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(54) **Title:** DETECTION OF QUANTITY OF WATER FLOW USING QUANTUM CLUSTERS

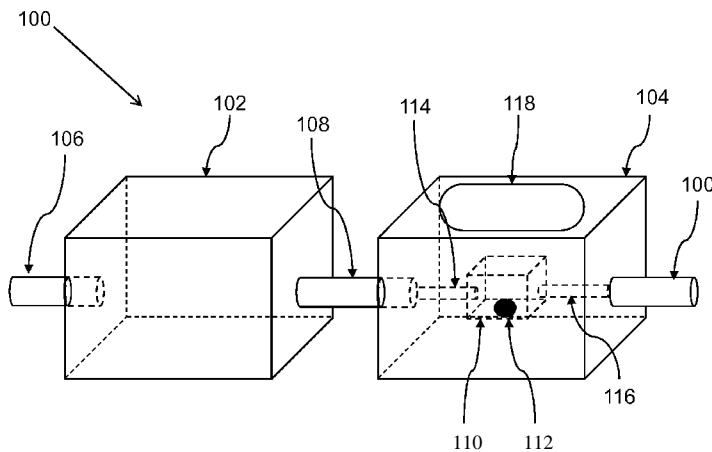


FIG. 1

(57) **Abstract:** The preparation of silver quantum clusters embedded in organic-templated-boehmite-nanoarchitecture (OTBN) and its use as a sensor for quantity of water flow measured by change of color in visible light upon flow of contaminated water have been provided. Silver quantum clusters-embedded OTBN are highly luminescent. Since the quantum clusters are embedded in the matrix, they are highly stable over a long period of time. The composition described here is utilized in the form of a device for 'visible / ultraviolet light color change-based detection' upon passage of water through a water purification device. Upon interaction with ions present in water, luminescent silver clusters undergo chemical transformation to Ag₂S nanoparticles. The transformation is reflected in the form of visible color change (from pink to black) and luminescence quenching (from red emission to negligible luminescence).



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DETECTION OF QUANTITY OF WATER FLOW USING QUANTUM CLUSTERS

BACKGROUND

TECHNICAL FIELD

[001] The present disclosure relates to the preparation of silver quantum cluster embedded in organic-templated-boehmite-nanoarchitecture (OTBN) and its use as a color changing sensor in the visible light or UV light for assessing the quantity of water passed through a water purification device.

TECHNICAL BACKGROUND

[002] The objective of providing safe and affordable drinking water is a global mission and it is eloquently articulated in United Nations Millennium Development Goal 2015, United Nations General Assembly resolutions (64/292 and 65/154) and article 47 of Indian Constitution. A major contribution to this can be made by providing an affordable safe drinking water at point-of-use, which is so far restricted largely due to un-availability of eco-conscious technology.

[003] For the past several years, various research groups are working on developing novel materials for water purification. An affordable and all-inclusive water purifier which removes broad range of contaminants such as pesticides has been disclosed by Indian patent 200767 and US patent 7968493, for removing microorganisms has been disclosed by Indian patent 20070608 and Indian patent applications 947/CHE/2011 and 4300/CHE/2011, for removing fluorides has been disclosed by Indian patent applications 2089/CHE/2009, 1529/CHE/2010 and 4062/CHE/2011, and for removing heavy metals has been disclosed by Indian patent applications 169/CHE/2009, 2433/CHE/2010 and 2563/CHE/2010. The water purification device is further described in Indian patent applications 2892/CHE/2010 and 1522/CHE/2011.

[004] An important aspect of a water purifier is to ensure delivery of quality output water throughout the stated life of the purifier. Usually it is quite difficult for a consumer to keep a note of volume of water passed through a water purifier. Unlike other consumer goods such as refrigerator, washing machine, etc., water purifier may still continue to function even though its performance may have shrunk significantly. The quality of output water directly relates to the health of consumer. Hence, it is necessary to ensure a reasonable check on the output water quality.

[005] As it would be evident from prior art that such a check on the output water quality is typically enforced using a flow meter which measures the volume of water passed. Owing to lack of actual water quality measurement at field, it is a first line of defense for output water quality. However, as it is well known that water quality across India varies significantly due to which the performance of water purification device also varies. Hence, it is important to have a second line of defense as simultaneous measurement of volume of water passed along with the input water quality. Depending on the input water quality, the measurement of volume of water should indicate if the water purification device is exhausted. This is an important premise of the invention articulated in this application.

[006] Quantum clusters of noble metals are a class of new materials which are less than 1 nm in core dimension, nearly equal to Fermi wavelength of an electron (0.5 nm for silver, M. A. H. Muhammed, T. Pradeep, in *Advanced fluorescence reporters in chemistry and biology II: Molecular constructions, polymers and nanoparticles*, Alexander P. Demchenko (ed.), 2010, Springer, Heidelberg). These are distinctly different from nanoparticles. In them band structure breaks into discrete energy levels, they have very high confinement in electronic structure, they exhibit molecular properties such as luminescence and plasmon resonance usually found with nanoparticles is absent. Due to these properties, quantum clusters have new utility in several applications such as optical storage, biological labels, catalysis, sensors, magnetism, optical absorption tunability, etc.

[007] Sensitivity of clusters to metal ions were reported by the group (Reactivity of Au₂₅ clusters with Au³⁺, M. A. Habeeb Muhammed, T. Pradeep, *Chem. Phys. Lett.*, 2007, 449, 186-190). Fluorescent clusters are used as sensitive and easy probes for

heavy metal ions in environmental samples such as pond water and soil by fluorescent turn-on mechanism (G.-Y. Lan, C.-C. Huang, H.-T. Chang, *Chem. Commun.*, 2010, 46, 1257-1259). A new class of water soluble silver clusters with high two-photon excitation cross-section providing tunability in excitation and emission wavelengths can be used as highly sensitive biolabels (S. A. Patel, C. i. Richards, J.-C. Hsiang, R. M. Dickson, *J. Am. Chem. Soc.*, 2008, 130, 11602-11603). DNA sequences templated silver clusters have been synthesized which can be tuned for fluorescence emission wavelength by varying the DNA template, implying useful biological applications (J. Sharma, H.-C. Yeh, H. Yoo, James H. Werner, J. S. Martinez, *Chem. Commun.*, 2010, 46, 3280-3282). Properties of water soluble fluorescent silver clusters can be varied by adopting different synthetic routes and their stabilizing polymer ligand (H. Xu, K. S. Suslick, *Adv. Mater.*, 2010, 22, 1078-1082). Water-soluble Ag-thioflavin T nanoclusters has been demonstrated for use in tracking of ultrasensitive biological assays both in vitro and in vivo (N. Makarava, A. Parfenov, i. V. Baskakov, *Biophys. J.*, 2005, 89, 572-580). An important biological analyte, cysteine can be sensed at low concentration by poly(methacrylic acid) templated silver clusters with specific fluorescent quenching mechanism (L. Shang, S. Dong, *Biosens. Bioelectron.*, 2009, 24, 1569-1573). Quantum optoelectronic logic operations can be created with electroluminescence of individual silver nanoclusters at room temperature (T.-H. Lee, J. i. Gonzalez, J. Zheng, R. M. Dickson, *Acc. Chem. Res.*, 2005, 38, 534-541). DNA-encapsulated Ag nanoclusters exhibit high fluorescence in the near IR, enabling a single-molecule-specific bunching feature (T. Vosch, Y. Antoku, J.-C. Hsiang, C. i. Richards, J. i. Gonzalez, R. M. Dickson, *PNAS*, 2007, 104, 12616-12621). Metal oxide supported silver quantum clusters are used as a catalyst (A. Leelavathi, T. U. B. Rao, T. Pradeep, *Nanoscale Res. Lett.*, 2011, 6, 123-132). Dehydrogenation of alcohols to carbonyl compounds by supported silver clusters has also been reported (K. Shimizu, K. Sugino, K. Sawabe, A. Satsuma, *Chem. Eur. J.* 2009, 15, 2341-2351). Alumina supported silver clusters have been used for direct amide synthesis from alcohols and amines with high selectivity (K. Shimizu, K. Ohshima, A. Satsuma, *Chem. Eur. J.* 2009, 15, 9977-9980). Poly(methacrylic acid) stabilized silver nanoclusters respond to the environment by having solvatochromic and solvato-fluorochromic (i.e., absorption and emission properties) responses useful for molecular sensing (I. Diez, M. Pusa, S. Kulmala, H. Jiang, A. Walther, A. S.

Goldmann, A. H. E. Muller, O. Ikkala, R. H. A. Ras, *Angew. Chem. Int. Ed.* 2009, 48, 2122-2125).

[008] Poly(methacrylic acid) stabilized silver nanoclusters prepared by sonochemical method can be used for bioimaging, chemical and biosensing, single-molecule studies, and possibly catalysis (H. Xu, K. S. Suslick, *ACS Nano*, 2010, 4, 3209-3214). Sub-nanometer clusters are used as Raman labels to identify true chemical information about single molecules (L. P.-Capadona, J. Zheng, J. I. Gonzalez, T.-H. Lee, S. A. Patel, R. M. Dickson, *Phys. Rev. Lett.*, 2005, 94, 058301). Silver clusters synthesized by micro-emulsion method display paramagnetic behavior (A. L.-Suarez, J. Rivas, C. F. R.-Abreu, M. J. Rodriguez, E. Pastor, A. H.-Creus, S. B. Oseroff, M. A. L.-Quintela, *Angew. Chem. Int. Ed.*, 2007, 46, 8823-8827). Water soluble fluorescent silver clusters have also been used for metal ion sensing (K. V. Mrudula, T. U. B. Rao, T. Pradeep, *J. Mater. Chem.*, 2009, 19, 4335-4342; B. Adhikari, A. Banerjee, *Chem. Mater.*, 2010, 22, 4365).

[009] Silver quantum clusters have also been studied from various perspectives: synthesis (various kinds of molecular clusters), characterization and utility (sensing and catalysis). Several other applications such as metal ion sensing and cell imaging were done with gold clusters as well. A representative list for silver clusters is given as follows:

[0010] Synthesis

- (i) Ag_7Au_6 : A 13 atom alloy quantum cluster, T. U. B. Rao, Y. Sun, N. Goswami, S. K. Pal, K. Balasubramanian, T. Pradeep, *Angew. Chem. Int. Ed.*, **2012**, 51, 2155-2159
- (ii) Conversion of double layer charge-stabilized $Ag@citrate$ colloids to thiol passivated luminescent quantum clusters, L. Dhanalakshmi, T. U. B. Rao, T. Pradeep, *Chem. Commun.*, **2012**, 48, 859-861
- (iii) A fifteen atom silver cluster confined in bovine serum albumin, A. Mathew, P. R. Sajanalal, T. Pradeep, *J. Mater. Chem.*, **2011**, 21, 11205-11212
- (iv) Ag_9 quantum cluster through a solid state route, T. U. B. Rao, B. Nataraju, T. Pradeep, *J. Am. Chem. Soc.*, **2010**, 132, 16304-16307
- (v) Luminescent Ag_7 and Ag_8 Clusters by interfacial synthesis, T. U. B. Rao, T. Pradeep, *Angew. Chem. Int. Ed.*, **2010**, 49, 3925-3929

[001 1] Characterization

(i) First principle studies of two luminescent molecular quantum clusters of silver, $\text{Ag}_7(\text{H}_2\text{MSA})_7$ and $\text{Ag}_8(\text{H}_2\text{MSA})_8$ based on experimental fluorescence spectra, Y. Sun, K. Balasubramanian, T. U. B. Rao, T. Pradeep, J. Phys. Chem. C, **2011**, 115, 42, 20380-20387

[001 2] Utility

- (i) Supported quantum clusters of silver as enhanced catalysts for reduction, A. Leelavathi, T. U. B. Rao, T. Pradeep, Nanoscale Research Letters, **2011**, 6, 123-132
- (ii) Investigation into the reactivity of unsupported and supported Ag_7 and Ag_8 clusters with toxic metal ions, M. S. Bootharaju, T. Pradeep, Langmuir, **2011**, 27, 8134-8143
- (iii) Luminescent sub-nanometer clusters for metal ion sensing: a new direction in nanosensors, I. Chakraborty, T. U. B. Rao, T. Pradeep, J. Haz. Mater., **2012**, 211-212, 396-403

[001 3] An important objective of providing clean and affordable drinking water to masses is to ensure delivery of pure water at the point-of-use. Ensuring the consumption of clean drinking water would facilitate realization of the fundamental right to life, of which clean water is a recognized component. This is also an important component of the United Nations Millennium Development Goal 2015.

[0014] In order to ensure quality drinking water at point-of-use, there are two possible approaches technologically. First is to develop an affordable sensor for detection of trace concentrations of drinking water contaminants, especially microorganisms. This approach is still under development at various research laboratories across the world. Second is to integrate a flow meter with a rigorously tested water purifier having a known life. Flow meter will tell the user when the known life of the water purifier is over and consumables such as the cartridge require a change. Indeed, the first approach is more reliable; however, since the technologies are still under development, it is wise to look at flow meters till a reliable solution is ready.

[0015] It is also to be noted that gravity-fed storage water purifiers can't operate with typical flow meters due to unavailability of high pressures ($P < 0.5$ psi). In such cases, a few approaches have been reported for the detection of volume of water passed.

[0016] **Ahmad** et al. in WO 2011/013142 have reported the use of a mechanical device along with a tablet made of sparingly water soluble salts. Intent is to have the tablet slowly dissolve upon passage of pre-determined volume of water. Once the tablet is dissolved, a mechanical action is initiated which blocks the flow of the liquid.

[0017] Another attempt is reported by Jambekar et al. in WO 2007/144256, wherein the biocide used is sparingly soluble in water and upon its dissolution, a mechanical action initiates the closure of water flow.

[0018] Ehara et al. in US patent number 5458766 have utilized battery along with a LED for determination of lifetime of the filter. Williams et al. in US patent number 7249524 have used an impeller device as a sensor for determining the flow and volume of water passing through the cartridge. Larkner et al. in US patent number 6585885 have reported a water purification system containing a sensing element coupled with an electronic control for accurately indicating the volume of water. Butts et al. in US patent number 491 8426 have reported an in-line filter consisting of a flow meter with no moving parts to measure the total volume of the fluid filtered. Chai et al. in US patent 7107838 have reported a water filter consisting of an electrode pair for sensing volume of the water dispensed. Guess et al. in US patent number 6613236 have used a tri-color LED emission for indicating volume of the water passed through the filter.

[0019] This invention reports the detection of volume of water passed through a water purification device, by use of a novel composition which undergoes change in the color upon continuous interaction with salts usually found in drinking water. The aspect of color change in nanomaterial, especially noble metal nanoparticles, upon interaction with ionic salts is well-studied. The conclusion from prior art is that nanoparticles undergo instant aggregation upon exposure to mild concentration of

salts. This is due to the reduction in surface energy of metal nanoparticles upon interaction with the counter ion. Usually, the aggregation of metal nanoparticles, especially silver, is almost instantaneous at salt concentrations of 100 ppm and above.

[0020] In light of the foregoing discussion, there exists a need to address the aforementioned problems and other shortcomings associated with the prior art methods and compositions. These needs and other needs are satisfied by the method and device described in the present disclosure.

SUMMARY

[0021] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, this disclosure, in one aspect, relates to water purification. Particularly the disclosure relates to the preparation of silver quantum cluster embedded in organic-templated-boehmite-nanoarchitecture (OTBN) and its use as a color changing sensor in the visible light or UV light for assessing the quantity of water passed through a water purification device.

[0022] An object of the present invention is to synthesize silver clusters in the OTBN matrix for protecting the silver quantum clusters from the segregation of common ions present in the drinking water.

[0023] Another object of the present invention is to provide a method for preparing a silver quantum clusters embedded in organic-templated-boehmite-nanoarchitecture (OTBN).

[0024] Yet another object of the invention is to device a low cost visible sensor for the volume of water passed through the cartridge so as to detect the lifetime of the water purifier.

[0025] Yet another object of the present invention is to provide a water purification device with a water flow meter having a silver quantum clusters embedded in OTBN to detect the quantity of water flowing.

[0026] Yet another object of the invention is to utilize the changes in color in the absorbed visible light with volume of water passed, as an indicator of lifetime of the water purification device.

[0027] Still another object of the invention is to utilize the changes in luminescence in the absorbed UV light with volume of water passed, as an indicator of lifetime of the water purification device.

[0028] In one aspect, the present disclosure provides a method for detecting the quantity of water flow using silver quantum clusters embedded in organic-templated-boehmite-nanoarchitecture (Ag QCs-OTBN). The OTBN matrix is used for protecting the silver quantum clusters. The method involves monitoring the color of the silver quantum clusters in a light. The change in color of the silver quantum clusters from a first color to a second color indicates a specific amount of contaminated water has been passed.

[0029] In another aspect of the present disclosure a water flow meter have been provided. The water flow meter includes a water inlet and a water outlet for flow of water in and out of the flow meter respectively, a sensor and a transparent casing. The sensor is present inside the flow meter. The sensor having silver quantum clusters embedded in organic-templated-boehmite nanoarchitecture (OTBN). The embedding of silver quantum clusters in OTBN protects silver quantum clusters from segregation of ions present in the contaminated water. The transparent casing allows monitoring the color of the sensor when the water is flowing. The change in color of the sensor from a first color to a second color indicates a specific amount of contaminated water have been passed through the water flow meter.

BRIEF DESCRIPTION OF FIGURES

[0030] The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

[0031] Fig. 1 shows a perspective view a water purification device, in accordance with an aspect of the present invention;

[0032] Fig. 2 shows a flowchart showing the method of detecting the quantity of water flow, in accordance with an aspect of the present invention;

[0033] Fig. 3 shows luminescence of glutathione protected Ag QCs embedded in OTBN under UV- lamp (preparation detailed in example 1), in accordance with an aspect of the present invention;

[0034] Fig. 4 shows color change observed during the passage of synthetic challenge water through Ag QCs embedded in OTBN (first row: photographs of disc in visible light, second row: photographs of disc in UV light). The color change mentioned here in visible light are 0 L: pink, 50 L: light brown, 100 L: dark brown, 150 L: dark yellow, 200 L: yellowish green, 250 L: black. The color change mentioned here in UV light is 0 L: red, 50 L: violet, 100 L: dull violet, 150 L: dark blue, 200 L: blue, 250 L: black. Images are shown in the shades of black and white in accordance with an aspect of the present invention;

[0035] Fig. 5 shows (a) TEM image of Ag QCs embedded in OTBN matrix (b) TEM image of Ag QCs-OTBN, upon electron beam irradiation for 20 minutes, in accordance with an aspect of the present invention;

[0036] Fig. 6 shows FTIR spectra of (a) OTBN, (b) Ag QCs embedded in OTBN and (c) Ag QCs embedded in OTBN, after passage of 250 L of synthetic challenge water, in accordance with an aspect of the present invention;

[0037] Fig. 7 shows luminescence spectra of (a) Ag QCs embedded in OTBN and those after the passage of (b) 50 L, (c) 150 L and (d) 250 L of water, excited at 450 nm, in accordance with an aspect of the present invention;

[0038] Fig. 8 shows X-ray diffractogram of (a) AlOOH (JCPDS PDF #832384), (b) chitosan, (c) OTBN, (d) silver quantum clusters embedded in OTBN, (e) silver clusters embedded in OTBN after the passage of 250 L of synthetic challenge water

and (f) silver sulfide (JCPDS PDF #893840), in accordance with an aspect of the present invention;

[0039] Fig. 9 EDAX spectrum of Ag QCs embedded in OTBN. Inset: elemental X-ray images of Al K α , O K α , C K α , Ag La and S Ka of the sample. The corresponding SEM image is also shown in the inset, in accordance with an aspect of the present invention; and

[0040] Fig. 10 EDAX spectrum of Ag QCs embedded in OTBN after the passage of 250 L of water. Inset: elemental X-ray images of Al Ka, O Ka, C Ka, Ag La, Si Ka, Ca Ka, Cl Ka and S Ka of the sample. The corresponding SEM image is also shown in the inset, in accordance with an aspect of the present invention.

DESCRIPTION

[0041] The present invention can be understood more readily by reference to the following detailed description of the invention and the examples included therein.

[0042] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0043] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

[0044] The novelty of the composition reported here is in the aspect of embedding the silver clusters in a nanoarchitecture matrix which enables protection of silver surface from various ions present in synthetic challenge water.

[0045] The present invention discloses the synthesis, characterization and application of silver quantum clusters impregnated organic-templated-boehmite-nanoarchitecture (Ag QCs-OTBN). The as-synthesized Ag QCs-OTBN composition is characterized by a number of spectroscopic and microscopic techniques. The utility of Ag QCs-OTBN as a visible sensor of quantity of water passed through a water purification device has been demonstrated.

[0046] The synthesized Ag QCs-OTBN is normally used in a water purification device. More specifically the Ag QCs-OTBN is used in the water flow meters to detect the quantity of water flowing.

[0047] A perspective view of a gravity fed water purification device 100 according to an embodiment of the disclosure is shown in Fig. 1. The various elements shown in Fig. 1 are for the representational purpose. It should be appreciated that the dimensions and design of the gravity fed water purification device 100 and their elements varies as per the requirements. The gravity fed water purification device 100 mainly includes a particulate filter 102 and a water flow meter 104. The gravity fed water purification device 100 is configured to purify the contaminated water.

[0048] In an embodiment of the disclosure, the water flow meter 104 is present after the water filter 102 as shown in Fig. 1. In another embodiment of the disclosure, the water flow meter is present before the water filter (not shown in the Fig.). It should be appreciated that the water flow meter 104 can also be used irrespective of the presence of the water filter 104. The use of water flow meter 104 is not limited to the particulate water filter 102. The use of any other type of water filter available in the market is well within the scope of this disclosure.

[0049] The contaminated water is provided to the particulate filter 102 through a first inlet 106. The contaminated water is filtered in the particulate filter 102 and passed on to the water flow meter 104 through a first outlet 108. Inside the water flow meter

104, a site 110 has been provided. The site 110 includes a sensor 112. The sensor 112 is silver quantum clusters embedded in the OTBN according to an embodiment of the disclosure. The embedding of silver quantum clusters in OTBN protects silver quantum clusters from segregation of ions present in the water. The water enters the site 110 through a second inlet 114 and goes out of the site 110 from a second outlet 116 as shown in Fig. 1. The water flow meter 104 further includes a transparent casing 118 or a transparent window 118. As the water flows over the silver quantum clusters, the color of silver quantum clusters changes from a first color to a second color. The transparent casing 118 allows a user to monitor the color of the silver quantum clusters embedded in the OTBN. The change in color indicates that a specific amount of water has been passed from the water flow meter and the same amount of water has been purified using the water purification device 100.

[0050] The change in the color of the silver quantum clusters is detected by using one of the visible light or the Ultraviolet light. The various changes in the color of the silver quantum clusters in the visible light or the Ultraviolet light are shown in Fig. 4 according to an embodiment of the disclosure.

[0051] A method for detecting the quantity of contaminated water using the water flow meter 104 is shown in a flowchart 200 of Fig. 2 in accordance with the embodiment of Fig. 1. At step 202, the sensor 112 is provided at the site 110. The sensor 112 is silver quantum clusters embedded in the OTBN. The embedding of silver quantum clusters in OTBN protects silver quantum clusters from segregation of ions present in the water. At step 204, the water is passed through the site 112. And finally at step 206, the color of the silver quantum clusters is monitored through the transparent casing 118. The change in color indicates that the specific amount of water has been passed through the water flow meter 104.

[0052] The novelty of the composition of silver quantum clusters reported in the disclosure is that the visible sensor based on Ag QCs-OTBN not only assesses the volume of water passed as a mechanical flow meter does; it assesses the lifetime of a cartridge based on the input water quality. A measure of the input water quality can be taken as ionic strength of the input water.

[0053] In an embodiment of the disclosure, the output reading of the sensor 112 is calibrated as per the requirement of the user. The sensor 112 is present at a fixed location. When the water flows inside the flow meter 104, then only a certain volume V_1 of water out of the total volume of water (coming in the flow meter 104) passes through the sensor 112. Thus, the passing of only certain volume V_1 results in color change of the Ag QCs-OTBN sensors from pink to black. For example, say the sensor is placed in such a way that only 10% of water coming in the flow meter 104 passes through the sensor 112. It is noted that the color of sensor 112 has been changed after a passage of 250 L. Since only 10 % is flowing through the sensor, so we calculate that a total of 2500 L has passed through the flow meter 104. Therefore, it is necessary to calibrate the output reading of the sensor 112.

[0054] In an illustrative embodiment, the present invention describes that the visible color change of the Ag QCs-OTBN from pink to black does not happen after a defined volume of any input water is passed. The color change happens in a reduced volume of water if TDS of the input water is greater than 1,000 ppm and will happen after much larger volume of water, if TDS of the input water is less than 100 ppm.

[0055] The efficiency of adsorption based removal of contaminants depends on ionic composition of input water. The interfering ions in the water are known to reduce the capacity/lifetime of the adsorption based filters. Therefore lifetime of the filter will be drastically reduced from the expected capacity if high ionic strength input water is passed. Hence, for any adsorption based filter, it is very important to have a lifetime sensor which works based on input water quality. The following experimental methods and their results describe such a color changing sensor in detail.

Experimental methods

Material characterization

[0056] The identification of the phase(s) of the as-prepared sample was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu-K α radiation at $\lambda = 1.5418 \text{ \AA}$. Surface morphology, elemental analysis and elemental mapping studies were done using a Scanning Electron Microscope (SEM) equipped with

Energy Dispersive Analysis of X-rays (EDAX) (FEI Quanta 200). For this, sample in the gel form was re-suspended in water by sonication for 10 min and drop casted on an indium tin oxide (ITO) conducting glass and dried. High Resolution Transmission Electron Microscopy (HRTEM) was done using JEM 3010 (JEOL, Japan). The samples were spotted on amorphous carbon coated copper grids and dried at room temperature. FT-IR spectra were measured using Perkin Elmer Spectrum One instrument and KBr crystals were used as the matrix for preparing samples. Luminescence measurements were carried out by using Jobin Vyon NanoLog instrument. The band pass for excitation and emission was set as 2 nm.

[0057] The accompanying examples and figures and examples, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention. This should, however, not be construed as limiting the scope of the invention.

Example 1

[0058] This example describes the in-situ preparation of silver quantum clusters protected by glutathione in the OTBN gel. OTBN was prepared as reported in the previous patent application (1529/CHE/2010). The filtered OTBN gel was used as a matrix for in-situ preparation of silver quantum clusters. The prepared OTBN gel was re-suspended in water, to which silver precursor (silver nitrate, silver fluoride, silver acetate, silver permanganate, silver sulfate, silver nitrite, silver salicylate or a combination thereof) was added drop-wise. The percentage of silver loading in OTBN gel was 3%. After stirring the gel for an hour, surface protecting agent (glutathione) was added drop-wise; then the solution was allowed to stir for an hour. Sodium borohydride was added drop-wise to the above solution at ice-cold condition (molar ratio of silver precursor to reducing agent ratio was 1:4). Then the solution was allowed to stir for an hour, filtered and dried at room temperature (28 °C).

Example 2

[0059] The method described in example 1 was modified to prepare the glutathione protected fluorescent silver quantum clusters in the OTBN gel material. Silver to glutathione ratio was varied from 1:1 to 1:10.

Example 3

[0060] The method described in example 1 was modified to prepare the glutathione protected fluorescent silver quantum clusters on OTBN gel material with various molar ratios of silver to sodium borohydride such as 1:4 and 1:8.

Example 4

[0061] The method described in example 1 was modified to prepare clusters with different surface protecting agents like mercaptosuccinic acid, polyvinyl pyrrolidone and trisodium citrate in OTBN gel.

Example 5

[0062] This example describes the in-situ preparation of silver quantum clusters protected with glutathione on the OTBN powder. The dried OTBN powder was crushed to a particle size of 100-150 μm . The powder was shaken in water using a shaker to which silver precursor (silver nitrate, silver fluoride, silver acetate, silver permanganate, silver sulfate, silver nitrite, silver salicylate or a combination thereof) was added drop-wise. The percentage of silver loading in OTBN powder was 3%. After shaking the dispersion for an hour, glutathione was added drop wise; then the dispersion was shaken for an hour. Sodium borohydride was added drop-wise to the above dispersion at ice-cold condition (molar ratio of silver to reducing agent ratio was 1:4). Then the dispersion was shaken for an hour, filtered and dried at room temperature (28 °C).

Example 6

[0063] This example describes the preparation of silver quantum clusters in a variety of chitosan-metal oxide/hydroxide/oxyhydroxide composite gels. The metal oxide/hydroxide/oxyhydroxide can be based on aluminum, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium, zirconium or a combination thereof. The synthetic procedure for such a composition is as follows: the chosen salt solution was added slowly into the chitosan solution (dissolved in 1 - 5 % glacial acetic acid or HCl or combination thereof) under vigorous stirring for 60 minutes and kept overnight at rest. Aqueous ammonia or NaOH solution was added slowly into the metal-chitosan solution under vigorous stirring to precipitate the metal-chitosan composites. These gels were used as matrices for the in-situ preparation of ligand protected silver quantum clusters.

Example 7

[0064] This example describes the preparation of fluorescent silver quantum clusters on magnetic materials. Superparamagnetic Fe_3O_4 was prepared by method as reported in prior art (M.T. Lopez-Lopez, J.D.G. Duran, A.V. Delgado, F. Gonzalez-Caballero, J. Colloid Interface Sci., **2005**, 291, 144-151). Freshly prepared superparamagnetic particles were added to the chitosan solution, allowed to stir for 2 h, precipitated at pH 9 using NaOH or aqueous ammonia and filtered to remove the salt contents. Superparamagnetic composite was re-suspended in water, to which silver precursor (silver nitrate, silver fluoride, silver acetate, silver permanganate, silver sulfate, silver nitrite, silver salicylate or a combination thereof) was added drop-wise. The percentage of silver loading in Fe_3O_4 -chitosan gel was 3%. After stirring the solution for an hour, surface protecting agent (glutathione) was added drop wise; then the solution was allowed to stir for an hour. Sodium borohydride was added drop-wise to the above gel at ice-cold condition (molar ratio of silver to reducing agent ratio was 1:4). Then the solution was allowed to stir for an hour, filtered and dried at room temperature (28 °C).

Example 8

[0065] This example describes the visible sensor for volume of water passed through a column using silver quantum clusters in organic-templated-boehmite-nanoarchitecture (Ag QCs-OTBN). A known quantity of Ag QCs-OTBN was packed as a disk of diameter anywhere between 35 mm to 55 mm, in a column. Challenge water having ionic concentration as prescribed by US NSF for testing contaminant removal was used in the study. The output water from a standard carbon block was passed through Ag QCs-OTBN disk at 60 to 120 mL/min flow rate. At periodic intervals, color of the disk was photographed and emission spectra of the material were collected. The change in color from pink to black was observed after the passage of 250 L of water. The material was collected, dried and analyzed using various techniques. Experiment was conducted with the carbon block at the output of the AgQCs-OTBN disk as well.

Example 9

[0066] This example describes the visible sensor based on fluorescence quenching of Ag QCs-OTBN to quantify volume of water passed through a column. A known quantity of Ag QCs-OTBN was packed in the form of a disk of diameter anywhere between 35 mm to 55 mm. The feed water was passed through this disk at a flow rate of 80 mL/min. At periodic intervals, color of the disk was photographed and emission spectra of the material were collected. The change in color from pink to black was observed after the passage of 250 L of water. The black material was collected, dried and analyzed using XRD and EDAX.

Results

[0067] Fig. 3 depicts in gray shades that the Ag QCs-OTBN is highly luminescent under UV light and luminescence can be observed even under low UV intensity (8 W low pressure Hg lamp), in accordance with an aspect of the present invention. The experiments results in the pink luminescence of Ag QCs-OTBN under UV light. 20 g of glutathione-Ag QCs-OTBN, taken in a petri dish and kept under an 8 W low pressure Hg UV lamp. The composition shown here was stable and it exhibited pink

luminescence intensity even after a few months of storage under ambient conditions. Fig. 3 displays various shades of black and white as luminescence in the central region of the petri dish. This is in contrast to other monolayer protected Ag clusters reported in the literature as they exhibit poor stability under ambient conditions. The stability of Ag QCs in OTBN is due to the presence of highly protective OTBN environment around the quantum cluster. The role of OTBN matrix in stabilizing nanoparticles has already been demonstrated in our previous patent application (947/CHE/201 1). It was shown that the presence of OTBN matrix ensures the stability of silver nanoparticles in synthetic challenge water conditions and can be used successfully for water treatment applications. AgQCs prepared in other matrices as described in Example 6, especially those of titanium, zinc, cerium, and zirconium were also luminescent.

[0068] Fig. 4 shows Ag QCs embedded in OTBN is used as a sensor for detecting the volume of water that can be filtered by a water filtration unit, in accordance with an aspect of the present invention. The figure shows the color of the Ag QCs embedded in OTBN changes from brighter shade of gray at 402 to darker shade of gray at 404 after the passage of particular amount of water. As lifetime of any water purifier depends on the input water quality, the Ag QCs-OTBN sensor should indicate the volume of water that can be passed through a filter and also should indicate whether the water purification device is exhausted or not. To achieve this, the output water from the water filtration unit is passed through the sensor material and collected in the storage container. After the passage of water, the color of the Ag QCs-OTBN changes as shown in Fig. 4. First row in Fig. 4 shows color of Ag QCs-OTBN disc in visible light and second row shows luminescence of Ag QCs-OTBN disc in UV light. Prior to the passage of water, the material is pink in color (brighter shade of gray at 402 is shown in Fig. 4) and exhibits high luminescence. Upon passage of water, the material undergoes gradual change and finally turns black (darker shade of gray at 404 is shown in Fig. 4) with quenching in luminescence. The color change mentioned here in visible light are 0 L: pink, 50 L: light brown, 100 L: dark brown, 150 L: dark yellow, 200 L: yellowish green, 250 L: black. The color change mentioned here in UV light is 0 L: red, 50 L: violet, 100 L: dull violet, 150 L: dark blue, 200 L: blue, 250 L: black. Images are shown in the shades of black and white in accordance with an aspect of the present invention. A blank trial with OTBN

matrix alone indicated that OTBN matrix does not contribute to the color change upon passage of water. This confirms that the change in color of the material is due to silver quantum clusters. Similar color change was seen in AgQCs prepared in matrices containing titanium, zinc, cerium, and zirconium.

[0069] Fig. 5 (a) shows the TEM image of Ag QCs embedded in OTBN, in accordance with an aspect of the present invention. Clusters in OTBN are not observable in TEM images. This is due to sub-nanometer size of the Ag QC. In the earlier report the formation of large size silver nanoparticles upon electron exposure on naked glutathione protected silver clusters was observed (T. U. B. Rao, B. Nataraju, T. Pradeep, J. Am. Chem. Soc, 2010, 132, 16304-16307). Unlike naked clusters, Ag QCs in OTBN described in this invention was stable under the electron beam (Fig. 5b). The stability of Ag QCs in OTBN under electron beam confirms that Ag cluster is highly protected by the OTBN matrix. Here, the electron beam induced aggregation of silver clusters did not happen as the clusters were embedded inside the OTBN matrix.

[0070] Fig. 6 depicts an FTIR spectra of (a) OTBN, (b) Ag QCs embedded in OTBN and (c) Ag QCs embedded in OTBN after passage of 250 L of synthetic challenge water, in accordance with an aspect of the present invention. Impregnation of Ag QCs in OTBN leads to change in the N-H stretching band around 1402 cm^{-1} (shown in curve b). After passage of 250 L synthetic challenge water, N-H band resembles the same as of OTBN. The features present in the region of $2000\text{-}500\text{ cm}^{-1}$ confirm the presence of glutathione (M. A. Habeeb Muhammed, S. Ramesh, S. S. Sinha, S. K. Pal and T. Pradeep, Nano Res., 2008, 1, 333-340). The spectra show a strong band at 3450 cm^{-1} due to hydrated water.

[0071] Fig. 7 shows a luminescence spectra of (a) Ag QCs embedded in OTBN and those after the passage of (b) 50 L, (c) 150 L and (d) 250 L of water, in accordance with an aspect of the present invention. The excitation spectrum was measured at 450 nm whereas corresponding emission spectrum was measured around 650 nm. It can be observed that the luminescence of Ag QCs-OTBN gradually decreases upon passage of synthetic challenge water. After the passage of 250 L, emission has fully

quenched. It is to be noted that peaks observed at $\lambda = 400$ nm and 475 nm are impurity lines of the excitation source.

[0072] Fig. 8 is a X-ray diffractogram of (a) AlOOH (JCPDS PDF #832384), (b) chitosan, (c) OTBN, (d) silver quantum clusters embedded in OTBN, (e) silver clusters embedded in OTBN after the passage of 250 L of synthetic challenge water and (f) JCPDS PDF #893840 of silver sulfide, in accordance with an aspect of the present invention. The peaks attributed to Ag_2S are marked in (e). The XRD of as-synthesized OTBN showed peaks corresponding to (120), (013), (051), (151), (200), (231) and (251) planes (Fig. 8c). All these peaks can be indexed to orthorhombic-AlOOH (JCPDS PDF #832384) (Fig. 8a). The broadened XRD peaks imply that the OTBN crystallite size is very small. The mean crystallite size calculated from the Scherrer formula shows that nanocrystals are of ~3.5 nm. The presence of organic template (chitosan) is also clear from the XRD data. The peaks corresponding to 2θ (in degrees) 18.7°, 20.6°, 41.2° in Fig. 8c are attributed to the presence of the organic template. XRD of Ag QCs-OTBN (Fig. 8d) is not different from OTBN (Fig. 8c). This is due to the fact that clusters are composed of very few atoms and is also smaller than wavelength of X-ray used. Fig. 8e shows that after the passage of 250 liters of water, new peaks appeared corresponding to silver sulfide. The new peaks are indexed based on the pattern of standard silver sulfide (JCPDS PDF #893840) (Fig. 8f). The labeled peaks (marked with \blacksquare) are designated as (-121) and (-112) respectively.

[0073] Fig. 9 and fig. 10 shows EDAX spectrum of as-synthesized QCs embedded in OTBN, in accordance with an aspect of the present invention. This confirms the presence all expected elements such as Ag, S, C and O. The inset shows SEM and its elemental mapping before the passage of water. EDAX spectrum after the passage of 250 L of synthetic challenge water is shown in Fig. 10 and it confirms the presence of all the expected elements such as Al, O K, C K, Ag L, Si K, Ca K, Cl K and S K. Ca, Si and Cl are from water. The inset shows the SEM and elemental maps of the material after the passage of water. The presence of Ca, Si and Cl on Ag QCs-OTBN indicates that the quenching in luminescence and change in color is due to salt induced aggregation of silver quantum clusters. Images in Fig. 9 and Fig.

10 are shown in the shades of black and white in accordance with an aspect of the present invention.

[0074] The described aspects are illustrative of the invention and not restrictive. It is therefore obvious that any modifications described in this invention, employing the principles of this invention without departing from its spirit or essential characteristics, still fall within the scope of the invention. Consequently, modifications of design, methods, structure, sequence, materials and the like would be apparent to those skilled in the art, yet still fall within the scope of the invention.

[0075] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A method for detecting the quantity of contaminated water flow, the method comprising:
 - providing a sensor at a site, wherein the sensor having quantum clusters embedded in organic-templated-nanometal oxyhydroxide, the embedding in organic-templated-nanometal oxyhydroxide protects quantum clusters from ions present in the contaminated water;
 - passing contaminated water through the site; and
 - monitoring the color of the sensor in a light, wherein the change in color from a first color to a second color indicating a specific amount of contaminated water have been passed through the site.
2. The method of claim 1, wherein the light is at one of a visible light or an Ultraviolet light.
3. The method of claim 1, wherein the organic-templated-nanometal oxyhydroxide is organic-templated-boehmite nanoarchitecture (OTBN).
4. The method of claim 1, wherein the quantum clusters is silver quantum clusters.
5. The method of claim 4, wherein the silver quantum clusters are embedded in OTBN by impregnating a plurality of silver ions with OTBN in the gel state, wherein the silver ions reduced to a zerovalent state by the use of a reducing agent and protecting by a surface protecting agent.
6. The method of claim 4, wherein silver quantum clusters are embedded in OTBN by contacting externally prepared silver quantum clusters with OTBN in the gel state.

7. The method of claim 4, wherein silver quantum clusters are embedded in OTBN by contacting externally prepared silver quantum clusters with OTBN in the solid state.
8. The method of claim 4 further includes the process of drop-wise addition of one of silver ion or silver quantum clusters to OTBN
9. The method of claim 4 further includes soaking of silver quantum clusters in OTBN for duration of about 30 minutes to about 12 hours.
10. The method of claim 1, wherein the organic template is prepared of at least one of a chitosan, a banana silk and cellulose.
11. The method of claim 5, wherein the reducing agent is sodium borohydride.
12. The method of claim 1 further includes a silver precursor used for the preparation of silver quantum clusters, wherein the silver precursor is made of at least one of a silver nitrate, silver fluoride, silver acetate, silver sulfate and silver nitrite.
13. The method of claim 1, wherein the weight ratio of silver quantum cluster to OTBN is about 0.01 % to about 10%.
14. The method of claim 1, wherein the weight ratio of silver quantum cluster to OTBN is about 0.01 % to about 5%.
15. The method of claim 5, wherein the concentration of the reducing agent is ranging from about 0.005 M to about 1 M.
16. The method of claim 1 wherein quantum clusters is based on at least one of a silver, gold, copper, iron, nickel, platinum and palladium.

17. The method of claim 1 wherein the nanometal is at least one of an aluminium, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium and zirconium.

18. A gravity fed water purification device comprising:

a particulate filter configured to filter the water;

a first inlet allowing water to move in the particulate filter;

a first outlet configured to pass the water out of the particulate filter;

and

a water flow meter configured to receive the water from the particulate filter, wherein the water flow meter comprising:

a sensor present inside the flow meter, wherein the sensor having silver quantum clusters embedded in organic-templated-boehmite nanoarchitecture (OTBN), the embedding of silver quantum clusters in OTBN protects silver quantum clusters from segregation of ions present in the water;

and

a transparent casing allows monitoring the change of color of the sensor when the water is flowing, wherein the change in color from a first color to a second color indicating a specific amount of contaminated water have been passed through the water flow meter.

19. A water flow meter comprising:

a second inlet for flowing of water inside the flow meter;

a second outlet for flowing of water outside the flow meter;

a sensor present inside the flow meter, wherein the sensor having silver quantum clusters embedded in organic-templated-boehmite nanoarchitecture (OTBN), the embedding of silver quantum clusters in OTBN

protects silver quantum clusters from segregation of ions present in the contaminated water; and

a transparent casing allows monitoring the color of the sensor when the water is flowing, wherein the change in color from a first color to a second color indicating a specific amount of contaminated water have been passed through the water flow meter.

20. The water flow meter of claim 19, wherein the OTBN is in the form of a plurality of granules.
21. The water flow meter of claim 19, wherein the particle size of the plurality of granules is from about 0.3 mm to about 5 mm.
22. The water flow meter of claim 19, wherein the particle size of the plurality of granules is from about 0.3 mm to about 1mm.

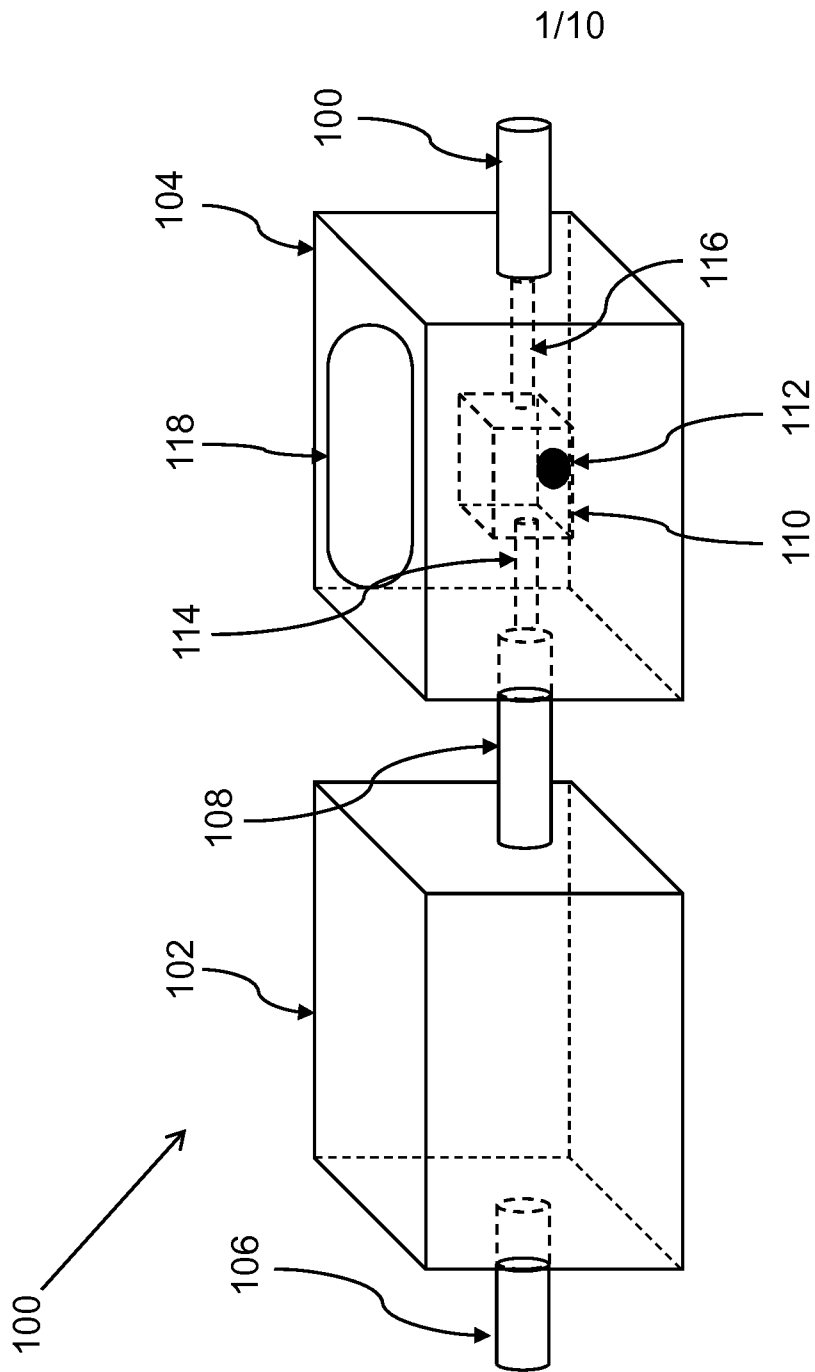


FIG. 1

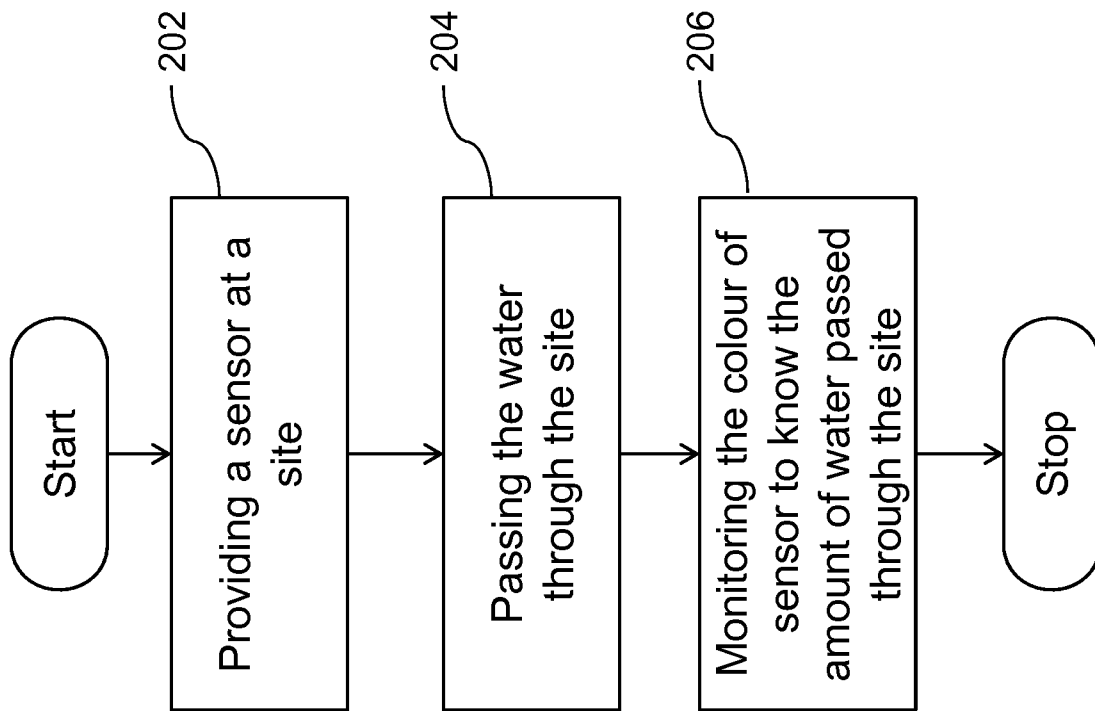


FIG. 2

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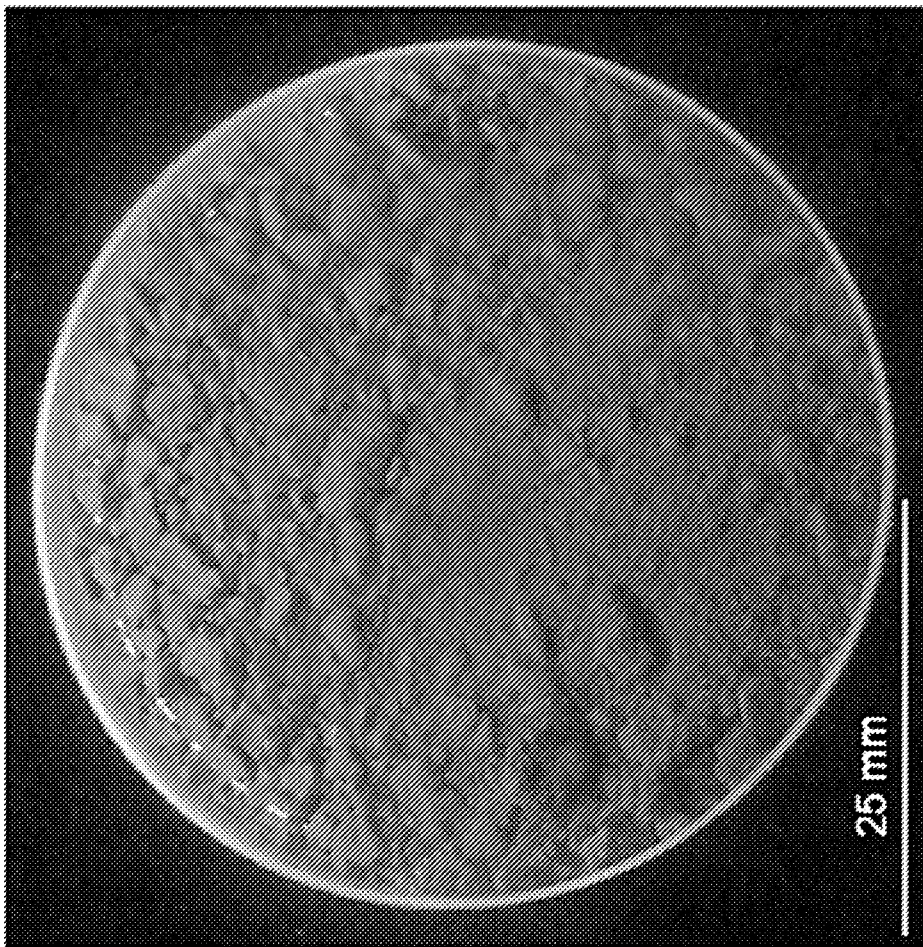


FIG. 3

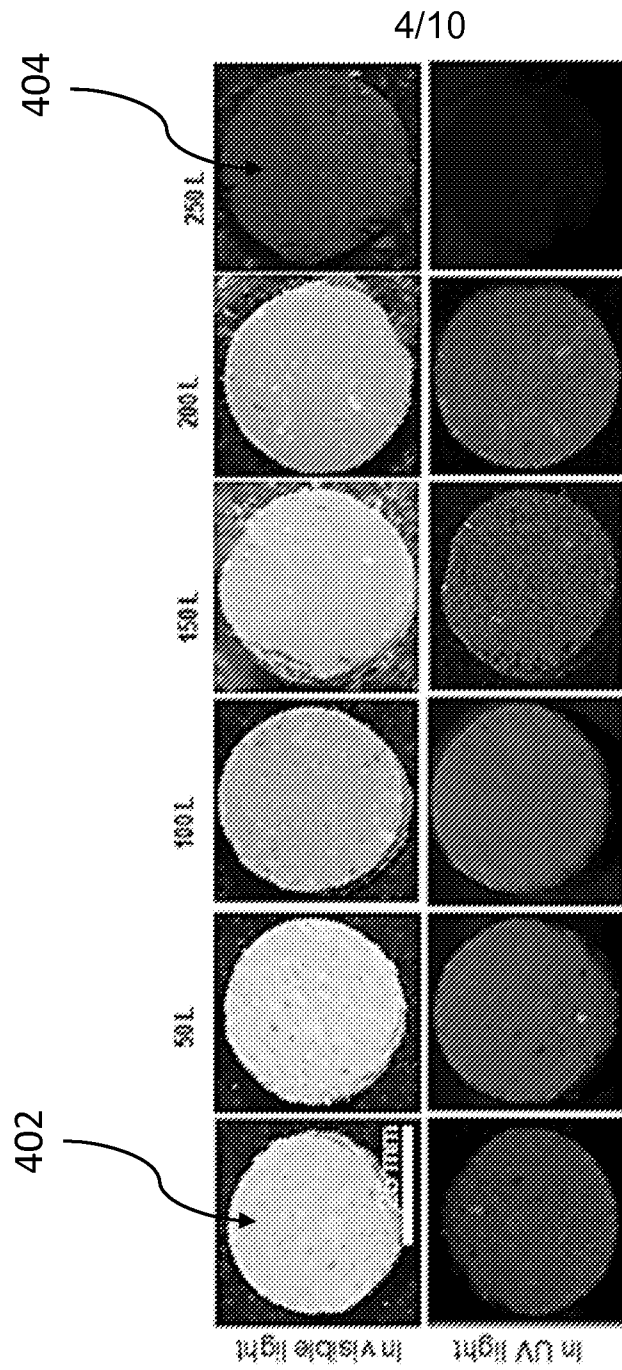


FIG. 4

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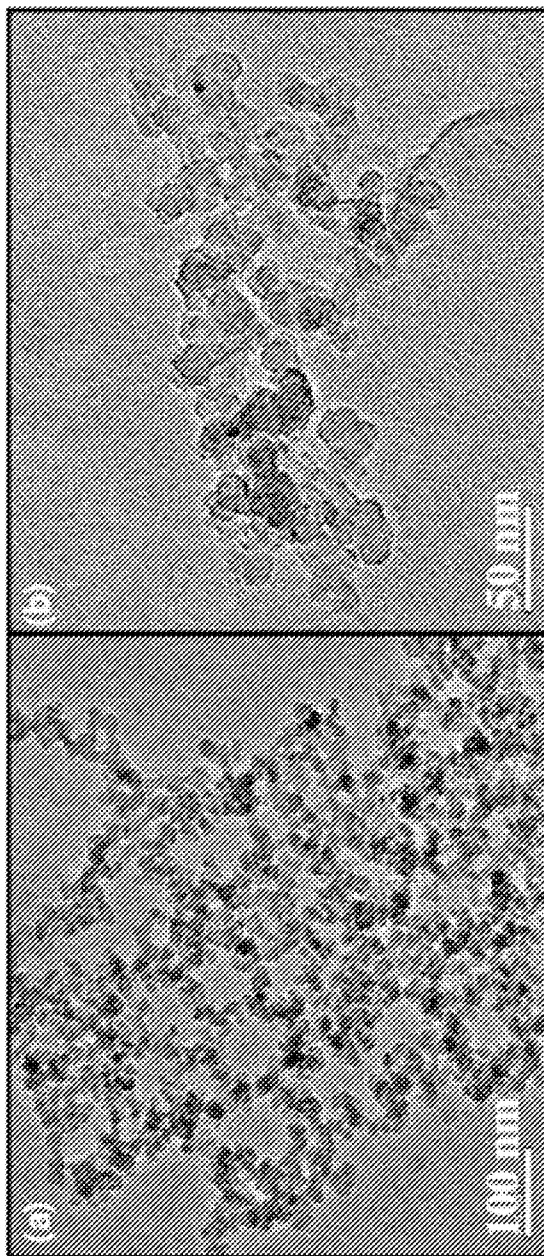


FIG. 5

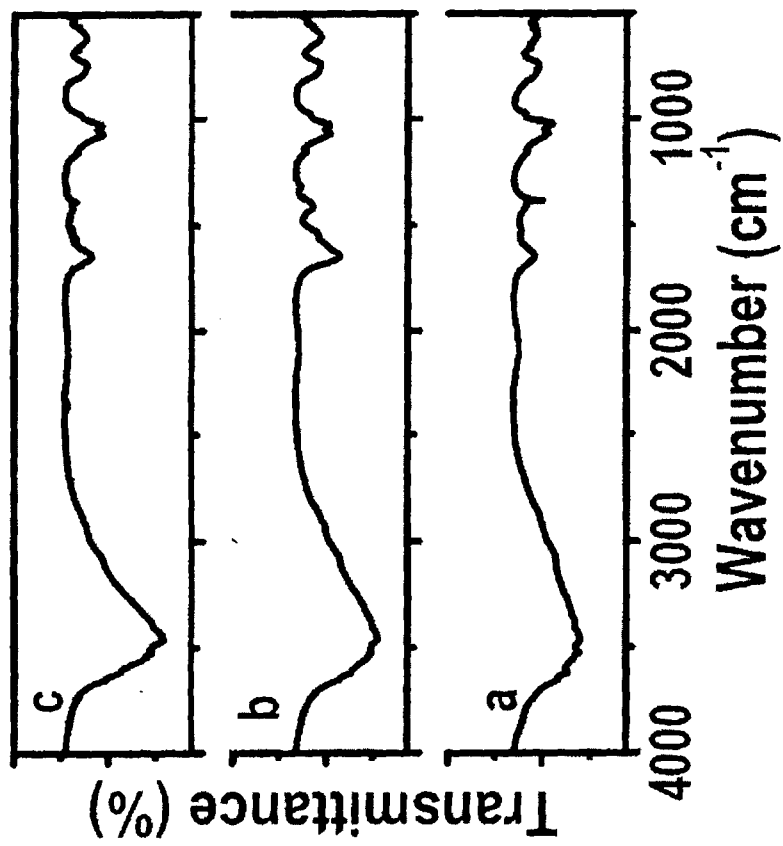


FIG. 6

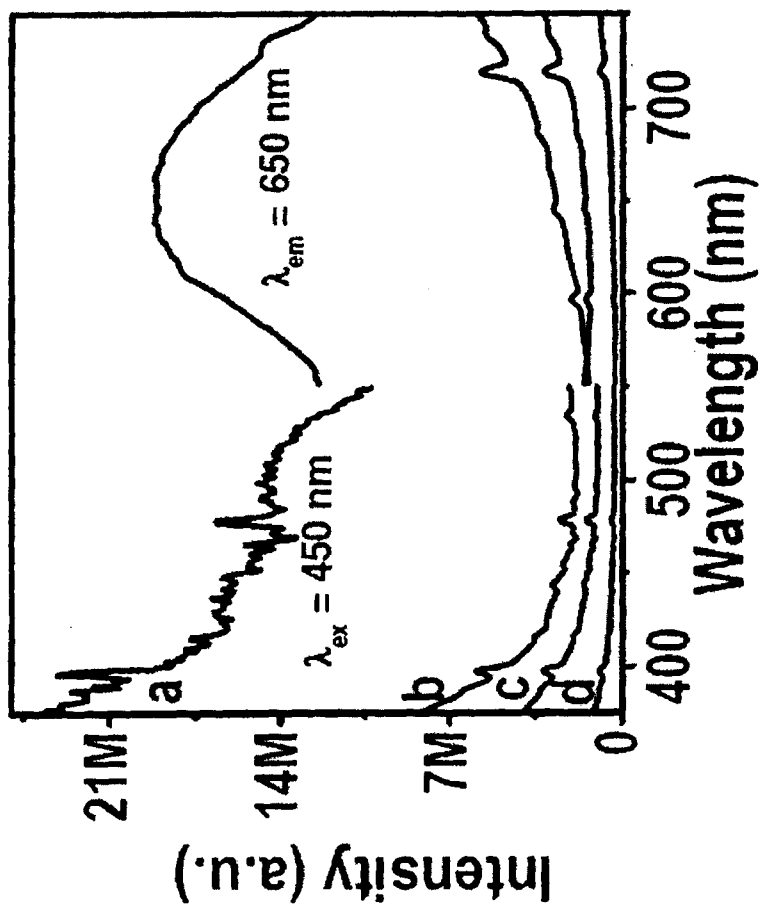


FIG. 7

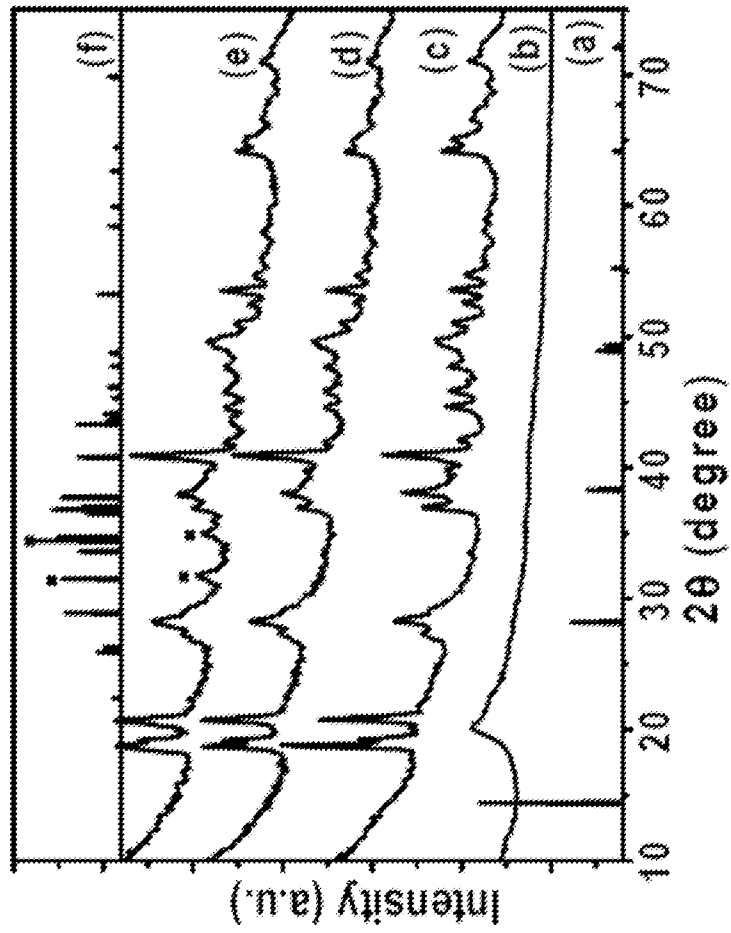


FIG. 8

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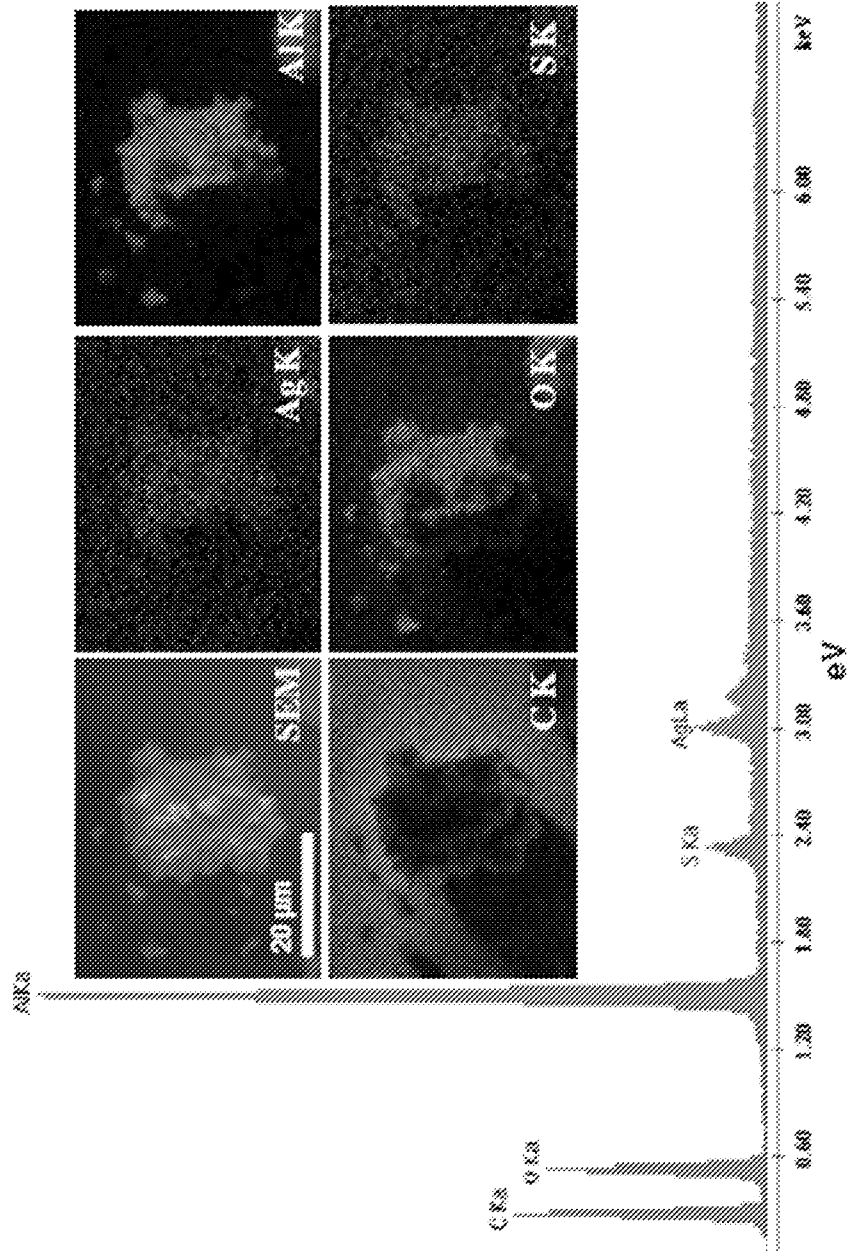


FIG. 9

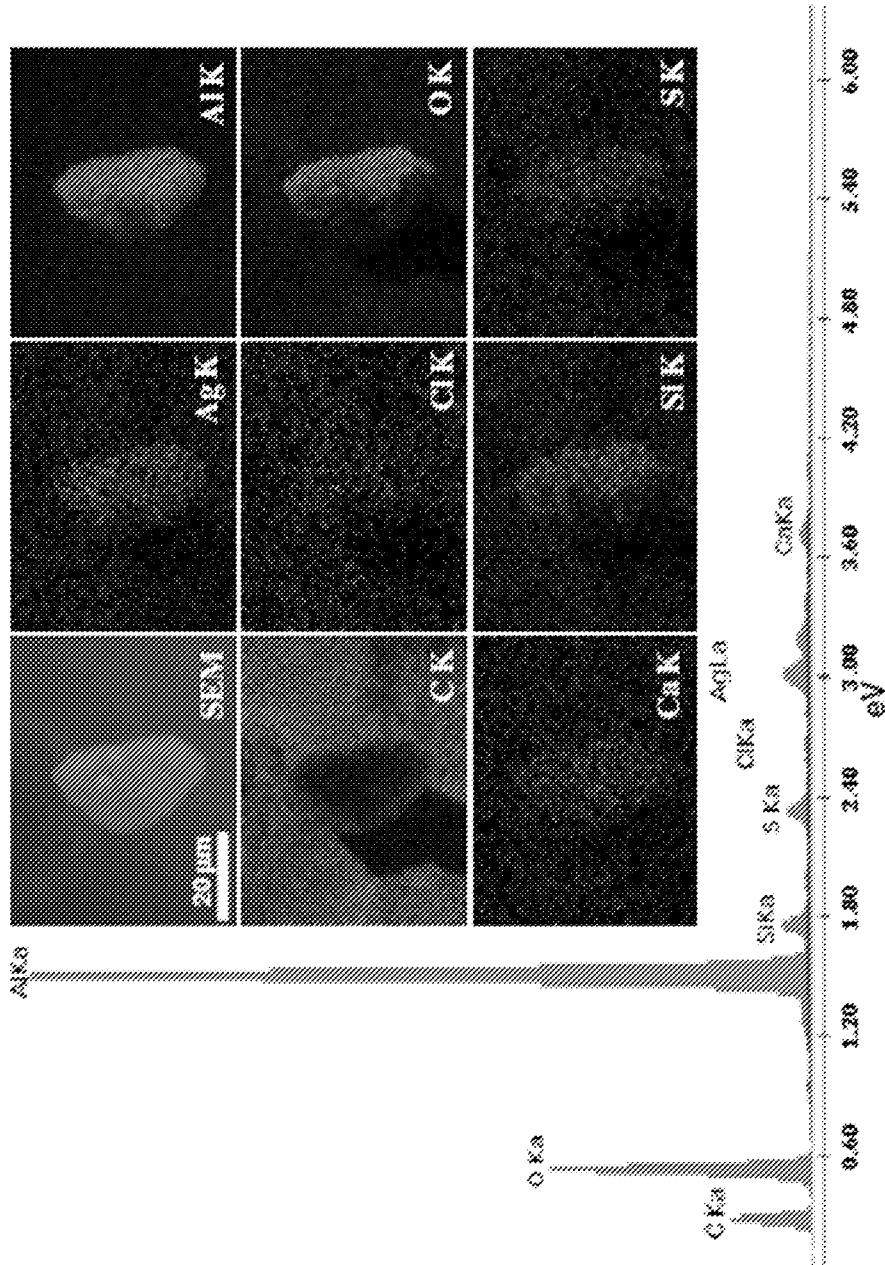


FIG. 10