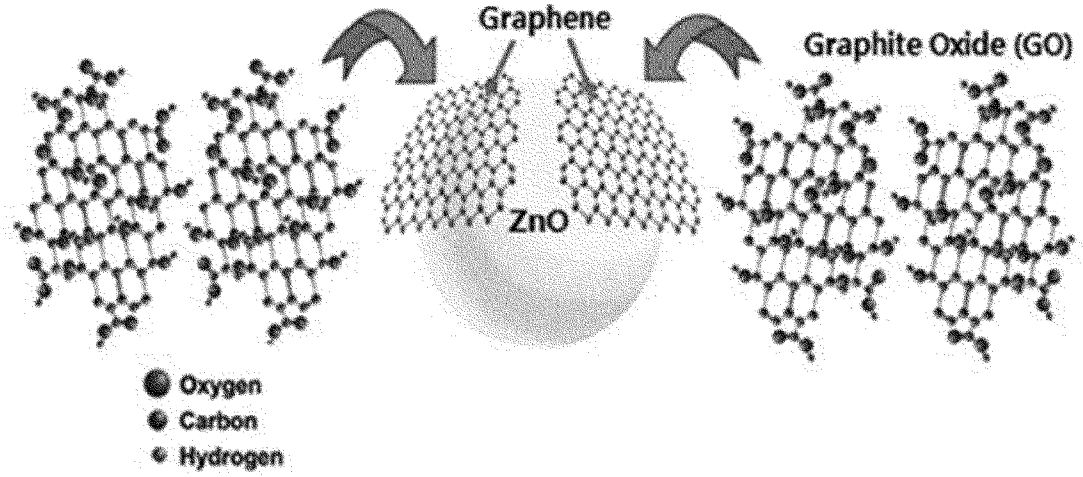
[Claim 7] The graphene according to Claim 6, which comprises 1-5 layers of carbon atoms.

[Claim 8] A nanoparticle having a metal oxide-graphene core-shell structure prepared from a reaction of graphite oxide with a metal oxide nanoparticle, wherein graphene encloses the metal oxide nanoparticle.

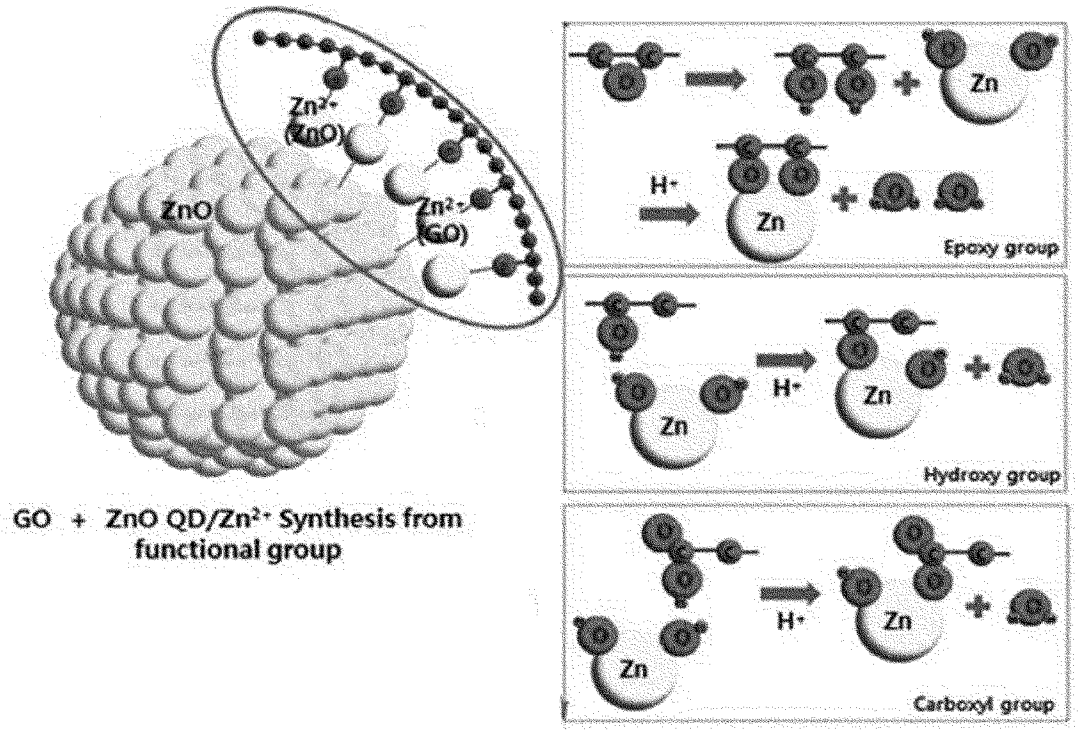
[Claim 9] The nanoparticle having a metal oxide-graphene core-shell structure according to Claim 8, wherein the metal oxide is selected from ZnO, CuO, $BaCO_3$, $Bi_2O_3$, $B_2O_3$, $CaCO_3$, $CeO_2$, $CrO_2$, $Cr_2O_3$, FeO, CoO, NiO, GeO, $Y_2O_3$, $ZrO_2$, MoO, $RuO_2$, PdO, AgO, CdO, SnO, $HfO_2$, $Ta_2O_5$, $Fe_2O_3$, $Ga_2O_3$, $In_2O_3$, $Li_2CO_3$, $LiCoO_2$, MgO, $IrO_2$, $Al_2O_3$, $SiO_2$, $P_2O_5$, $PO_2$, CaO, $Sc_2O_3$, $Mn_2O_3$, $MnCO_3$, $MnO_2$, $Mn_3O_4$, $Nb_2O_5$, PbO, $Sb_2O_3$, $SnO_2$, $SrCO_3$, $Ta_2O_5$, $TiO_2$, $BaTiO_3$, $VO_2$, $V_2O_5$, $WO_3$, $Bi_2O_3$ and $ZrO_2$.

Not Furnished Upon Filing

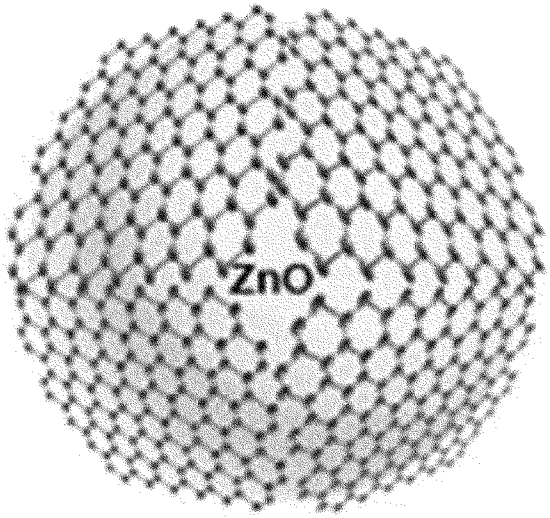
[Fig. 1]


Graphene
Graphite Oxide (GO)
ZnO
Oxygen
Carbon
Hydrogen

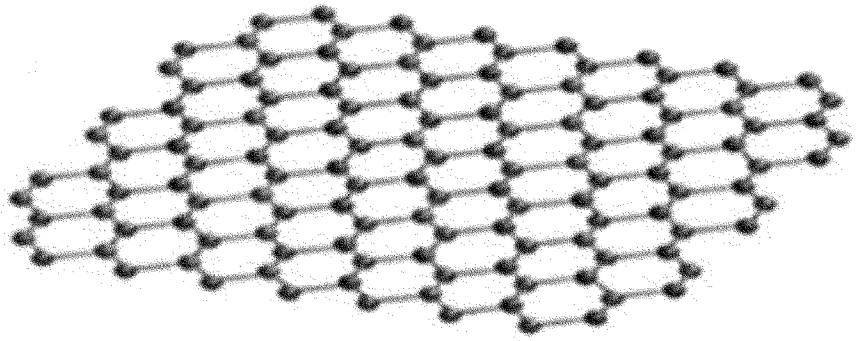
[Fig. 2]


Zn2+ (ZnO)
ZnO
Zn2+ (GO)
GO + ZnO QD/Zn2+ Synthesis from functional group
H+
Zn
Epoxy group
Hydroxy group
Carboxyl group

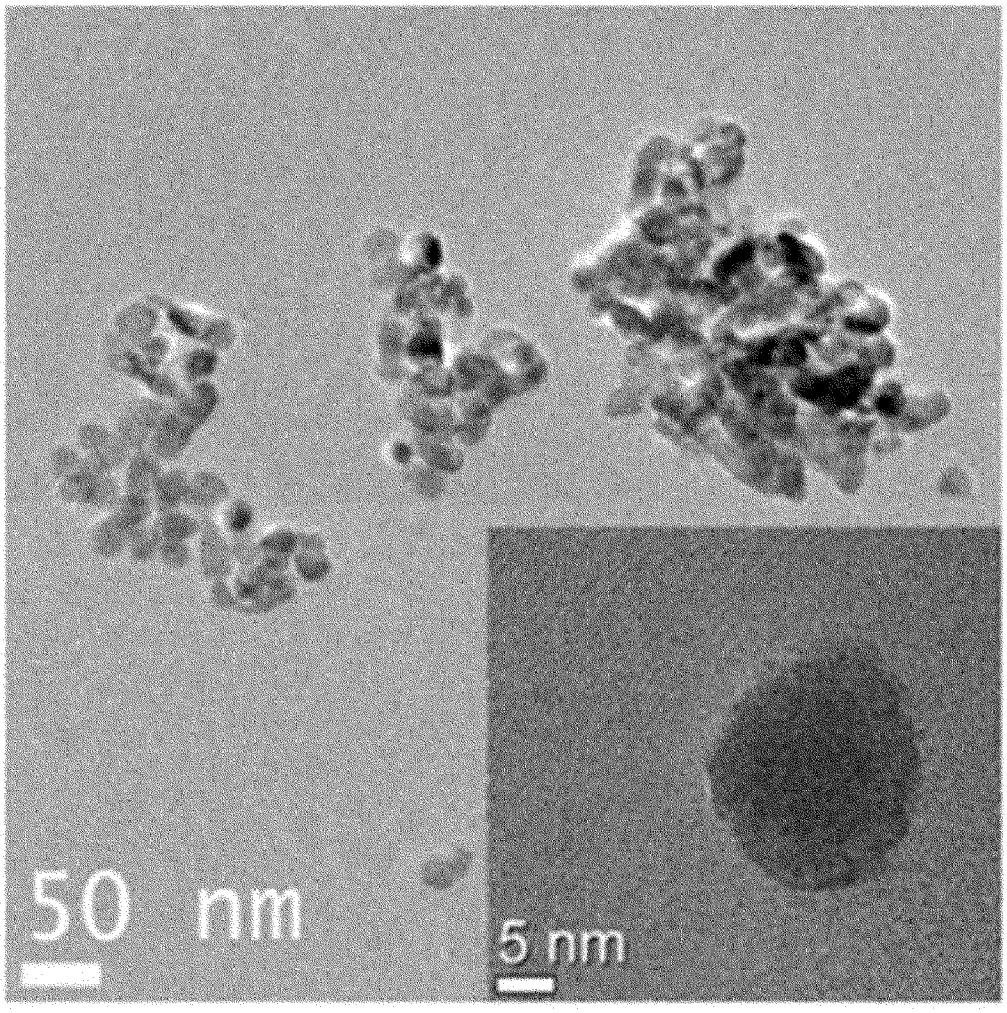
[Fig. 3]



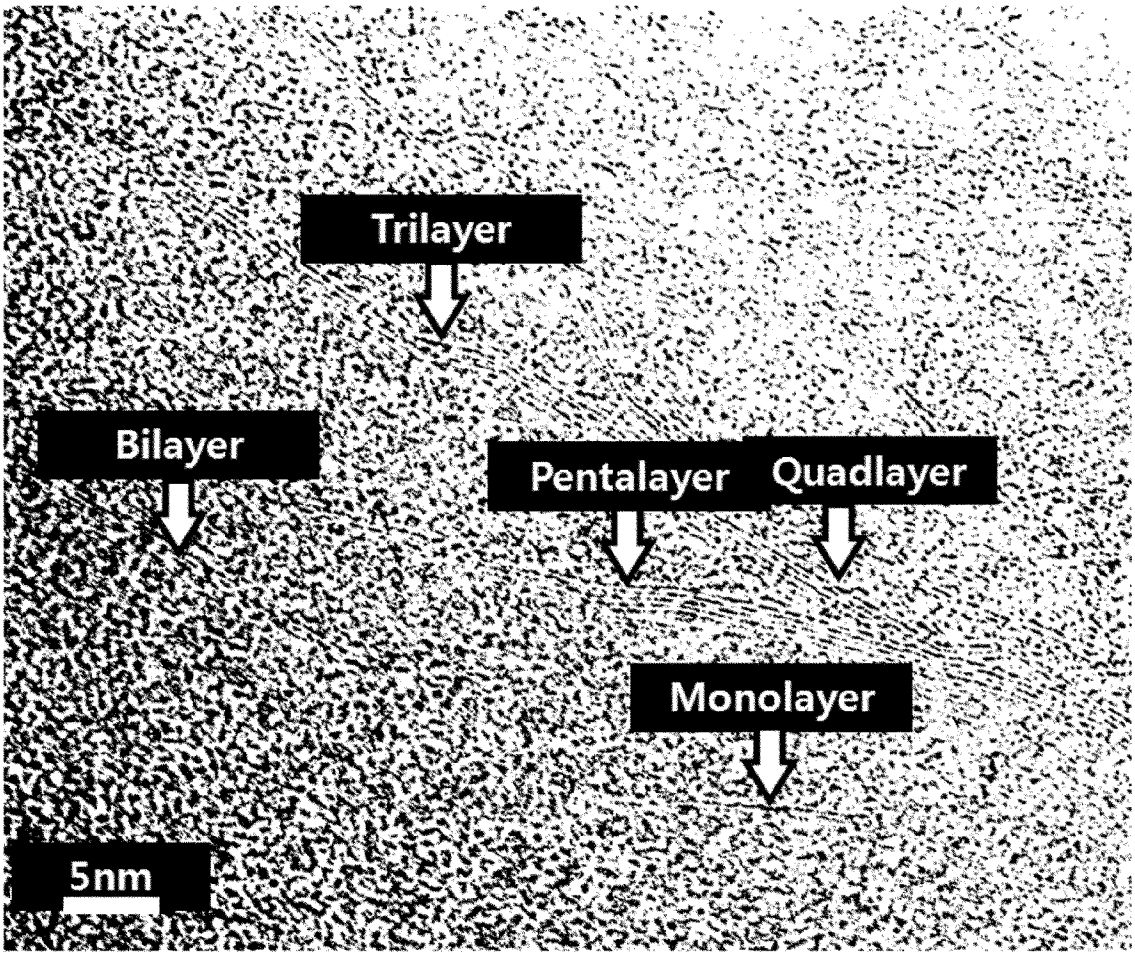

[Fig. 4]



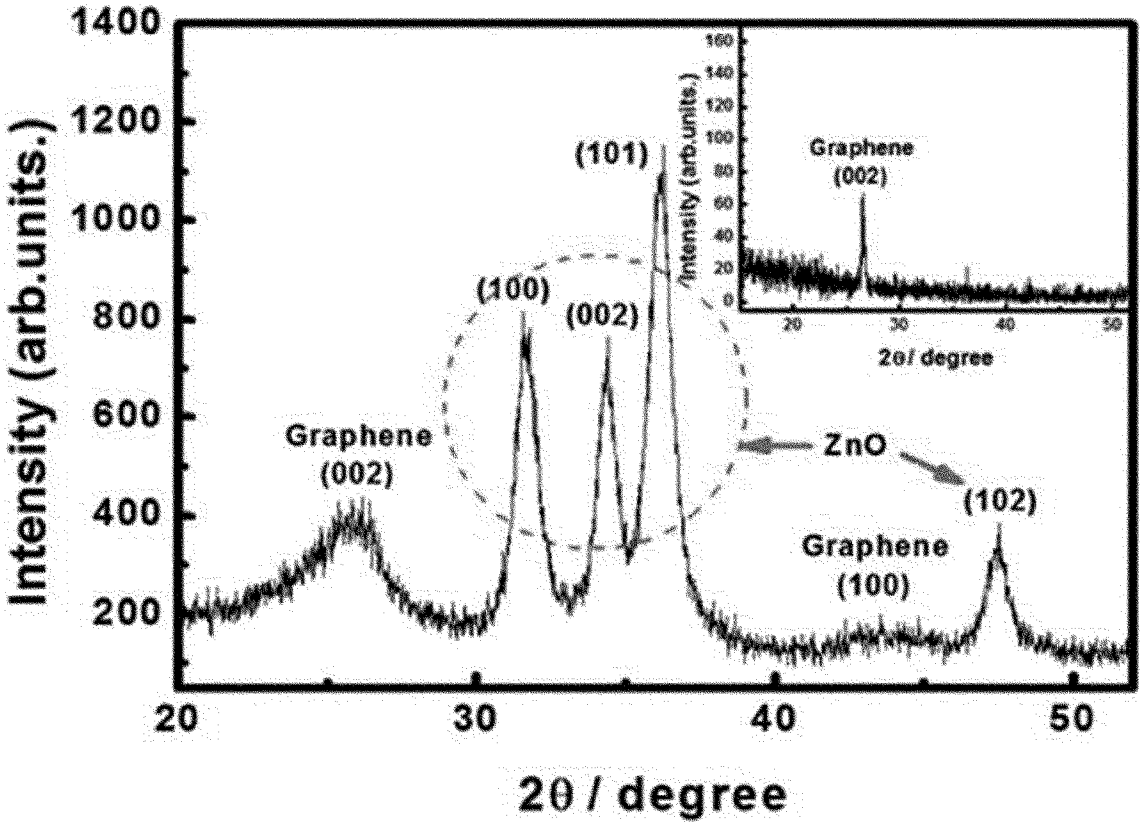
[Fig. 5]



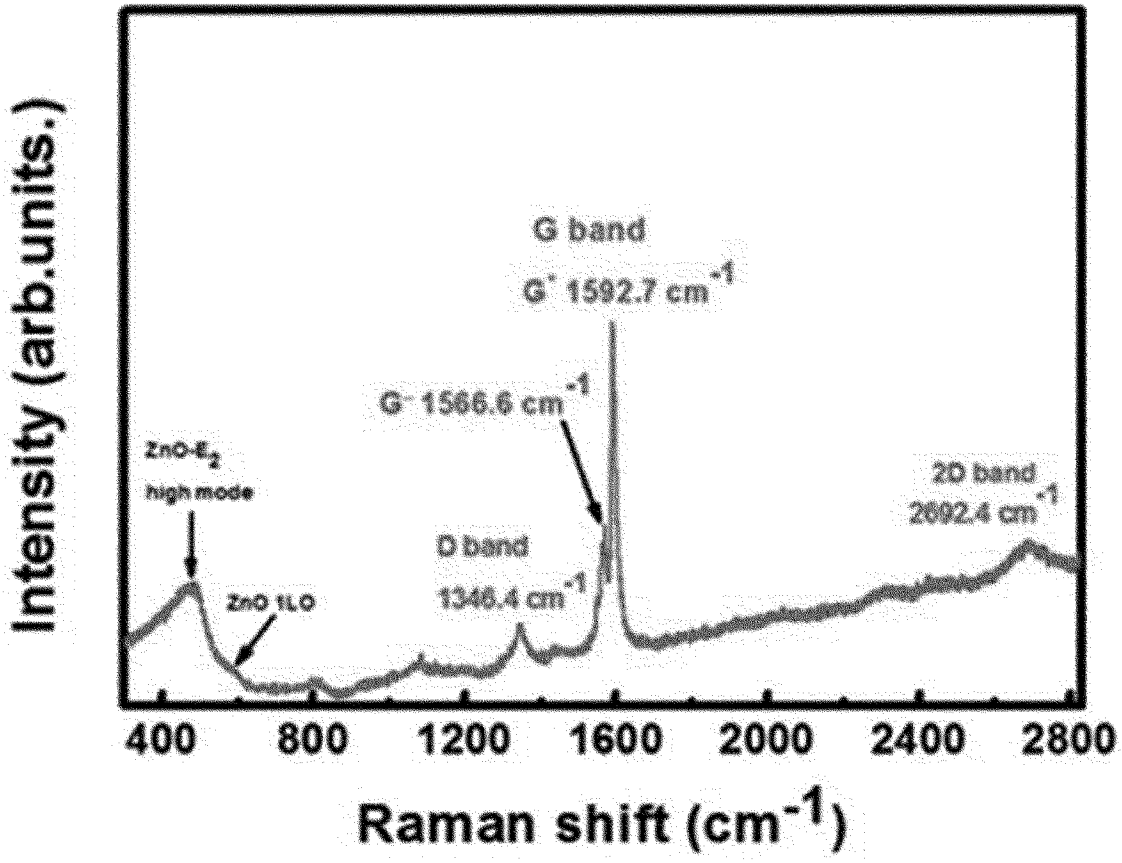
[Fig. 6]


Trilayer
Bilayer
Pentalayer
Quadlayer
Monolayer
5nm

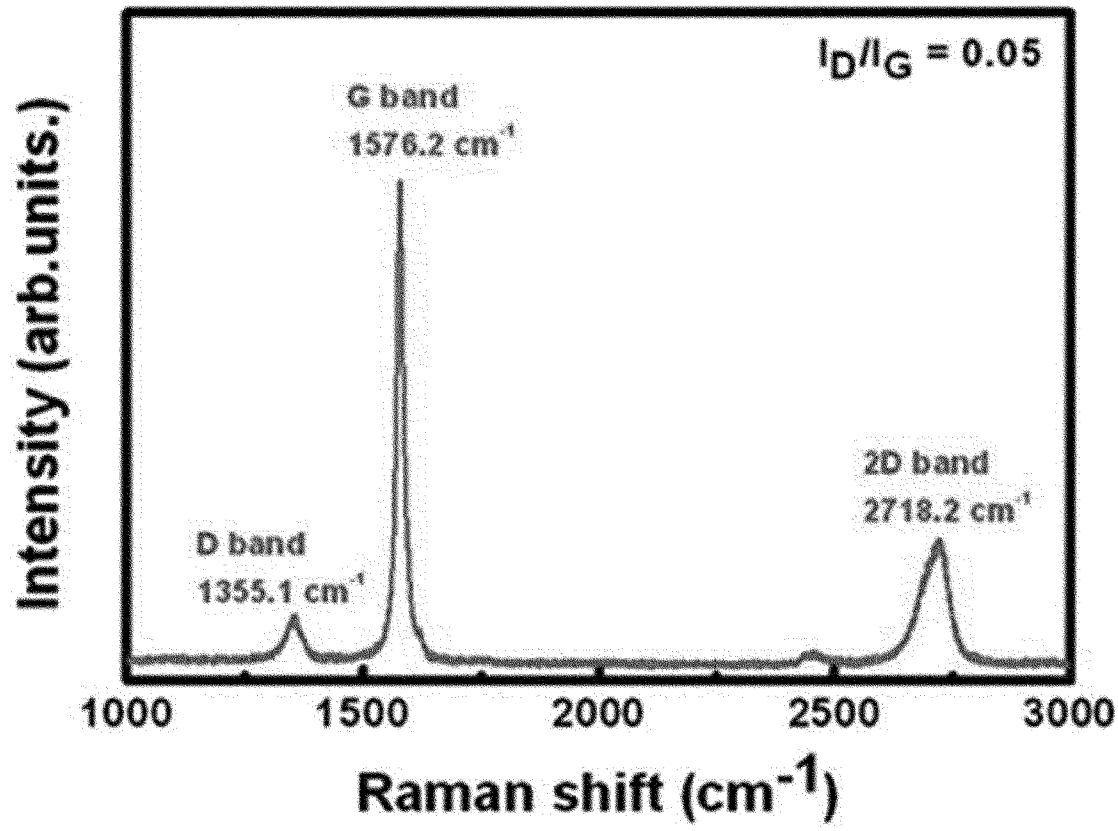
[Fig. 7]


Intensity (arb.units.)
2θ / degree
(101)
(100)
(002)
Graphene
(002)
ZnO
(102)
Graphene
(100)
Intensity (arb.units.)
2θ/ degree

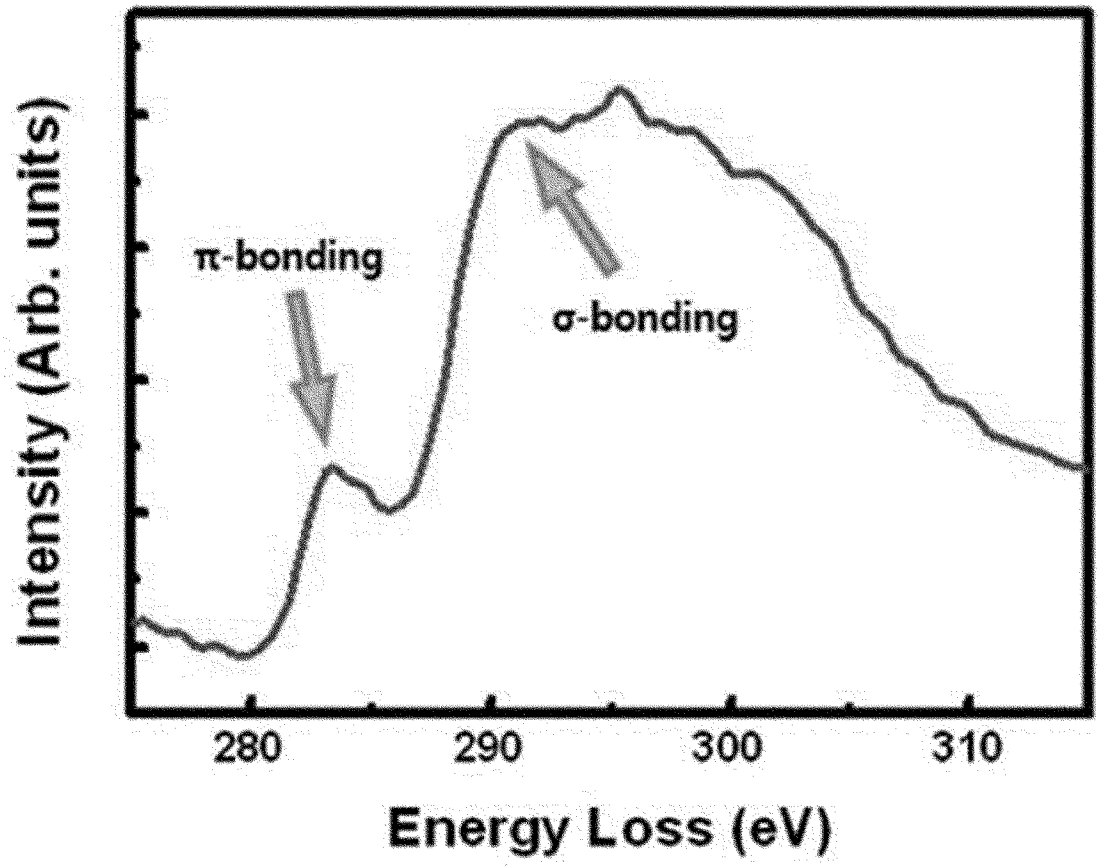
[Fig. 8]


Intensity (arb.units.)
G band
G+ 1592.7 cm-1
G- 1566.6 cm-1
ZnO-E2
high mode
ZnO tLO
D band
1346.4 cm-1
2D band
2692.4 cm-1
400
800
1200
1600
2000
2400
2800
Raman shift (cm-1)

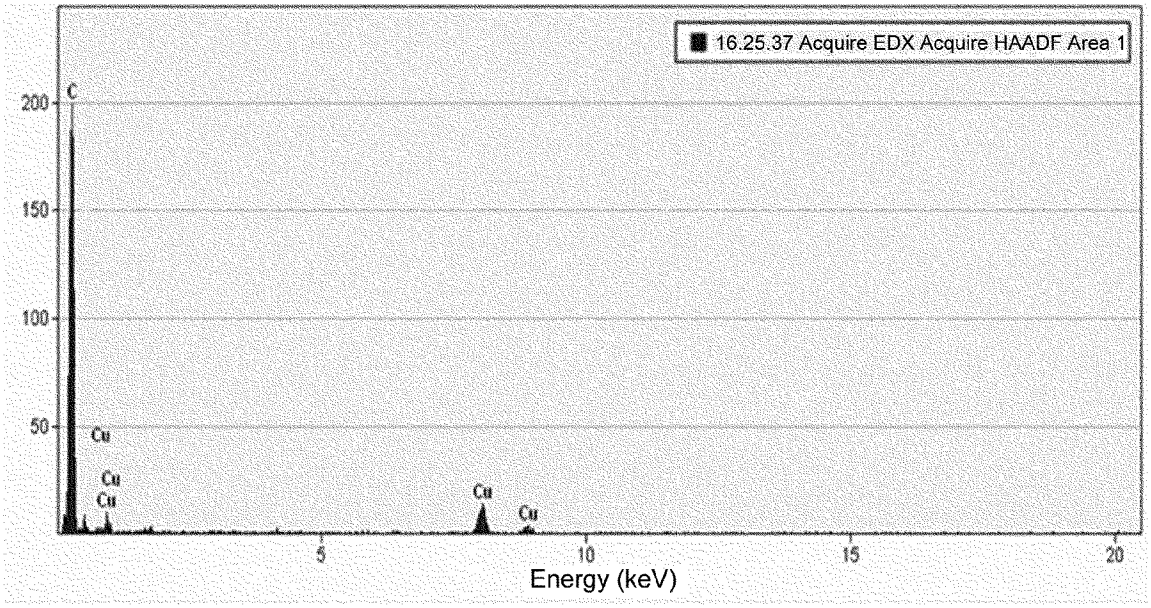
[Fig. 9]


ID/IG = 0.05
Intensity (arb.units.)
G band
1576.2 cm-1
D band
1355.1 cm-1
2D band
2718.2 cm-1
1000
1500
2000
2500
3000
Raman shift (cm-1)

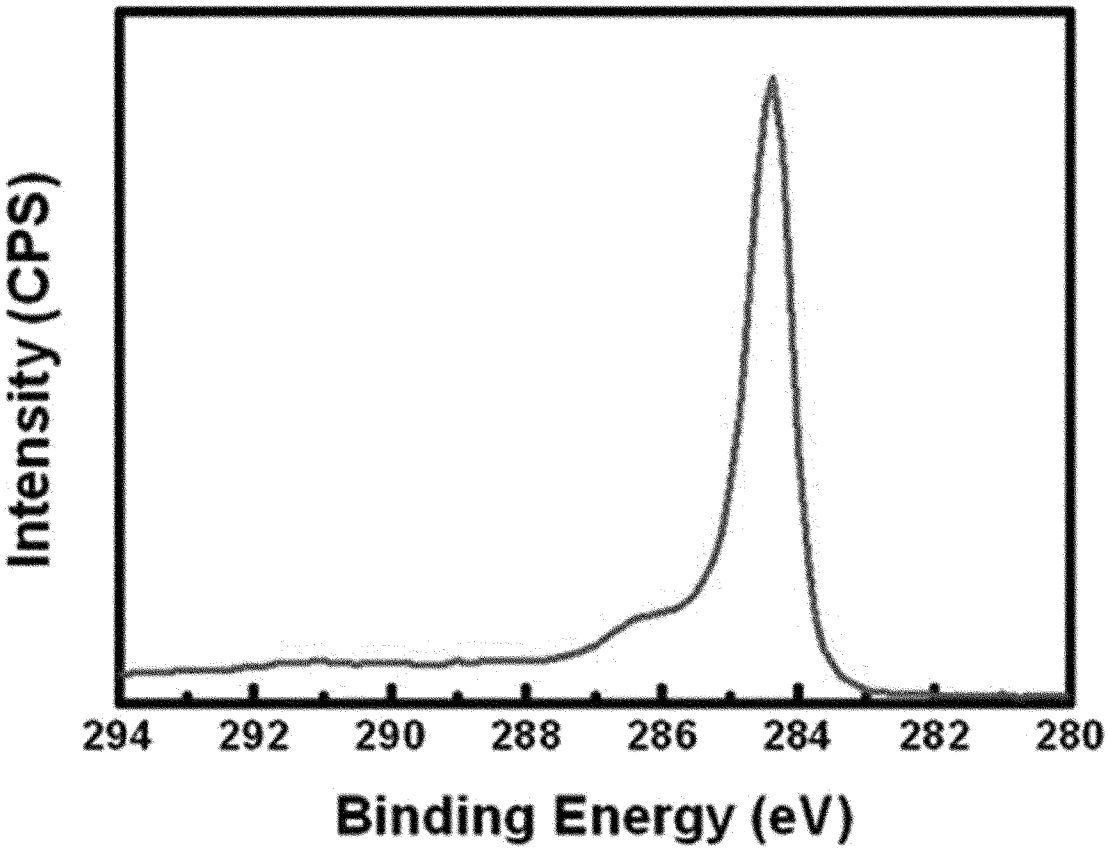
[Fig. 10]


Intensity (Arb. units)
π-bonding
σ-bonding
280
290
300
310
Energy Loss (eV)

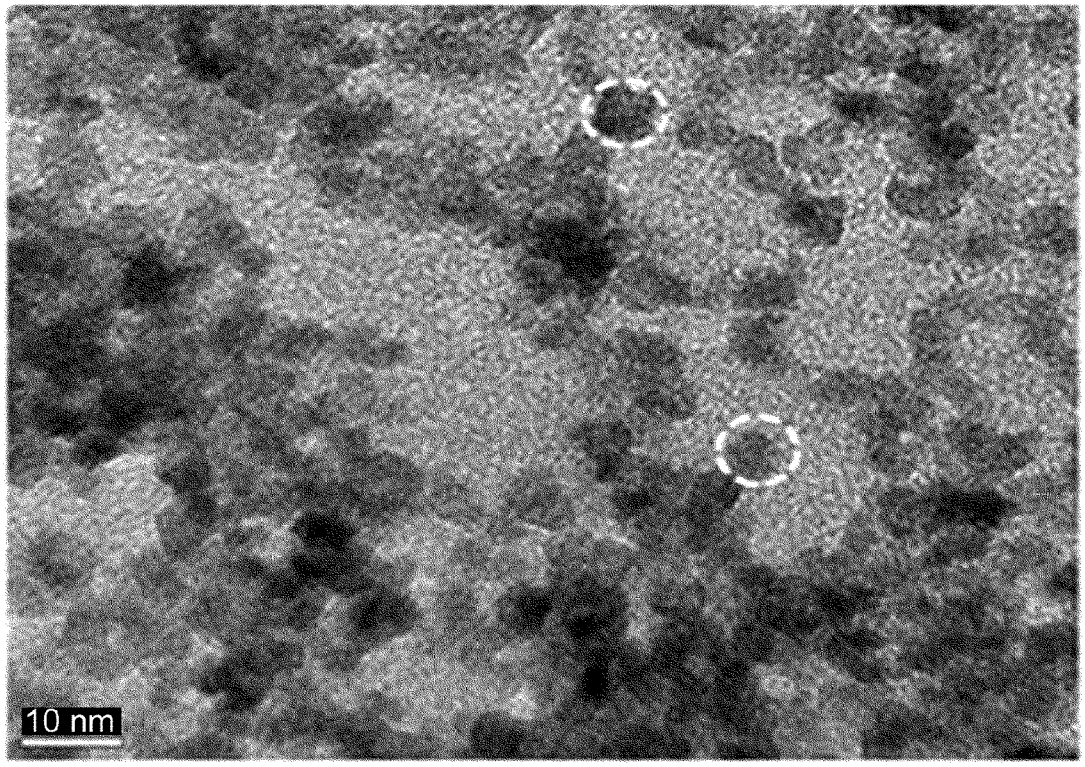
[Fig. 11]


16.25.37 Acquire EDX Acquire HAADF Area 1
C
Cu
Cu
Cu
Cu
Cu
200
150
100
50
5
10
15
20
Energy (keV)

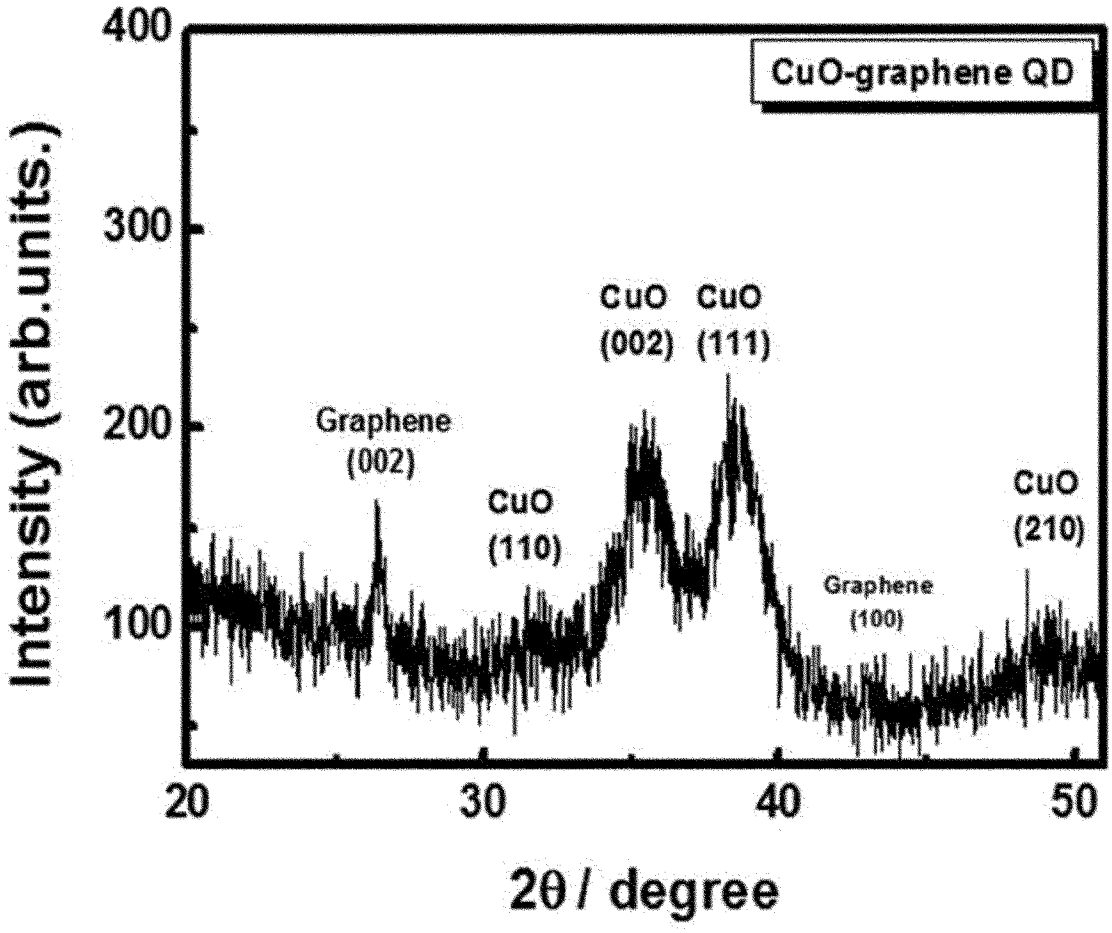
[Fig. 12]


Intensity (CPS)
294
292
290
288
286
284
282
280
Binding Energy (eV)

[Fig. 13]


10 nm

[Fig. 14]


CuO-graphene QD
Intensity (arb.units.)
400
300
200
100
20
30
40
50
2θ / degree
Graphene
(002)
CuO
(110)
CuO
(002)
CuO
(111)
Graphene
(100)
CuO
(210)

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/KR2012/001433**

**A. CLASSIFICATION OF SUBJECT MATTER**

***C01B 31/02(2006.01)i, C01G 9/02(2006.01)i, B82B 3/00(2006.01)i***

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)
C01B 31/02; C08F 301/00; D01F 9/12; C01B 31/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: graphene, graphite oxide, metal oxide, acid, nanoparticle, core-shell structure

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 2011-0014111 A1 (MARY ANNE LEUGERS et al.) 20 January 2011<br>See abstract, claims 1, 18-19 | 1-9 |
| A | US 2005-0271574 A1 (BOR Z. JANG et al.) 08 December 2005<br>See abstract, claims 1, 6 | 1-9 |
| A | US 2009-0028777 A1 (ARUNA ZHAMU et al.) 29 January 2009<br>See abstract, claims 1, 12 | 1-9 |
| A | US 2010-0105834 A1 (JAMES M. TOUR et al.) 29 April 2010<br>See abstract, claims 1, 3, 34 | 1-9 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"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
"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
"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
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 21 AUGUST 2012 (21.08.2012) | **22 AUGUST 2012 (22.08.2012)** |


Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
LEE, Young Wan
Telephone No. 82-42-481-5560

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/KR2012/001433**

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 2011-0014111 A1 | 20.01.2011 | CN 101765560 A | 30.06.2010 |
| | | EP 2176163 A1 | 21.04.2010 |
| | | JP 2010-535148 A | 18.11.2010 |
| | | JP 2010-535148 T | 18.11.2010 |
| | | KR 10-2010-0051681 A | 17.05.2010 |
| | | WO 2009-018204 A1 | 05.02.2009 |
| US 2005-0271574 A1 | 08.12.2005 | None | |
| US 2009-0028777 A1 | 29.01.2009 | None | |
| US 2010-0105834 A1 | 29.04.2010 | CA 2762430 A1 | 10.02.2011 |
| | | CA 2765492 A1 | 23.12.2010 |
| | | EP 2327085 A1 | 01.06.2011 |
| | | EP 2432733 A2 | 28.03.2012 |
| | | EP 2443062 A1 | 25.04.2012 |
| | | JP 2012-500179 A | 05.01.2012 |
| | | KR 10-2011-0050523 A | 13.05.2011 |
| | | TW 201012749 A | 01.04.2010 |
| | | WO 2010-022164 A1 | 25.02.2010 |
| | | WO 2010-022164 A9 | 17.06.2010 |
| | | WO 2010-096665 A1 | 26.08.2010 |
| | | WO 2010-147859 A1 | 23.12.2010 |
| | | WO 2010-147860 A1 | 23.12.2010 |
| | | WO 2011-016889 A2 | 10.02.2011 |