



(43) International Publication Date
21 October 2004 (21.10.2004)

PCT

(10) International Publication Number
WO 2004/090199 A1

(51) International Patent Classification⁷: C25D 5/20,
5/02, 7/12

(74) **Agent: JETTER, Neil, R.;** Akerman Senterfitt, 222 Lakeview Avenue, Suite 400, P.O. Box 3188, West Palm Beach, FL 33402-3188 (US).

(21) International Application Number:
PCT/US2004/009806

(22) International Filing Date: 31 March 2004 (31.03.2004)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) Priority Data:
60/459,376 31 March 2003 (31.03.2003) US

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

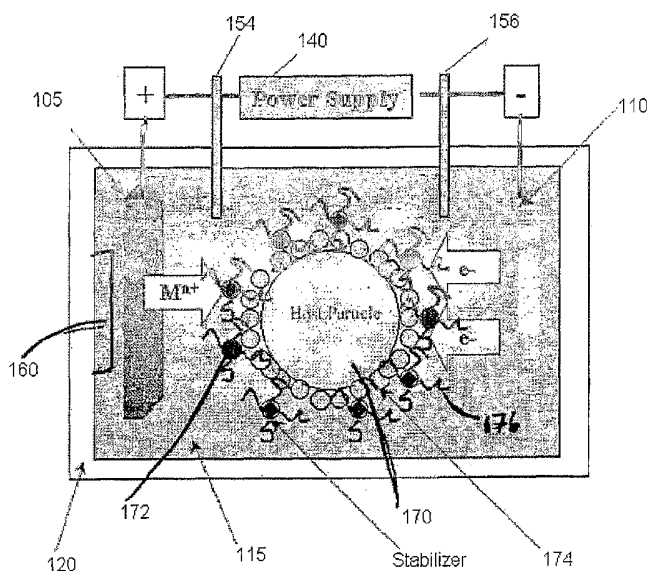
(71) Applicant (for all designated States except US): UNIVERSITY OF FLORIDA [US/US]; 223 Grinter Hall, P.O. Box 115500, Gainesville, FL 32611-5500 (US).

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors: SINGH, Rajiv, K.; 8615 S.W. 19th Road, Gainesville, FL 32607 (US). CHOI, Han-Ho; 2919 S.W. 13th Street, #98, Gainesville, FL 32608 (US).

[Continued on next page]

(54) Title: ELECTROCHEMICAL PARTICLE COATING METHOD AND DEVICES THEREFROM



100

(57) Abstract: An electrochemical method of forming nanocoated particles includes the steps of suspending a plurality of host core particles in a solution, providing a plurality of cations in the solution, and electrochemically forming a plurality of nanosize coating particles from reduction of the cations. A portion of the nanosize coating particles formed are deposited on surfaces of the host core particles. Continuous coatings as thin as 1 nm on core particles can be produced using the invention.

WO 2004/090199 A1



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ELECTROCHEMICAL PARTICLE COATING METHOD AND DEVICES THEREFROM

FIELD OF THE INVENTION

[0001] The invention relates to nanoscale coatings on core particles, more specifically, an electrochemical method for forming nanoscale coatings on core particles.

BACKGROUND

[0002] In recent years, nanostructured materials and particulate encapsulation have stimulated intensive research due to their unique properties and numerous potential technological applications. Host particles encapsulated by a layer comprising nanosized particles can provide unique electric, magnetic, optical and mechanical properties which are significantly different from those of the uncoated particles. Applications for nanoparticle coated core particles include electronics, chemical mechanical planarization (CMP) for use in slurries, displays, and energy.

[0003] Several efforts have been made to develop particulate encapsulation with nanosized particles using approaches such as gas phase synthesis, wet chemical synthesis (e.g. sol-gel, microemulsion) and dry coating synthesis. The dry coating synthesis method is one of the simplest methods to produce large quantities of coated particulates. Drawbacks of this coating method include contamination and impurities. In wet chemical synthesis, controlling the chemical reaction rate is very difficult, making it hard to achieve uniformly coated particulates. The main disadvantages of gas phase synthesis include low volume production and high cost.

[0004] One important application of nano-encapsulated coatings is in the area of catalysts due to their high surface area and chemical activity. CuO supported catalysts are potential candidates in the field of heterogeneous catalysis, especially as oxidation catalysts. They have also been considered as low-cost substitutes for noble metal-based emission control catalysts because their efficiency of CO oxidation is comparable to that of noble metal catalysts.

[0005] Another important application of nanoencapsulated coatings is in the area of phosphor anodes which are commonly used for field emission display (FED) applications. The reduction in ZnS:Ag phosphor degradation from electron bombardment is critical for FED applications which generally operate at high current densities.

[0006] In a FED, electrons are emitted from a cathode and impinge on phosphors coated on the back of an optically transparent cover plate to produce an image. The particle size of phosphors used in conventional FEDs is several microns, or more. Such a cathodoluminescent process is known as one of the most efficient methods for generating light. Contrary to a conventional CRT device, each pixel or emission unit in a FED has its own electron source, typically an array of emitting microtips. A voltage difference between a cathode and a gate electrode extracts electrons from the cathode and accelerates them toward the phosphor coating, which is typically ZnS:Ag. Although FEDs are promising, the ZnS:Ag phosphor coating generally used has been reported to have a short lifetime which has been attributed to electron beam induced surface reactions and charging effects on the surface. Recently, several largely unsuccessful attempts have been made to slow the degradation process to enhance the cathodoluminescent lifetime.

[0007] Yet another important application for nanoencapsulated coatings is for forming coated particles for use in chemical-mechanical polishing (CMP) in semiconductor fabrication. CMP is generally used with a damascene process to form certain layers, such as copper. Used in CMP slurries, coated particles can provide properties and certain desirable results that are not available from a single component slurry particle.

SUMMARY OF THE INVENTION

[0008] An electrochemical method of forming nanocoated particles includes the steps of suspending a plurality of host core particles in a solution, providing a plurality of cations in the solution, and electrochemically forming a plurality of nanosize coating particles from reduction of the cations. A portion of the nanosize coating particles are deposited on surfaces of the host core particles. The plurality of cations can be generated from a sacrificial anode. In one embodiment, the method further comprises the step of providing a gaseous species to the solution, wherein the gaseous species reacts with the plurality of cations to form the coating layer. The gaseous species can comprise O₂.

[0009] The solution can include at least one surfactant. The method can also include the step of generating ultrasonic waves in the solution, wherein the electrochemically forming step proceeds in the presence of ultrasonic waves.

[0010] The coating layer comprises a metal oxide, such as CuO, SnO₂, In₂O₃ and ZnO. The host core particles can comprise silica particles. In one embodiment, the host core particles can comprise ZnS:Ag particulates.

[0011] The host core particles can be relatively large particles of > 1μm, or be nanoparticles. An average thickness of the coating layer can be less than 20 nm, such as 15 nm, 10 nm, 8 nm, 7 nm, 6 nm, 5 nm, 4 nm, 3 nm, 2 nm, or 1 nm.

[0012] A field emission display (FED) having enhanced cathodoluminescent lifetime includes a plurality of microtips for emitting electrons towards an anode. The anode includes an optically transparent plate having a plurality of light emitting core phosphor particles coated with a nanoscale coating layer comprising a plurality of optically transparent nanoparticles disposed thereon. The coating layer can provide full surface coverage on the phosphor particles. The phosphor particles can

comprise ZnS:Ag, while the plurality of optically transparent nanoparticles can be metal oxide particles such as CuO, SnO₂, In₂O₃ or ZnO. An average thickness of the coating layer can be less than about 10 nm, and an average size of the core phosphor particles can be nanoscale.

[0013] The optical transmittance of the nanoscale coating layer can be at least 40% throughout the full visible light range, defined herein to be about 400 to 750 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] A fuller understanding of the present invention and the features and benefits thereof will be accomplished upon review of the following detailed description together with the accompanying drawings, in which:

[0015] FIG. 1 illustrates an exemplary electrochemical cell and associated process dynamics, according to an embodiment of the invention.

[0016] FIG. 2A shows an enlarged, cross-sectional view of a conventional field emission display (FED) device.

[0017] FIG. 2B shows a completed FED structure which includes coated phosphor particles according to an embodiment of the invention.

[0018] FIG. 3 illustrates field emission-scanning electron microscope (FE-SEM) images for (a) uncoated silica particles and (b) CuO coated silica particles.

[0019] FIGs. 4(a) and (b) are transmission electron microscope (TEM) images of silica particles coated with nanosized CuO particles, while FIG. 4(c) is a TEM image of nanosized CuO particles and FIG. 4(d) is the optical absorption spectrum of an as-synthesized CuO suspension.

[0020] FIG. 5 shows x-ray diffraction (XRD) patterns for silica particles coated with nanosized CuO particles and as-synthesized CuO particles.

[0021] FIG. 6 are Zeta potential curves of uncoated silica, silica coated with CuO nanoparticles, and CuO nanoparticles as a function of pH.

[0022] FIGs. 7(a) is a FE-SEM, while FIGs. 7(b) and (c) are TEM images of a ZnS:Ag particle coated with nanosized ZnO particles.

[0023] FIG. 8(a) is a XRD pattern of nanosized ZnO particles, while FIG. 8(b) is a UV-VIS transmittance and absorption spectra of a ZnO suspension.

[0024] FIGs. 9(a) and (b) are X-ray photoelectron spectroscopy (XPS) results for the Zn 2p_{3/2} peak for uncoated ZnS:Ag powder, and ZnS:Ag powder coated with nanosized ZnO particles, respectively.

[0025] FIG. 10 illustrates cathodoluminescence degradation curves for uncoated and ZnS:Ag particulates coated with nanosized ZnO particles.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The invention includes electrochemical methods for forming thin nanoscale coatings on host core particles. The method can be easily scaled to a manufacturing process. The invention is based on the formation of nanoparticles on the surface of host particles suspended in solution by the application of electrochemical driving forces. A significant advantage of the inventive method is the ability to control the coating thickness and surface coverage of the coating layer on the host particles. Applications for the invention include catalysts including photocatalysts, composite particles for CMP slurries, and field emission displays (FEDs). Full encapsulating coating layers may be electrochemically formed on host particles using the invention. As used herein the phrase "full encapsulation" refers to a nanoscale coating layer that covers at least 95%, such as 96%, 97%, 98%, 99% or 100% of the surface area of the host particles.

[0027] As used herein, the term "nanoscale" as applied to the coating layer refers to a coating layer which is less than 1 μm thick. The electrochemically synthesized coating layer thickness is preferably from about 1 nm to about 300 nm, but more preferably from about 2 nm to 20 nm. The host particle size can generally range from a few nanometers (e.g. 3 to 5 nm) up to 20 μm . However, the method can also be used with larger particles, such as 20 μm to 500 μm core particles.

[0028] FIG. 1 illustrates an exemplary electrochemical cell 100 and its associated process dynamics for forming nanoscale coatings on host particles, according to an embodiment of the invention. Electrochemical cell 100 includes electrodes anode 105 and cathode 110, each made of electrically conductive materials, such as metals, carbon, or a composite material. In FIG. 1, the anode is a sacrificial anode which provides metal cations M^{n+} ($n=1, 2, \dots$) to electrolyte containing solution 115,

while cathode 110 provides electrons to electrolyte containing solution 115.

Alternatively, cations can be directly added to the solution, such as from dissolved salts in the solution. Those salts can comprise metal hydroxides, metal carbonates, metal chlorides, metal sulfates, metal nitrates and metal organics. Solution 115 can include one or more additional species, such as additional electrolytes, and/or surfactants. Power supply 140 provides electrode bias to anode 105 and cathode 110 and provides the current required by the cell 100 during operation of the electrochemical process.

[0029] The cell container 120 is preferably made of an inert material, such as glass or plexiglass. Ultrasonic source 160 provides turbulence for the process. Ultrasonic source 160 generally includes an ultrasonic converter (not shown) driven by a power supply (not shown) to produce a sufficiently strong pulse-repetitive multifrequency train of mechanical oscillations or pulses. An acoustical load (not shown) is driven by the incoming frequency and amplitude modulated pulse-train and starts producing its own vibration and transient response, oscillating in one or more of its vibration modes or harmonics which produces ultrasonic waves in solution 115.

[0030] Inlet gas line 154 provides gas to cell 100 which provides added turbulence and optionally provides one or more reactant species. For example, air or O₂ can be supplied if a metal oxide coating is to be formed or an inert gas can be used if a metal coating is to be formed. For example, in the case of ZnO formation, inlet gas line 154 supplies an oxygen containing gas and the applicable reaction is

$$\text{Zn}^{2+} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{ZnO}_{\text{nanoparticles}}$$
 In the case of metal coatings, such as Cu, Zn or Sn, an inert gas is generally supplied to the solution to provide additional turbulence while avoiding oxidation of the metal coating. Outlet gas line 156 is provided to vent gas from cell 100.

[0031] The process begins by suspending a plurality of host particles 170 in the electrolyte solution 115. Power supply 140 is turned on to provide at least the required potential to drive the intended electrochemical reaction. Gas is supplied to cell 100 via gas inlet 154. Ultrasonic source 160 is also preferably activated.

[0032] As shown in FIG. 1, coating of a host particle 170 is believed to occur when cations 172 provided by anode 105 react with electrons provided by cathode 110 and optionally with one or more species, such as a species provided by inlet gas line 154. A plurality of coating nanoparticles 174 are formed which become disposed on host particle 170. Surfactant molecules 176 present in solution 115 generally aid the reaction.

[0033] The electrolyte solution 115 preferably includes at least one surfactant, such as the cationic surfactant dodecyltrimethylammonium bromide ($C_{12}TAB$). However, the surfactant additive can be anionic, zwitterionic, non-ionic or another cationic surfactant, or a combination of surfactants. An alcohol, such as isopropyl alcohol (IPA), can also be added to the electrolyte solution to provide additional solution conductivity. Certain alcohols can also provide surfactant properties.

[0034] Energetic waves are also preferably applied during processing to provide turbulence sufficient to improve dispersion of the core particles, such as using ultrasonic source 160. For example, waves having a frequency from about 100 Hz to several MHz can be provided in a power range generally from 100 mW to several MWs.

[0035] As noted above, the sacrificial anode 105 in FIG. 1 can be used to provide a supply of metal cations to the electrolyte solution. For example, when the desired coating comprises copper or a copper compound, a copper plate (>99.9%) can be used as a sacrificial anode. The cathode 110 can be any suitable electrode material,

such as a stainless steel plate. The applied current to drive the electrochemical reaction is generally from about 1 to 10 mA/cm², and preferably from 3 to 5 mA/cm².

[0036] The coating thickness can be controlled using parameters including current, process time, turbulence, temperature, and particle concentration. The coating thickness can be determined using methods such as x-ray powder diffraction for crystalline products and transmission electron microscopy.

[0037] The electrochemical coating process can electrochemically coat a wide variety of coating compositions, such as oxides (e.g. metal oxides), nitrides and metals. Mixed coatings, such as metal alloys can also be produced using the invention. Exemplary oxides include SnO₂, In₂O₃, In₂O₃-SnO₂ typically 90-10% (ITO), ZnO, CuO, TiO₂. Exemplary metal coatings include Cu, Zn, Sn and Ag. A wide variety of core particles can be used including metal, oxide, carbide, sulphide and oxysulphide, and mixed type core particles such as ZnS:Ag which are known to be useful as phosphors.

[0038] As demonstrated in the Examples, using the invention, silica core particles have been coated with nanosized CuO particles. In addition, ZnS:Ag core particles have been coated with metal oxides including ZnO, In₂O₃ and SnO₂. Alumina has also been coated with Sn using the invention.

In the case of ZnS:Ag core particles coated with nanoscale ZnO, In₂O₃ or SnO₂ coating layers, the coating layer has been found to significantly enhance the cathodoluminescent lifetime of ZnS:Ag phosphors.

The coating can provide full surface coverage on the host core particles. For example, zeta potential analysis has been used to successfully demonstrate the presence of a CuO coating layer which provides full encapsulation (100%) on the surface area of underlying silica core particles.

[0039] For coatings on the order of several nanometers thick, the optical absorption spectrum exhibited by semiconducting coatings such as CuO can also be verified on the basis of the quantum confinement effect. The quantum confinement effect shifts the inherent semiconductor bandgap energy to a higher bandgap energy when a semiconducting layer thickness is on the order of several nm, or less.

[0040] Coatings using the invention can provide continuous coverage over the surface of core particles, having a thickness as little as 1 nm and still providing continuous coverage. The deposited films can be substantially non-porous. In addition, the particle-to-particle layer coating uniformity can be quite high.

[0041] In one embodiment, nanoscale coated phosphor core particles according to the invention and used to produce improved FED devices having enhanced lifetimes. Referring initially to FIG. 2A, an enlarged, cross-sectional view of a conventional field emission display device 10 is shown. The FED device 10 is formed by depositing a resistive layer 12 of typically an amorphous silicon base film on a glass substrate 14. An insulating layer 16 of a dielectric material and a metallic gate layer 18 are then deposited and formed together to provide metallic microtips 20 and a cathode structure 22 is covered by the resistive layer 12 and thus, a resistive but somewhat conductive amorphous silicon layer 12 underlies a highly insulating layer 16 which is formed of a dielectric material such as SiO₂. It is important to be able to control the resistivity of the amorphous silicon layer 12 such that it is not overly resistive but yet, it will act as a limiting resistor to prevent excessive current flow if one of the microtips 20 shorts to the metal layer 18.

[0042] A completed FED structure 30 including anode 28 mounted on top of the structure 30 is shown in FIG. 2B which includes nanocoated phosphor particles 32 according to the invention. It is to be noted, for simplicity reasons, the cathode layer

22 and the resistive layer 12 are shown as a single layer 22 for the cathode. The microtips 20 are formed to emit electrons 26 from the tips of the microtips 20. In operation, the gate electrodes 18 are provided with a positive charge, while the anode 28 is provided with a higher positive charge. The anode 28 is formed by a glass plate 36 which is coated with phosphorous particles having an optically transparent nanoscale coating layer thereon. The total thickness of the FED device is only about 2 mm, with vacuum pulled in between the lower glass plate 14 and the upper glass plate 36 sealed by sidewall panels 38 (shown in FIG. 1B).

[0043] As noted above, the particle size of phosphors used in conventional FEDs is several microns, or more. Although it is known to coat phosphor particles to enhance emitter lifetime, nanoscale coating layers according to the invention significantly enhance the adhesion of phosphors on the glass plate 36, such as during screen printing because of the much higher surface area provided by the nanoscale coating layer. In a preferred embodiment of the invention, the nanoscale coating layer is disposed on nanoscale size phosphor core particles. In one embodiment, an average thickness of the coating layer can be less than about 10 nm. As a result, the invention can significantly enhance the lifetime FEDs by decreasing surface charging, decreasing sulfur desorption, decreasing the formation of non-luminescent layer such as ZnO, and preserving the light transmittance characteristics from the phosphors.

[0044] The average size of the phosphor particles can also have a nanoscale size. The average size of the phosphor core particles can be less than 900 nm, such as 800 nm, 700 nm, 600 nm, 500 nm, 400 nm, 300 nm, 200 nm, or 100 nm.

Examples

[0045] The present invention is further illustrated by the following specific Examples. The Examples are provided for illustration only and are not to be construed as limiting the scope or content of the invention in any way.

Example 1; CuO coated Silica Nanoparticles

[0046] The host core material used was spherical sol-gel silica particles, which had a non-agglomerated average particle size was about 0.52 μm based on measurements using field emission scanning electron microscopy (FE-SEM, JEOL JSM 6300F) and a particle size analyzer (Microtrac UPA 150). The deposition process was carried out in an electrochemical cell made of glass. Silica host particles were suspended in isopropyl alcohol (IPA) along with dodecyltrimethylammonium bromide (C_{12}TAB , 0.1 mol/L) which acts as both an electrolyte and a surfactant. The silica particles were uniformly dispersed with the use of ultrasonic-waves with 300 W of power before and during the coating process.

[0047] A copper plate (>99.9%) was used as a sacrificial anode, and a stainless steel plate was used as the cathode. Both the anode and cathode plates were parallel to one another and separated by a distance of 1 cm in the cell. The applied current was kept constant at a current density of from 3 to 5 mA/cm^2 . The electrochemical cell was purged with air to complete the oxidation reaction which results in the formation of CuO nanoparticles and the coating of the silica core particles with the CuO formed. After deposition, the coated samples were washed several times by centrifugation and dried at 80 $^{\circ}\text{C}$ for 24 hours.

[0048] The particle shape, size, and CuO coating layer thickness on the surface of silica particles were investigated using transmission electron microscopy (TEM,

JEOL 2010F) and FE-SEM. The crystallinity, phase constituents, and the crystallite size of nanosized CuO particles and coated silica particles were identified by X-ray diffraction (XRD, Philips APD 3720). The UV-visible absorption spectrum of CuO suspension was examined using a UV/VIS spectrometer (PerkinElmer Lambda 800). Zeta potential measurements were carried out with a Zeta Plus (Brookhaven Instruments Corporation).

[0049] Figure 3(a) shows well-defined and smooth surface morphology of the uncoated individual silica host core particles. In contrast, as shown in FIG. 3(b), the rough and textured layer of CuO particles formed becomes clearly distinguishable on the surface of smooth silica particles. Thus, the surface texturing of CuO coated silica provides clear evidence for the presence of CuO coating layer on the surface of silica particles. Most of the coated silica particles formed had a uniform and continuous CuO coating layer. The uniformity of the coating is believed to be aided by the high dispersion stability of the silica suspension provided by the applied ultrasonic-waves during processing.

[0050] Typical TEM images of the CuO coated silica particles and as-synthesized CuO particles are shown in FIGs. 4(a) and (b), respectively. It can be seen that the silica surfaces were covered with uniform and continuous CuO coating layers. Both FIGs. 4(a) and 4(b) indicate that the morphology of the CuO particles seems somewhat aggregated with a spherical shape, and the CuO coating layer can be measured to be from a few nm to 20 nm thickness, which corresponds to a few individual CuO particle layers.

[0051] A typical TEM image of nanosized CuO particles prepared under the same experimental conditions except without the silica support particles in the deposition solution is presented in FIG. 4(c). The particle size distribution of as-synthesized

CuO particles can be estimated to a few nm to about 7 nm. These values are in good agreement with the particle sizes of CuO particles in the coating layer. UV-Visible absorption spectrum of the as-synthesized CuO nanoparticles is shown in FIG. 4(d). This spectrum shows a broad absorption peak whose center is about 275 nm, corresponding to a semiconducting bandgap energy of about 4.5 eV.

[0052] The absorption spectrum and onset of absorption were quite similar to the CuO nanoparticles which exhibit the quantum confinement effect. Since CuO has an indirect allowed band gap of 1.35 eV and a direct allowed inter band transition at 3.25 eV, the absorption behavior of a CuO suspension was predominantly dependent on the direct inter-band transition effect. The quantum size effect induced about a 1.25 eV shift to a higher bandgap energy. This shift comes from the result that the primary particle sizes in both TEM and XRD analysis were in the range of Bohr excitation radius. Therefore, the quantum confinement effect gives further evidence of formation of CuO nanocrystals with dimensions on the order of a few nanometers.

[0053] Figure 5 shows XRD patterns of both the CuO coated silica particles and the as-synthesized CuO particles, respectively. The XRD pattern of CuO coated silica particles is labeled as (a) in FIG. 5, while the XRD pattern of the as-synthesized CuO particles is labeled as (b). The featureless XRD pattern shown in (a) indicates the amorphous nature of the silica support particles, with no CuO peaks evident. This is attributed to a very small amount of CuO in the overall coated particle samples. Based on the amount of copper consumed in the electrochemical reaction, it is estimated that the total amount of CuO is less than 1 wt % of the coated silica samples. Thus, to determine the characteristics of the CuO surface layer, the CuO particles must generally be separately formed.

[0054] As shown in (b) in FIG. 5, the as synthesized CuO particles formed without a silica core demonstrates characteristic diffraction peaks of CuO. The broadened diffraction lines shown in (b) clearly indicate randomly oriented nanoscale crystals. The XRD pattern shown is essentially identical to that of pure CuO with a monoclinic structure. The mean crystallite sizes estimated from XRD peak width of (200) using the Scherrer equation and the Rietveld method were 7.2 nm and 5.3 nm, respectively. These values obtained are in good agreement with TEM analysis. Palker et al (V. R. Palker, P. Ayyub, S. Chattopadhyay, and M. Multani, Phys. Rev., B 53, 2167 (1996) proposed that CuO nanoparticles which have sizes less than 25 nm are not stable and transform into Cu₂O phase. The results shown in (b) in FIG. 5 contradict the Palker et al. proposal as the CuO layer tested was thinner than 25 nm and CuO rather than Cu₂O was detected.

[0055] Figure 6 shows the zeta potential behavior and isoelectric point of uncoated silica, CuO encapsulated silica, and CuO nanoparticles as a function of pH in the pH range of 2 to 10. The zeta potential curve of CuO encapsulated silica particles is similar to that of CuO nanoparticles, and the isoelectric point (IEP) of CuO encapsulated silica is shifted nearly to the value (pH 9.53) of CuO nanoparticles. Based on the apparent surface coverage (ACS) estimation, over 95% of the silica surface was covered with CuO nanoparticles. This result also indicates that silica particles have a uniform and continuous CuO nanoparticle coating layer.

[0056] Some have previously demonstrated the formation of CuO nanoparticles and other oxide particles using an electrochemical deposition processes. The proposed electrochemical reactions to form CuO are given as follows:



[0057] In contrast to the electrochemical formation of oxide nanoparticles themselves, such as CuO, the invention electrochemically forms oxide nanoparticles on host particles. Applicants, not seeking to be bound to theory, present the following mechanism for electrochemical formation of coating layers on host core particles. In the case of formation of CuO coated host particles, it is believed that copper ions (Cu^{2+}) which are generated from a copper sacrificial anode get oxidized to form CuO nanoparticles by applying a sufficient cathodic potential according to reaction (2). Consequently, the CuO nanoparticles were successfully synthesized in a solution saturated with dissolved oxygen that behaves like a reactive oxygen species complexing the copper cations in reaction (2).

[0058] When silica support particles were suspended in the deposition solution under the same experimental conditions, the nanosized CuO particles synthesized by electrochemical deposition were coated on the surface of silica particles. This result confirms that nanosized CuO particles can be electrochemically formed and simultaneously deposited on the surface of host core particles, such as silica particles.

[0059] It was also demonstrated the nucleation and aggregation of CuO nuclei occurred at the surface silica particles to overcome the surface energy during nucleation and growth with an electrochemical reaction (2). As-synthesized CuO particles (0.02g) and silica particles (2 g) were mixed and dispersed at the same experimental condition without applying the current noted above. Subsequent TEM analysis showed that there was no indication of formation of a CuO particle coating layer on the surface of the silica particles. The CuO and silica particles were individually dispersed, so that these two particles could readily be separated through

the centrifugation. These results suggest that the surface of silica particles plays an important role for the nucleation and growth of CuO particles during the electrochemical reaction.

Example 2; ZnO coated ZnS:Ag nanoparticles

[0060] ZnS:Ag phosphor core particles were provided having an average particle size of about 11.2 μm , which was estimated from field emission scanning electron microscopy (FE-SEM, JEOL JSM 6300F) and a particle size analyzer (Coulter LS 230). The ZnS:Ag particulates were suspended in isopropyl alcohol (IPA) with dodecyltrimethylammonium bromide (C_{12}TAB). A zinc plate was used as the sacrificial anode, and a stainless steel plate was used as the cathode. Both the anode and cathode plates were parallel to one another and separated by a distance of 1 cm in the cell. The current was constantly applied with a current density of 3 mA/cm^2 through the deposition process. Air was purged into the electrochemical cell to complete oxidation resulting in formation of nanosized ZnO particles.

[0061] After deposition, the ZnO coated ZnS:Ag particulates were washed by centrifugation and subsequently dried at 80 C for 24 hours. The particle shape, particle size, and coating thickness of ZnO on the ZnS:Ag particulates were investigated by transmission electron microscopy (TEM, JEOL 2010F) and FE-SEM. The crystallinity, phase constituents, and crystallite size of nanosized ZnO and the coated particulates were identified by x-ray diffractometry (XRD, Philips APD 3720). The surface chemistry was analyzed by x-ray photoelectron spectroscopy (XPS, KRATOS XSAM 800). The UV-visible transmittance and absorption spectra of ZnO suspension was examined by UV/VIS spectrometer (PerkinElmer Lambda 800).

[0062] The samples were irradiated with an e-beam using a PHI model 545 electron gun at an energy of 4 keV in a ultra high vacuum (UHV) of 3×10^{-9} Torr chamber. The electron current density was kept constant to a 130 A/cm^2 and the electron beam area was 0.011 cm^2 . The emission spectrum and peak intensities were measured in reflection mode by an Oriel 77400 multi-spectrometer coupled with a CCD array detector. The value of electron dose was determined by the product of irradiation time and current density.

[0063] Some have previously demonstrated the formation of ZnO nanoparticles using electrochemical deposition processes. The proposed electrochemical reactions are given as follows:



[0064] The zinc cations (Zn^{2+}) can be generated in organic medium from a zinc sacrificial anode in the described experimental condition. Reaction (4) has an $E^0_{\text{ZnO}} = 0.88 \text{ V}$ versus the normal hydrogen electrode (NHE). Consequently, the formation of ZnO nanoparticles is believed to be made possible thermodynamically by applying a sufficient cathodic potential according to reaction (4). The ZnO nanoparticles were successfully synthesized in a solution saturated with dissolved oxygen which was controlled by bubbling under the above-described conditions. The dissolved oxygen behaves as a reactive oxygen species which complexes the zinc cations in reaction (4). When ZnS:Ag particulates were suspended in the deposition solution at the same experimental condition, the nanosized ZnO particles synthesized by electrochemical deposition were coated on the surface of ZnS:Ag particulates.

[0065] Analogous to the CuO coating process described above, it is likely that the nucleation and the aggregation of ZnO nuclei occurred at the core surface (ZnS:Ag) to overcome the surface energy during nucleation and growth during electrochemical reaction (4). This hypothesis was proven by synthesizing ZnO particles and mixing them with ZnS:Ag particulates dispersing the mixture under the same experimental conditions, except no current was applied. Subsequent TEM analysis showed that there was no indication of a ZnO particle coating layer on the surface of the ZnS:Ag particulates. This result suggests that the surface of ZnS:Ag particulates play an important role for the nucleation and growth of ZnO particles during electrochemical reactions.

[0066] Figure 7(a)-(c) are FE-SEM and TEM micrographs for ZnO coated ZnS:Ag particulates. It is noted that the surface of the ZnS:Ag particulates is partially covered with a discontinuous layer consisting of nanosized ZnO particles. Figures 7(a) and 7(b) indicate that the morphology of the ZnO seems somewhat aggregated with a spherical shape. As shown in FIG. 7(c), the particle size distribution of ZnO can be estimated to be from a few nm to 10 nm, while the coating layer measured to be from a few nm to about 100 nm in thickness.

[0067] The x-ray diffraction lines of the ZnS:Ag particulates coated with ZnO were identified as only ZnS with no indication of the ZnO phase. This is attributed to a very small amount of ZnO in the coated samples. Based on the amount of zinc consumed in the electrochemical reaction, it is estimated that the total amount of ZnO is less than about 0.5 wt%. Thus, to determine the characteristics of the surface layer, the ZnO particles were separately formed.

[0068] Figure 8(a) is an XRD pattern of nanosized ZnO particles. The broadened diffraction lines clearly indicate the nanoscale crystallinity of the ZnO particles. The

mean sizes of the crystallites estimated from XRD peak width of (101) based on the Scherrer equation and the Rietveld method were calculated to be 7.1 nm and 5.5 nm, respectively. Slightly lower values (10% less) were obtained when (110) peak is used for analysis. The small difference of this result might be attributed to the distortion of the (101) peak by (002) peak which introducing some errors in the estimation. These values obtained are in good agreement with the TEM analysis.

[0069] The suspension of ZnO nanoparticles showed excellent UV-absorption capacity and high transparency of at least about 40% transmittance across the visible light spectrum as shown in FIG. 8(b). This result suggests that ZnO particles seem well-dispersed maintaining high stability with less agglomeration, which in turn can reduce the scattering of light and increase the transmittance of visible light.

[0070] The absorption spectrum and onset of absorption were quite similar to what is typically observed for the ZnO suspension which exhibits no quantum confinement effect. Since ZnO has bandgap energy of about 3.2 eV, the absorption behavior of ZnO suspension was predominantly dependent on the valence band-to-conduction band transition effect. The quantum size effect is not shown in this absorption spectra because the primary particle sizes in both TEM and XRD analysis were much larger than the Excitation Bohr diameter which is about 1.25 nm. Furthermore, the ZnO particles are continuously connected to each other, thus, suppressing the quantum confinement effect. As a result, there was no significant difference of transmittance between the uncoated and the coated samples with ZnO particles. This can be attributed to the high transparency in visible light of the ZnO suspension.

[0071] The XPS results of the Zn 2p_{3/2} peak for the uncoated and the coated phosphors with ZnO particles are shown in FIGs. 9(a) and (b). The atomic ratio of zinc to sulfur in the coated sample was twice as much as in uncoated sample in

quantitative XPS analysis. This indicates that ZnO particles were successfully coated on the surface of the ZnS:Ag particulates as evidenced by the estimated electron inelastic mean free path being less than a few nanometers in length in XPS analysis.

[0072] The Zn $2p_{3/2}$ peaks of the uncoated and coated samples are located at 1021.1 eV and 1022.6 eV, respectively. This gives a small difference of 0.5 eV which might be accounted for with the higher concentration of ZnO particles at the surface of the ZnS:Ag particulates. The presence of the ZnO coating layer induces a 0.5 eV shift to a higher binding energy. This peak shift arises because the binding energy of the Zn $2p_{3/2}$ peak in ZnO is higher than that of ZnS.

[0073] The results of cathodoluminescent degradation on the uncoated and coated ZnS:Ag particulates are plotted in FIG. 10. After exposure under a coulombic dose of 2 C/cm² at 4 keV, which corresponds to an exposure time of about 4.3 hours, the coated phosphors exhibited about a 25% higher relative brightness than the uncoated phosphors, and a lower rate of degradation was observed as well. The normalized relative intensities of the uncoated and coated phosphors decreased drastically up to about 1 and 0.4 C/cm², respectively and then the degradation rates of both phosphors were retarded up to 2 C/cm². Based on the XPS analysis described above, the optically transparent electrically conducting nanosized ZnO particles on the surface of ZnS:Ag particulates played a critical role to suppress the decomposition of sulfur on the phosphor surface and to retard the formation of non-luminescent layer. The longer lifetime and the lower rate of degradation of coated phosphors might be attributed to this result.

Example 3; Sn coated platey alumina particles

[0074] The average particle size of the platy alumina was about 10 μm , which was estimated from field emission scanning electron microscopy (FE-SEM, JEOL JSM 6300F) and particle size analyzer (Coulter LS 230). Platy alumina particulates were obtained from Advanced Nano Technologies which is a joint venture between Advanced Powder Technology (APT) of Australia and Samsung Corning of Korea. "Platey" alumina is made up of single crystal, non-agglomerated, hexagonal plates of alumina. Each plate was approximately 50 nm thick. The particle size range was between 2 and 10 microns in diameter, with an average diameter of about 6 microns. The alumina was suspended in isopropyl alcohol (IPA) with dodecyltrimethylammonium bromide (C_{12}TAB) which acts as both an electrolyte and a surfactant.

[0075] A tin plate was used as the sacrificial anode, and a stainless steel plate was used as the cathode. Both the anode and cathode plates were parallel to each other at a distance of 1 cm. The current was constantly applied with a current density of 3 mA/cm^2 through the deposition process. Argon gas was purged into the electrochemical cell to prevent oxidation and form tin metallic particles. After deposition, the platy alumina particulates were washed by centrifugation and subsequently dried at 50°C for 24 hours.

[0076] TEM micrographs taken demonstrated that the surface of the tin particulates became partially covered with a discontinuous layer consisting of nanosized tin metallic particles. An EDS line scan taken confirmed that metallic tin was present on the surface of platy alumina particles.

Example 4; SnO₂ coated ZnS:Ag phosphors

[0077] The average particle size of the ZnS:Ag phosphors was about 11.2 μm , which was estimated from field emission scanning electron microscopy (FE-SEM, JEOL JSM 6300F) and particle size analyzer (Coulter LS 230). ZnS:Ag particulates were suspended in isopropyl alcohol (IPA) with dodecyltrimethylammonium bromide (C₁₂TAB) which acts as an electrolyte and a surfactant. A tin plate was used as the sacrificial anode, and a stainless steel plate was used as the cathode. Both the anode and cathode plates were parallel to each other at a distance of 1 cm. The current was constantly applied with a current density of 3 mA/cm² through the deposition process. Air was purged into the electrochemical cell to complete oxidation resulting in formation of nanosized tin oxide particles. After deposition, the ZnS:Ag particulates were washed by centrifugation and subsequently dried at 80°C for 24 hours.

[0078] FE-SEM and TEM micrographs of the coated ZnS:Ag particulates revealed that the surface of the ZnS:Ag particulates was partially covered with a discontinuous layer consisting of nanosized tin oxide particles. The morphology of the tin oxide coating was determined to be somewhat aggregated with a generally spherical shape. The particle size distribution of tin oxide was estimated to a few nm to 10 nm, and the coating layer was measured to be from a few nm to 50 nm in thickness.

Example 5; In₂O₃ coated ZnS:Ag phosphors

[0079] The average particle size of the ZnS:Ag phosphors was about 11.2 μm , which was estimated from field emission scanning electron microscopy (FE-SEM, JEOL JSM 6300F) and particle size analyzer (Coulter LS 230). ZnS:Ag particulates

were suspended in isopropyl alcohol (IPA) with dodecyltrimethylammonium bromide ($C_{12}TAB$) which acts as an electrolyte and a surfactant. A indium plate was used as the sacrificial anode, and a stainless steel plate was used as the cathode. Both the anode and cathode plates were parallel to each other at a distance of 1 cm. The current was constantly applied with a current density of 3 mA/cm^2 through the deposition process. Air was purged into the electrochemical cell to complete oxidation resulting in formation of nanosized indium oxide particles. After deposition, the ZnS:Ag particulates were washed by centrifugation and subsequently dried at 80°C for 24 hours.

[0080] FE-SEM and TEM micrographs taken of the coated ZnS:Ag particulates revealed that the surface of the ZnS:Ag particulates was partially covered with a discontinuous layer consisting of nanosized indium oxide particles. The morphology of the indium oxide was found to be somewhat aggregated with a generally spherical shape. The particle size distribution of indium oxide was estimated to a few nm to 10 nm, and the coating layer was measured to be from a few nm to 50 nm thickness.

[0081] It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, that the foregoing description as well as the examples which follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

CLAIMS

We claim:

1. An electrochemical method of forming nanocoated particles, comprising the steps of:
 - suspending a plurality of host core particles in a solution,
 - providing a plurality of cations in said solution, and
 - electrochemically forming a plurality of nanosize coating particles from reduction of said cations, wherein a portion of said nanosize coating particles are deposited on surfaces of said host core particles.
2. The method of claim 1, wherein said plurality of cations are generated from a sacrificial anode.
3. The method of claim 1, further comprising the step of providing a gaseous species to said solution, wherein said gaseous species reacts with said plurality of cations to form said coating layer.
4. The method of claim 1, wherein said gaseous species comprises O₂.
5. The method of claim 1, wherein said solution comprises at least one surfactant.
6. The method of claim 1, further comprising the step of generating ultrasonic waves in said solution, wherein said electrochemically forming step proceeds in the presence of said ultrasonic waves.

7. The method of claim 1, wherein said coating layer comprises a metal oxide.
8. The method of claim 7, wherein said metal oxide comprises at least one selected from the group consisting of CuO, SnO₂, In₂O₃ and ZnO.
9. The method of claim 1, wherein said host core particles comprise silica particles.
10. The method of claim 1, wherein said host core particles are ZnS:Ag particulates.
11. The method of claim 1, wherein said host core particles are nanoparticles.
12. The method of claim 1, wherein an average thickness of said coating layer is less than 20 nm.
13. A field emission display (FED), comprising:

a plurality of microtips for emitting electrons towards an anode, said anode including an optically transparent plate having a plurality of light emitting core phosphor particles coated with a nanoscale coating layer comprising a plurality of optically transparent nanoparticles disposed thereon.
14. The display of claim 13, wherein said coating layer provides full surface coverage on said phosphor particles.

15. The display of claim 13, wherein said phosphor particles comprise ZnS:Ag.
16. The display of claim 13, wherein said plurality of optically transparent nanoparticles are metal oxide particles selected from the group consisting of CuO, SnO₂, In₂O₃ and ZnO.
17. The display of claim 16, wherein said metal oxide particles comprise ZnO.
18. The display of claim 13, wherein an average thickness of said coating layer is less than 10 nm.
19. The display of claim 13, wherein an optical transmittance of said coating layer is at least 40% throughout the full visible light range.

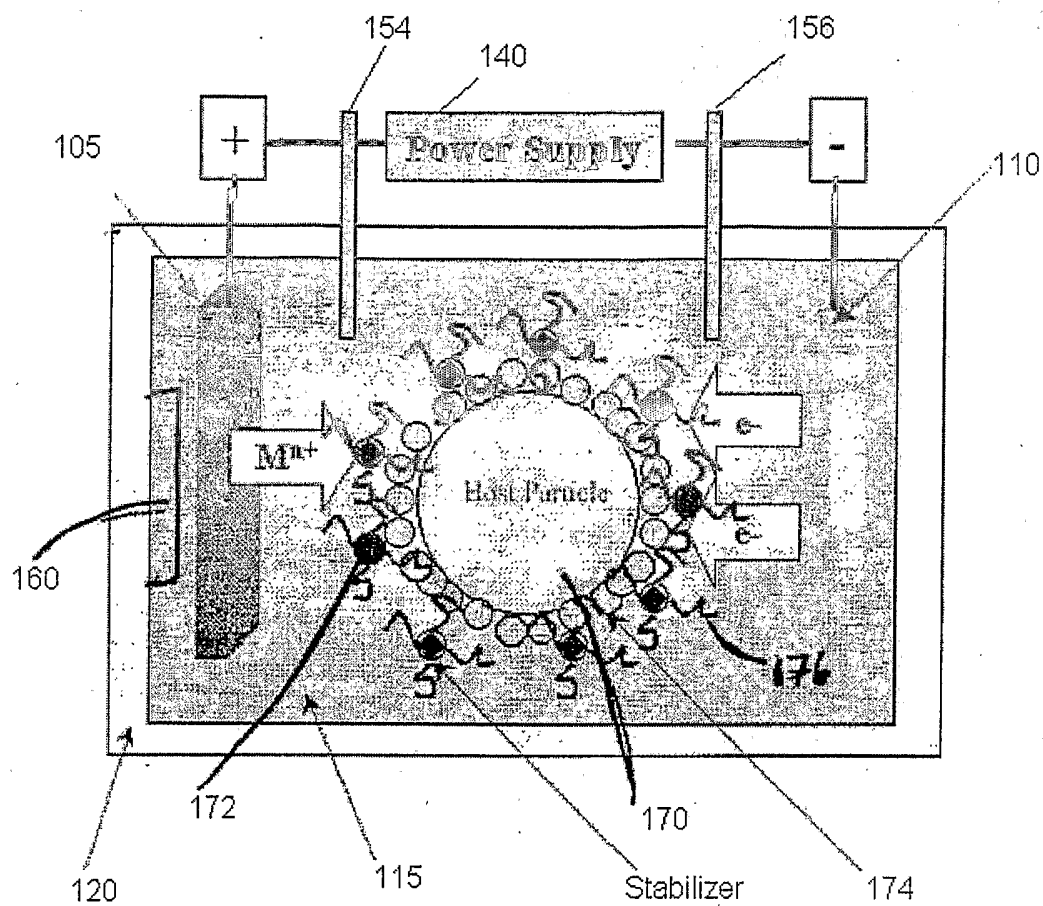
100

FIG. 1

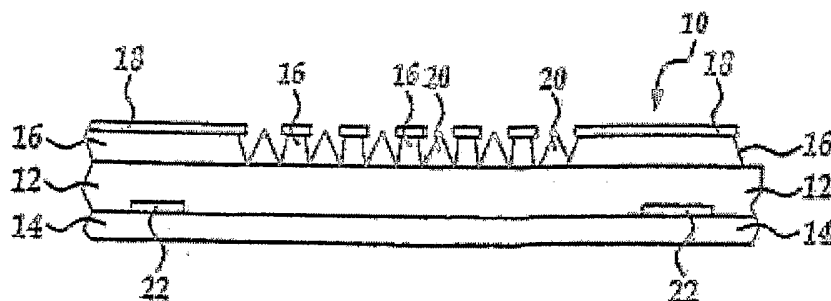


FIG. 2a
PRIOR ART

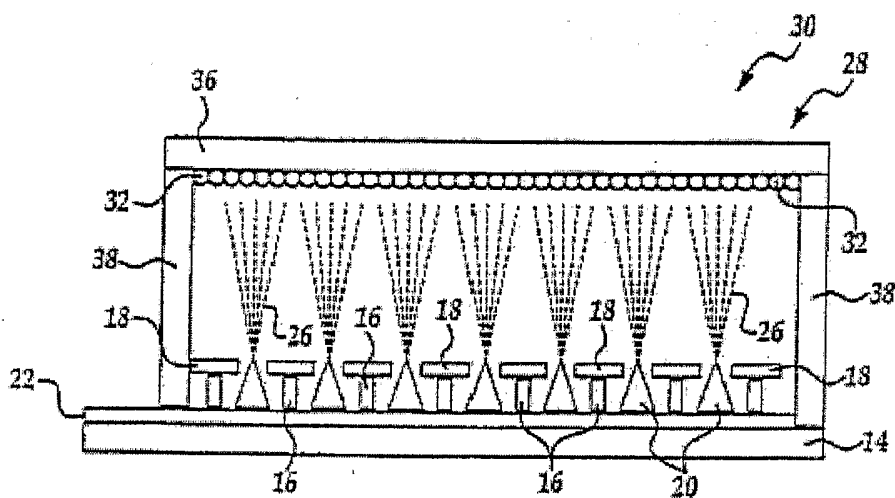


FIG. 2b

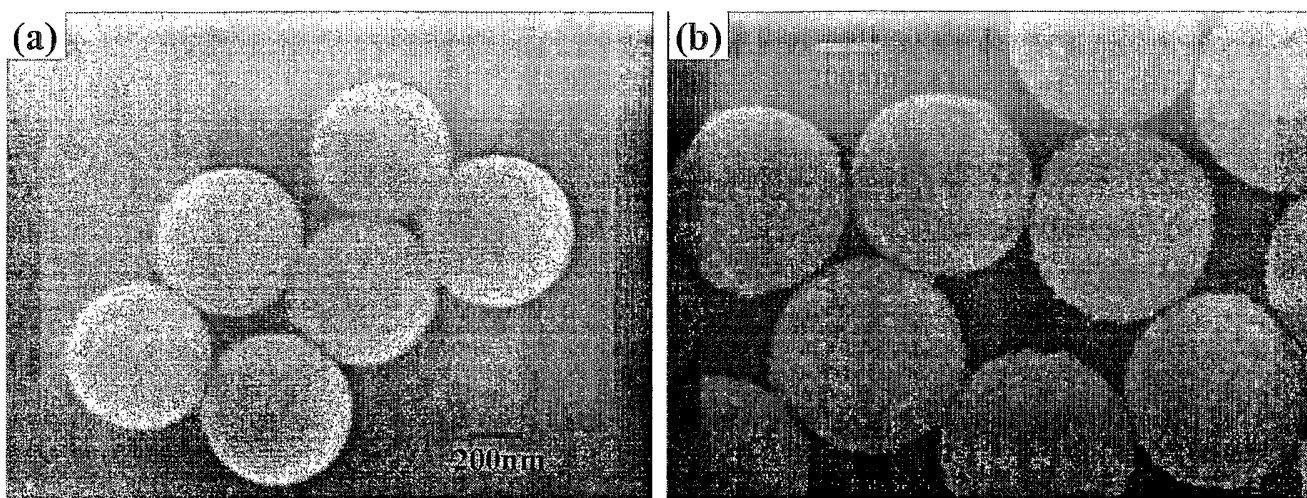


FIG. 3

4/9

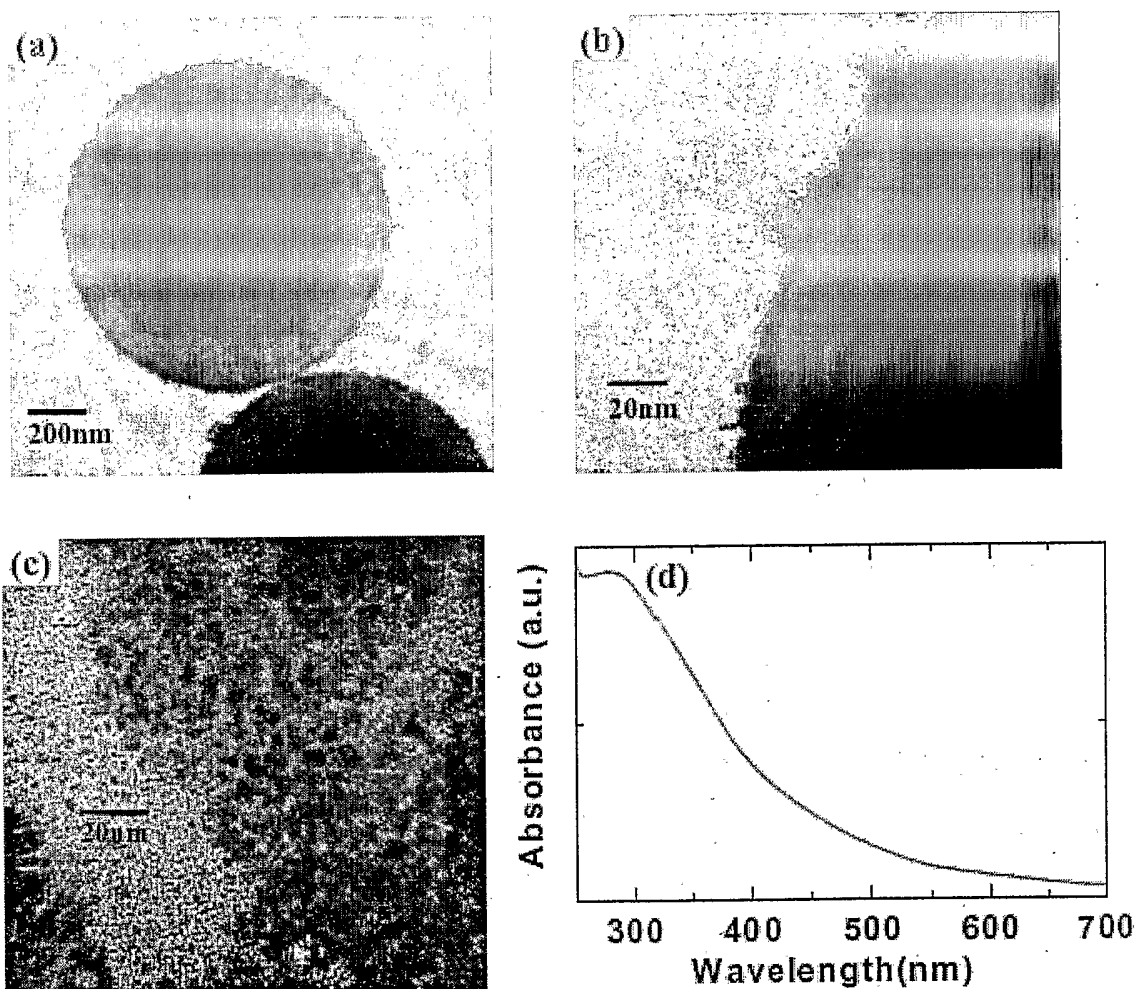


FIG. 4

5/9

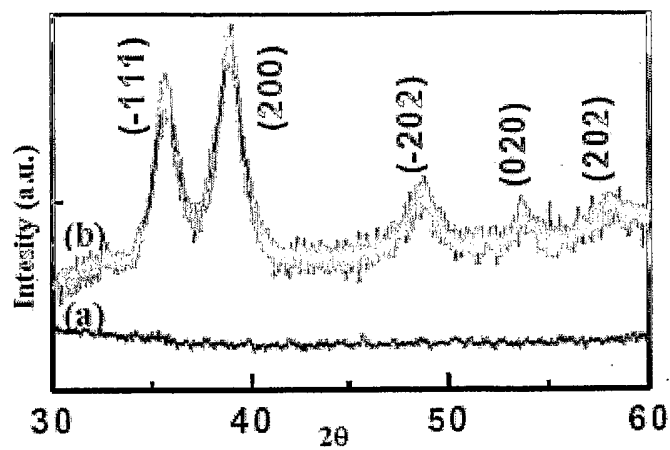


FIG. 5

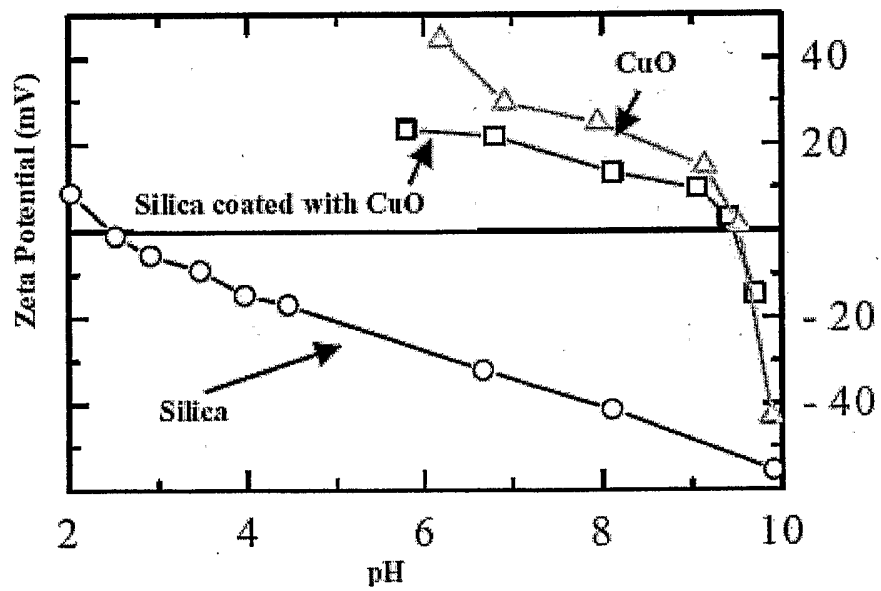


FIG. 6

6/9

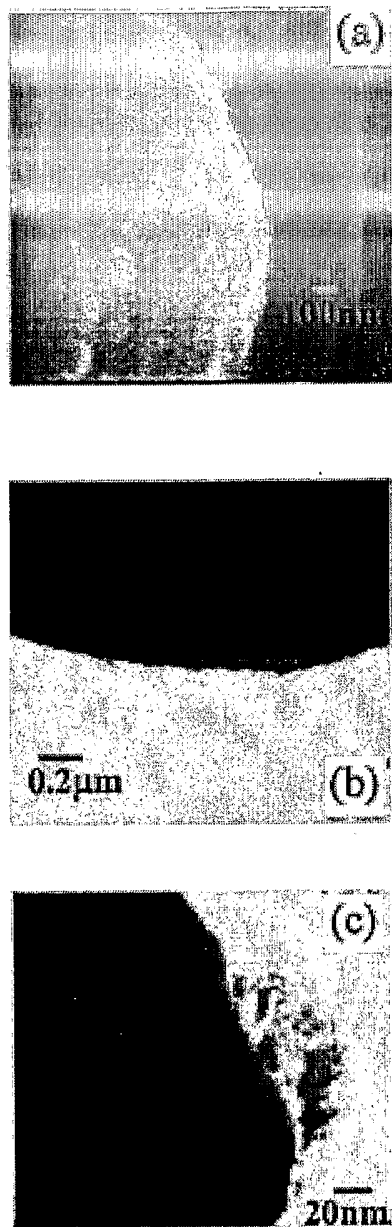


FIG. 7

7/9

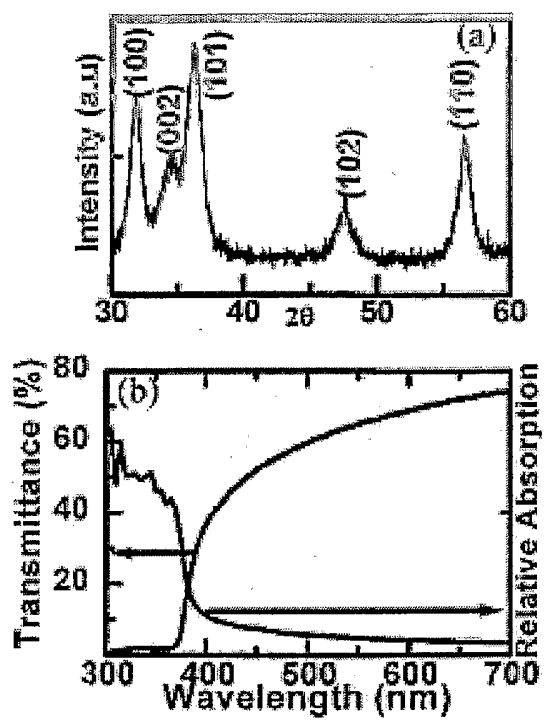


FIG. 8

8/9

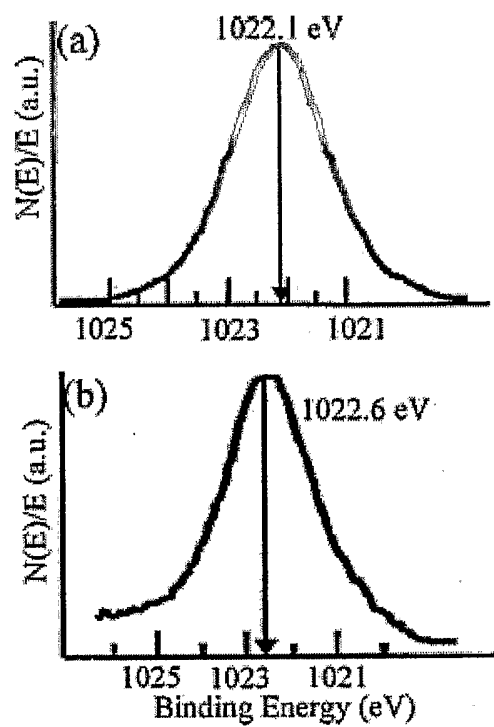


FIG. 9

9/9

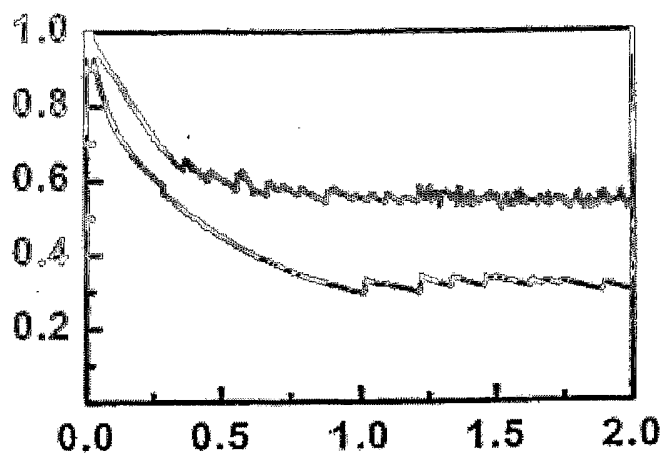


FIG. 10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/009806

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D5/20 C25D5/02 C25D7/12

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)

IPC 7 C25D

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 03/044247 A (TRUSTEES OF THE UNIVERSITY OF) 30 May 2003 (2003-05-30) page 2, line 16 - line 26 page 5, line 5 - page 6, line 15 -----	1, 7-12
A	US 2002/104762 A1 (DIETZ LOUIS J ET AL) 8 August 2002 (2002-08-08) paragraphs '0011!, '0013!, '0045!, '0082! - '0085!, '0097!; examples 1, 3 -----	1-12
A	US 6 361 660 B1 (GOLDSTEIN AVERY N) 26 March 2002 (2002-03-26) column 4, line 30 - line 63 -----	1-12
A	US 6 235 179 B1 (DUBOC JR ROBERT M ET AL) 22 May 2001 (2001-05-22) column 1, line 45 - line 63; claims 1-22 -----	13-19



Further documents are listed in the continuation of box C.



Patent family members are listed in 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 document 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 another 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

5 August 2004

Date of mailing of the international search report

19/08/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Teppo, K-M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/009806

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 03044247	A	30-05-2003	US 2003089611 A1	15-05-2003
			CA 2462295 A1	30-05-2003
			WO 03044247 A1	30-05-2003
US 2002104762	A1	08-08-2002	AU 9646001 A	15-04-2002
			EP 1337694 A1	27-08-2003
			WO 0229136 A1	11-04-2002
			US 2003209427 A1	13-11-2003
			AU 1495101 A	10-05-2001
			AU 7746200 A	10-05-2001
			AU 7844800 A	10-05-2001
			CA 2386047 A1	12-04-2001
			CA 2386165 A1	12-04-2001
			CA 2387992 A1	12-04-2001
			EP 1222609 A1	17-07-2002
			EP 1227929 A1	07-08-2002
			EP 1238125 A1	11-09-2002
			JP 2003529128 T	30-09-2003
			JP 2003511556 T	25-03-2003
			JP 2003511675 T	25-03-2003
			WO 0125002 A1	12-04-2001
			WO 0126038 A1	12-04-2001
			WO 0125510 A1	12-04-2001
US 6361660	B1	26-03-2002	US 6060026 A	09-05-2000
US 6235179	B1	22-05-2001	TW 500837 B	01-09-2002
			WO 0070127 A1	23-11-2000
			US 6731061 B1	04-05-2004