Partially passivated quantum dots, process for making, and sensors therefrom.

Swadeshmukul Santra  
*University of Central Florida*

Yang Heesun  
*University of Florida Research Foundation, Inc.*

Paul Halloway  
*University of Florida Research Foundation, Inc.*

Subir Sabui  
*University of Central Florida*

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A partially passivating core shell particle includes a luminescent nanocrystal core, and a partially passivating semiconducting core shell on a surface of the nanocrystal. The shell allows selected analytes to alter a luminescent response of the core shell particle. A quantum dot-based sensing system includes at least one partially passivating core shell particle, a light source for irradiating the partially passivating core shell particle, and a light detector for receiving emissions from the particle, wherein emissions from the core shell particle change in response to the presence of at least one analyte.
OTHER PUBLICATIONS


* cited by examiner
Fig. 2

(a) Core (CdS:Mn)

(b) Ln1 = Pb

(c) Ln2 = Hg

(d) Ln3 = Cd

210 Shell (ZnS)

Lns
Receiving leg

Glass plate slot in the fiber probe head attached to the fiber probe

Chemical coated glass plate

Transmitting leg

Chemical coated fiber core

Light Source

Fig. 3a

Fig. 3b
Cd acetate
Mn acetate
in water

AOT
heptane

Sodium sulfide
in water

AOT
heptane

Zn acetate
in water

AOT
heptane

Cd²⁺/Mn²⁺
micellar
solution

addition of Cd/Mn
micellar solution

15 min mixing

S²⁻
micellar
solution

(CdS:Mn + surplus of S²⁻)
micellar solution

controlled addition of
Zn micellar solution
(1.5 ml/min)

CdS:Mn/ZnS
micellar
solution

Fig. 4
Synthesis of CdS:Mn/ZnS Core/Shell Quantum Dots:

<table>
<thead>
<tr>
<th>Qdot Sample ID</th>
<th>[Zn2+/Cd2+] Initial (Calculated)</th>
<th>Cd acetate + Mn acetate + water + AOT + heptane</th>
<th>Sodium sulfide + water + AOT + heptane</th>
<th>Zn acetate + water + AOT + heptane</th>
<th>Microemulsion Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD 1</td>
<td>8</td>
<td>A (= 96 mg + 1.24mg + 3.6 ml + 8.92 g + 100 ml)</td>
<td>B (= 562.4 mg + 10.8 ml + 26.76 g + 300 ml)</td>
<td>C (= 528.4 mg + 10.8 ml + 26.76 g + 300 ml)</td>
<td>700</td>
</tr>
<tr>
<td>QD 1-4</td>
<td>8</td>
<td>A/4</td>
<td>B/4</td>
<td>C/4</td>
<td>175</td>
</tr>
<tr>
<td>QD 1-8</td>
<td>8</td>
<td>A/8</td>
<td>B/8</td>
<td>C/8</td>
<td>87.5</td>
</tr>
<tr>
<td>QD 1-16</td>
<td>8</td>
<td>A/16</td>
<td>B/16</td>
<td>C/16</td>
<td>43.75</td>
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<tr>
<td>QD 1-20</td>
<td>8</td>
<td>A/20</td>
<td>B/20</td>
<td>C/20</td>
<td>35</td>
</tr>
</tbody>
</table>

F.W. (Cd-acetate: 266.52; Mn-acetate: 245.09; Zn-acetate: 183.48)
FIG. 6
Synthesis of CdS:Mn/ZnS Core/Shell Quantum Dots: Controlling crystal growth via scale-down approach

<table>
<thead>
<tr>
<th>Qdot Sample ID</th>
<th>[Zn²⁺/Cd²⁺] Initial (Calculated)</th>
<th>[Zn²⁺/Cd²⁺] Final (XPS data)</th>
<th>Microemulsion Volume (ml)</th>
<th>Luminescence intensity at 584 nm (355 nm excitation)</th>
<th>Luminescence intensity at 584 nm (370 nm excitation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD 1</td>
<td>8</td>
<td>6.02</td>
<td>700</td>
<td>2635000</td>
<td>2554610</td>
</tr>
<tr>
<td>QD 1-4</td>
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<td>8.17</td>
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<td>5259010</td>
<td>5110030</td>
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<tr>
<td>QD 1-8</td>
<td>8</td>
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<td>87.5</td>
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<td>667160</td>
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<tr>
<td>QD 1-16</td>
<td>8</td>
<td>3.31</td>
<td>43.75</td>
<td>618610</td>
<td>593390</td>
</tr>
<tr>
<td>QD 1-20</td>
<td>8</td>
<td>8.58</td>
<td>35</td>
<td>1498800</td>
<td>1344270</td>
</tr>
</tbody>
</table>

*Qdots were dispersed in 3 ml heptane + 100 µl W/O microemulsion.

FIG. 7
FIG. 8
A quantum dot (Qdot) is a semiconductor crystal whose size is on the order of just a few nanometers. Qdots contain anywhere from 100 to 1,000 essentially free electrons and range from about 2 to 10 nanometers in size, or about 10 to 50 atoms, in diameter.

One of the optical features of excitonic Qdots noticeable to the unaided eye is coloration. While the material which makes up a quantum dot is significant, more significant in terms of coloration is the size. The larger the Qdot, the redder (the more towards the longer wavelength end of the electromagnetic spectrum) they fluoresce. The smaller the dot, the bluer (the more towards the short wavelength end) it is. The coloration is directly related to the energy levels of the Qdot. Quantitatively speaking, the bandgap energy that determines the energy (and hence color) of the fluorescent light is approximately inversely proportional to the square of the size of the Qdot. Larger Qdots have more energy levels which are more closely spaced. This allows the Qdot to absorb photons containing less energy, i.e. those closer to the red end of the spectrum.

Regarding fabrication, in semiconductors, Qdots are small regions of one material buried in another with a larger energy (band) gap. Qdots sometimes may occur spontaneously in quantum well structures due to monolayer fluctuations in the well's thickness. Self-assembled quantum dots nucleate spontaneously under certain conditions during molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE), when a material is grown on a substrate to which a metal dopant. In one embodiment, the partially passivating core shell provides a band gap of at least 4 eV at 25°C. The composition can further comprise an analyte selective shell covalently attached to the core shell, such as a Macro-Cyclic Crown Ligand (MCCL).

A method of sensing analytes comprising the steps of providing at least one partially passivating core shell particle comprising a luminescent nanocrystal core and a partially passivating semiconducting core shell on a surface of the nanocrystal. The shell allows selected analytes to alter a luminescent response of the core shell particle. A light source is provided for irradiating the partially passivating core shell particle. A light detector receives emissions from the partially passivating core shell, wherein the emissions change in response to the presence of at least one analyte. The system can further comprise at least one optical fiber including a transmitting leg and a receiving leg covered with at least one of the partially passivated core shell particles. In one embodiment, an analyte selective shell is covalently attached to the partially passivating core shell, such as a MCCL.

The nanocrystal can comprise a metal chalcogenide and the partially passivating core shell can comprise a metal chalcogenide. In one embodiment, the nanocrystal comprises CdS and the partially passivating core shell comprises ZnS or ZnSe.

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

FIG. 1 is a schematic representation of a partially passivated quantum dot (partially passivated Qdot) according to an embodiment of the invention.
metal ions and a large energy gap material (e.g. ZnS) partially passivating a Qdot core. The MCCLs at least partially encapsulate the partially passivated core. FIG. 2(b)-(d) show some exemplary MCCLs, shown as Ln1, Ln2 and Ln3, respectively.

FIGS. 3(a) and (b) show simplified representations of an intrinsic and an extrinsic fiber optic based sensor system, respectively, according to an embodiments of the present invention.

FIG. 4 shows a flow chart for the synthesis of Cds:Mn/ZnS core/shell Qdots using a water-and-oil (W/O) microemulsion according to the invention.

FIG. 5 is a Table showing the experimental protocol used having a constant microemulsion composition to demonstrate a scale-down effect where the microemulsion volume becomes an important process control parameter. FIG. 6 shows emission spectra for the various Qdot samples showing very significant spectral changes based solely on the microemulsion volume used in the microemulsion system (the scale-down effect).

FIG. 7 provides data including XPS data for the various samples described above evidencing a variation in Zn$^{2+}$/Cd$^{2+}$ ratio between the sample groups.

FIG. 8 shows the effect of metal ion concentration on the luminescence intensity for the metal ions Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$, as a function of concentration of the metal ion.

DETAILED DESCRIPTION

The present invention is more particularly described in the following description and examples that are intended to be illustrative only since numerous modifications and variations therein will be apparent to those skilled in the art. As used in the specification and in the claims, the singular form "a," "an," and "the" may include plural referents unless the context clearly dictates otherwise. Also, as used in the specification and in the claims, the term "comprising" may include the embodiments "consisting of" and "consisting essentially of". In addition, unless indicated otherwise, a description of a layer being disposed on another layer, includes both embodiments where the layer is directly on the other layer or the layer has one or more intermediate layers interposed between the layer and the other layer.

As noted in the Background, it is well known to provide surface passivation layers for Qdots to achieve maximum brightness. Besides providing maximum brightness, such conventional passivation coatings are designed to also provide a reduction in the sensitivity of Qdots to various environmental conditions. Significantly, however, the Inventors have unexpectedly found that a partially passivating semiconductor coating layer disposed on the luminescent nanocrystal dot core which provides a significantly lower brightness compared to a fully passivated layer, provides useful sensing properties that can be used for a variety of chemical/biological sensing applications.

A partially passivating core shell particle according to the present invention comprises one or more partially passivated quantum dots. FIG. 1 shows an exemplary partially passivated quantum dot 100 according to an embodiment of the present invention. The nanocrystal core 105 has an average size less than 100 nm, generally being about 1 to 10 nm in size. A partially passivating semiconductor coating layer 110 is disposed on the surface of the luminescent nanocrystal core. As used herein, "partially passivated layer" or "partially passivating layer" is defined by reference to its luminescence intensity measured at the emission band (e.g., 590 nm for Mn doped CdS) as compared to the luminescence intensity of both a fully (optimal) passivated Qdot control and an unpassivated control. Specifically, partially passivated Qdots according to the present invention as defined herein to provide a luminescence intensity range as follows:

1. a maximum intensity level that is at least 30% less than the luminescence of a fully (optimal) passivated Qdot control, and
2. a lower intensity level that is the greater of 85% less than the luminescence of the same fully passivated Qdot control and 30% more than the luminescence intensity of an unpassivated control.

The thickness of the semiconductor coating 110 is generally one to two atomic layers, but can be somewhat thicker, such as three to five atomic layers. The coating is preferably a wide band gap semiconductor, selected to have a larger band gap, such as 0.5 to 1 eV higher, as compared to the band gap provided by the core nanocrystal 105. The partially passivated surface coating according to the present invention exposes at least a portion of the exterior of the luminescent nanocrystalline material to external influences. Although shown in FIG. 1 as being a continuous coating, the surface coating can be discontinuous as well. The semiconductor coating 110 can be a luminescent or non-luminescent coating.

Although not required to practice the present invention, Applicants, not seeking to be bound by theory, believe that by using luminescent core nanoparticles having a significant portion of their surface area exposed to external influences allows certain materials to change the electron-hole recombination process behavior, which results in a change in the photoluminescence (PL) response. Through interaction of the luminescent nanocrystalline material with certain outside influences, and a resulting change in photoluminescence (PL) intensity or PL lifetime, certain outside influences can thus be sensed and identified based on unique PL signatures for a variety of analytes.

Although generally described using a Cds core and a ZnS coating, the invention is in no way limited to any particle luminescent nanocrystalline material or coating. Although the passivating coating is generally an inorganic layer, organic layers may also be used. In some embodiments, the luminescent nanocrystals can be doped with a transition or lanthanide metal.

In one specific embodiment, the luminescent nanocrystalline material is a doped metal chalcogenide, such as Mn doped CdS. Cds:Mn nanocrystals have been found to show efficient broad photoluminescence (PL) around 2.1 eV. Similar PL is observed in bulk Cds:Mn. This is attributed to the intra-3d transition of Mn$^{2+}$ ions. Moreover, the PL excitation spectrum of Cds:Mn nanocrystals has been found to be similar to the absorption spectrum of Cds nanocrystals. These observations suggest that efficient energy transfer of carriers occurs from Cds nanocrystals to Mn$^{2+}$ ions.

As a result of partial surface passivation according to the present invention, compositions according to the invention behave as if the emission is internally quenched. This arrangement and the discovery of an efficient method to form partially passivating semiconductor coating layers disposed on the luminescent nanocrystals (described below) allows the formation of new Qdot-based analyte sensors. Such sensors have been found to provide high levels of sensitivity toward pH, various metal ions (including bivalent Cd, Pb, Hg cations) and certain organic molecules, and are expected to
provide selectivity for organics including nitroaromatic explosives, such as TNT. It is expected that environmentally-sensitive Qdots will also have potential for the biosensing. For example, alteration in the Qdot PL signature is expected once reactive oxygen species (such as associated with superoxide, nitric oxide and peroxide) will interfere with the electron-hole recombination processes at the surface of the luminescent nanoparticle. Accordingly, portable heavy metal detection devices for Hg, Pb, As, Cd ions (samples including contaminated water) can make use of fluorescence signatures upon exposure to heavy metals.

Regarding heavy metal detection using partially passivated Qdots according to the invention, results obtained described below indicated significant sensitivity. Moreover, such Qdots were found to be extremely photostable in solution as was confirmed by the continuous exposure to 450 W Xenon excitation for several hours. However, in certain applications where multiple analytes may be present, such Qdots may not have sufficient selectivity. For instance, when exposed to both Hg$^{2+}$ and Pb$^{2+}$, luminescence quenching of the 584 nm Mn$^{2+}$-Tl$^{4+}$A$_{2}$ band was observed in each case. Moreover, an unconverted soil contaminated or water sample may contain various cationic and anionic species, other than toxic heavy metal ions. In this situation, it would be challenging to selectively detect any specific heavy metal.

To improve selectivity of partially passivated Qdots according to the invention, a new core-shell-shell QHMDP design was developed by the present Inventors. Although described below as being a shell to improve heavy metal selectivity, selectivity enhancing shells can be used to improve selectivity for a variety of non-heavy metal analytes. The core here is defined to be a partially passivated core-shell Qdot according to the present invention and is designed to achieve high optical sensitivity (e.g. luminescence quenching of Mn doped CdS 584 nm emission for both Hg$^{2+}$ and Pb$^{2+}$ ions). In one embodiment, the Qdot shell will be synthesized by covalently attaching the core to heavy metal selective ligands, such as Macro-Cyclic Crown Ligands (MCCLs), to provide a Qdot based Heavy Metal Detection Probe (QHMDP) 200 according to the present invention, as shown in FIG. 2(a). QHMDP 200 is shown having a Mn doped CdS core 205, a partially passivating ZnS coating 210, and a plurality of selective ligands 215 (shown as Ln) bound to the ZnS coating 210. In one embodiment the selective ligands 215 are MCCLs which are designed to capture specific heavy metals from a mixture heavy metal ions. It is noted that the MCCL or other selective ligands 215 is preferably directly attached to the Qdot surface without a spacer. The purpose for direct attachment is to obtain essentially zero-space surface passivation that will create a non-flexible MCCL coating. In the case of a MCCL coating, such a robust coating should prevent undesired metal ions diffusion to the core. The shell design shown reduces interference due to non-specific binding of undesired metal ions. In a practical situation, however, there will always be a chance of non-specific interaction once the probe is allowed to interact with the sample for a longer period of time. Therefore, when implementing a detection method using QHMDPs according to the present invention, a brief exposure (e.g. <1 minute) of QHMDP to the sample and rapid detection procedure will generally be desirable.

FIGS. 2(b)-(d) show exemplary MCCL coatings for the selective detection of Pb$^{2+}$, Hg$^{2+}$, and Cd$^{2+}$. Although generally covalently attached, it is possible to attach MCCLs to Qdots according to the present invention by certain non-covalent means. Ln1 shown in FIG. 2(b) is not a fully closed ring. As shown in FIG. 2(b)-(d), the MCCLs (e.g. Ln1, Ln2 and Ln3) are shown surrounding their respective selective analytes, Pb$^{2+}$, Hg$^{2+}$, and Cd$^{2+}$, respectively.

MCCLs have been widely used in separation chemistry and treatment of heavy metal poisoning. During the past two decades, several synthetic strategies have been developed to make metal selective MCCLs. Crown ether based chemosensors for the specific detection of Hg (shown in FIG. 2(c)) are disclosed in Yoon, S., et al., Screening mercury levels in fish with a selective fluorescent chemosensor. Journal of the American Chemical Society, 2005. 127(46): p. 16030-16031; hereafter “Yoon et al.”. Crown ether based chemosensors for the specific detection of Pb (shown in FIG. 2(b)) are disclosed in He, Q. W., et al., A selective fluorescent sensor for detecting lead in living cells. Journal of the American Chemical Society, 2006. 128(29): p. 9316-9317; hereafter “He et al.”.

The present invention replaces fluorescein reporter molecules with highly-sensitive, photostable and environmentally-sensitive Qdot probes according to the invention. For example, for the detection of Cd$^{2+}$, Ln3 (FIG. 2(d) can be used. Ln3 shown in FIG. 2(d) is disclosed in Bronson et al. [Bronson, R. T., et al., Efficient immobilization of a cadmium chemosensor in a thin film: Generation of a cadmium sensor prototype. Organic Letters, 2005. 7(6): p. 1105-1108].

The present invention can be used in a variety of sensor systems. Sensor systems generally comprise a light source for irradiating the partially passivated Qdots. A light detector is provided for receiving emissions (typically fluorescence) from the nanocrystals, wherein the emissions change (intensity, wavelength, decay time) in response to the presence of at least one analyte. A detector for measuring electrical conductivity of the nanocrystals can also be included. The analyte can be in liquid or vapor form. The nanocrystals can be secured to a surface or held in solution. For example, the nanoparticles can be arranged on a packed bead bed or in a particle dispersion on a substrate. In another embodiment, selective shell covered partially passivated Qdots according to the invention are dip coated inside the core of a fiber optic fiber.

FIG. 3(a) shows an intrinsic fiber-optic based hand-held sensor probe 300 according to an embodiment of the present invention. The fiber includes a transmitting leg 305 and a receiving leg 310. Between the transmitting leg 305 and a receiving leg 310 is a core portion 312 having at least one, and generally a plurality of selective shell covered partially passivated Qdots according to the invention coated inside to provide analyte specificity. An inlet region 316 to core region 312 is provided for introducing samples suspected of including one or more targets. A light source (e.g. laser) 315 and lens 320 are provided for coupling light into the transmitting leg 305 of the fiber. A detector 325 is coupled to the output of receiving leg 310. Although not shown, a supervisory computer and processor is preferably included for characterizing the luminescence intensity and/or luminescence lifetime and determining whether a specific analyte is present.
ing multiple fibers all having different selective sheaths between light source/lens and detector, probes according to the present invention can be used to simultaneously sense a plurality of different analytes.

FIG. 3(b) shows an extrinsic fiber-optic based hand-held sensor probe 350 according to an embodiment of the present invention. The fiber includes a transmitting leg 355 and a receiving leg 360. Probe 350 includes positions for insertion of plates having selective shell covered partially passivated Qdots according to the invention coated thereon. As with FIG. 3(a), although not shown, a supervisory computer and processor is preferably included for generating a luminescence spectrum from data provided and determining whether a specific analyte is present. Probes according to the invention are expected to rapidly and selectively detect toxic heavy metal ions at trace levels, such as in the range between parts per billion (ppb) or parts per trillion (ppt).

Besides detecting highly toxic heavy metal ions (Cd²⁺, Hg²⁺, Pb²⁺ and As³⁺ ions), biological reactive species (nitrile oxide, superoxide and peroxides), or explosives (e.g. explosive nitro-aromatics) as noted above, nanosensors according to the present invention can also be useful for detection of sodium, potassium, magnesium ions, as well as amino acids and other materials.

Reactive oxygen species (ROS), such as superoxide, nitric oxide, and peroxides are of particular interest as they are responsible for oxidative stress and ageing. Superoxides are known to cause oxidative stress and are directly linked to many neurodegenerative diseases such as Alzheimer’s, Parkinson’s, and Huntington’s diseases. Nitric oxide (NO) is an important bioregulatory agent in a range of physiological processes from vasodilation and platelet aggregation to neurotransmitter and penile erection. In biology, hydrogen peroxide is considered as a reactive oxygen species that could lead to serious tissue damage. Sensitive detection of these ROS is highly desirable for early diagnosis and monitoring disease progression. Superoxide radicals will be generated in solution by the reaction between xanthine oxidase and hypoxanthine, followed by the treatment with Qdots. Sodium (Z)-1-(N,N-diethylamino)diaceto-1,2-diolate will be used to generate nitric oxide in solution and will then be treated with Qdots. ROS will generally interfere with the electron-hole recombination process. It is expected that sensitive responses will be provided by partially passivated Qdots according to the invention. Exemplary explosive nitro-aromatics include 2,4,6-trinitrotoluene (TNT), peroxides and picric acid.

A new room temperature operable synthesis protocol allows synthesis of doped semiconductor nanocrystals, such as CdS:Mn nanocrystals, having variety of surface passivation layers, such as a ZnS layer. Through controlling the process as described below, the surface passivation layer can be continuous or sufficiently thin or discontinuous to be partially passivating. Regarding the new process, as demonstrated in the Examples below, solution volume has unexpectedly been found to be a process parameter which enables formation of a partially passivating passivation layer.

Generally, the method comprises the steps of providing a metal ion comprising at least a first and a second metal, providing a chalcogenide ion comprising water-in-oil micellar solution, and mixing the metal ion comprising water-in-oil micellar solution and the chalcogenide ion comprising water-in-oil micellar solution, wherein a stoichiometric surplus of the chalcogenide is provided. A plurality of first or second metal chalcogenide nanoparticles are formed. A third metal comprising water-in-oil micellar solution is then sequentially or simultaneously added, wherein a coating comprising the third metal and chalcogenide forms on the plurality of first or second metal chalcogenide nanoparticles. By using a total volume of reactants sufficiently low, generally less than 400 ml, a partially passivating coating layers is formed on the nanoparticles. Nanoparticles formed by the present method also generally include a plurality of surfactant molecules on their outer surface.

FIG. 4 shows a flow chart for one method suitable for the synthesis of CdS:Mn/ZnS core/shell Qdots using a water/oil (W/O) microemulsion according to the invention. In this embodiment, the oil is heptane and the surfactant is sodium dioctyl sulfosuccinate (AOT, 99%, Sigma Chemical Co., St. Louis, Mo.). The water/AOT ratio can be about 10.

EXAMPLES

It should be understood that the Examples described below are provided for illustrative purposes only and do not in any way define the scope of the invention.

While attempting to synthesize CdS:Mn/ZnS Qdots on a small scale (small volume) using a AOT/heptane W/O microemulsion system based on the process described in FIG. 4, an unexpected dramatic scale-down effect of reaction volume on the growth of the ZnS surface passivation layer (shell) onto the CdS:Mn Qdot core was discovered. The Table shown in FIG. 5 described below details the scale-down protocol of Qdot synthesis showing a constant composition using different microemulsion volumes, from about 700 ml to 35 ml.

FIG. 6 shows emission spectra for the various Qdot samples surprisingly showing very significant spectral changes based only the microemulsion volume used in the microemulsion system, referred to herein as the scale-down effect. For all sensing tests 50 µg of nanoparticles were dispersed in 3 ml of methanol along with less than 1% water (V/V). QD1-4 which resulted in a continuous coatings was found to be the brightest. QD1, QD1-8 and QD1-16 which resulted in a partially passivating coating were found to have intermediate (moderate) emission intensity. QD1-20 which resulted in a minimal coating was found to have the lowest emission intensity. Except QD1-20, all samples showed only variation in luminescence intensity at 884 nm, confirming the effect of surface passivation. Sample QD1-20 showed dual emission at 584 nm and 645 nm. The emission at 645 nm could be due to the ionic defect emission (e.g. sulfur vacancies).

As expected, well-surface passivated Qdots showed the brightest intensity and the poorly-passivated Qdots showed very weak emission. However, Qdots with complete surface passivation are expected to be insensitive to the outside environment, while Qdots with partial surface passivation were found to be responsive to the outside environment. As noted above, partially passivated Qdots are believed to possess localized surface states in the band gap as well as ionic defects (e.g. sulfur vacancies in case of CdS:Mn/ZnS Qdots). Therefore, the Inventors determined that the partially passivated Qdots can be used as an environmentally-sensitive probe as it is possible to further quench or enhance the luminescence intensity of the Qdots in the presence of certain analytes.
Several experiments were conducted. Using a dioctyl sulfosuccinate, sodium salt (AOT)/heptane/water W/O micro-emulsion technique, CdS:Mn core/ZnS shell Qdots were produced based on the process flow described generally in FIG. 4. Typically, Cd(CH$_2$COO)$_2$.2H$_2$O, Mn(CH$_2$COO)$_2$.4H$_2$O, Na$_2$S$_2$O$_3$, and Zn(CH$_2$COO)$_2$.2H$_2$O were used for the preparation of (Cd$_{25}$+ Mn$_{2-}$), S$^{2-}$, and Zn$^{2+}$ containing the standard aqueous solutions. Each aqueous solution was stirred with an AOT/heptane solution, forming the micellar solution. Mn doped CdS core nanocrystals were formed by mixing (Cd$_{25}$+Mn$_{2-}$) and S$^{2-}$ containing micellar solutions rapidly for 10-15 min. The W/W value for the W/O microemulsion was 10. For the growth of a shell layer, a Zn$^{2+}$-containing micellar solution was added at a very slow rate (1.5 ml/min) into the CdS:Mn nanocrystal micellar solution (having maintained a surplus of 15 nol containing DI water (maximum value (i.e. 8)). Fluorescence emission spectra recorded for all samples described above. Significantly, the Zn$^{2+}$/Cd$^{2+}$ ratio varied from the nominal calculated value of 8, to values above and below 8. A high Zn$^{2+}$/Cd$^{2+}$ ratio may be evidence of a partially passivated surface.

To demonstrate the environmental sensitivity of partially passivated Qdots according to the invention, QD1 and QD1-8 were intentionally selected as the test samples as they are about 2 and 7.4 times dimmer than QD1-4 and thus should be partially surface-passivated. As noted above, for fluorescence measurements, all experimental Qdot solutions (concentration: 50 μg/ml) were prepared at room temperature in methanol containing DI water (maximum 0.01% (V/V)). Again, all experimental Qdot solutions were transparent and no light-scattering was observed in the visible range. When exposed to highly toxic heavy metal ions (e.g. Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$ ions etc.), quenching of 584 nm Qdot emission was observed in a unique fashion for each type of metal ion. It was observed that with respect to luminescence quenching, both QD1 and QD1-8 samples had similar response.

FIG. 8 shows the effect of increased amounts of metal ion concentration on the luminescence intensity of QD1-8. The luminescence quenching efficiency of Hg$^{2+}$ was at least three orders of magnitude higher than Cd$^{2+}$ ions. The higher sensitivity of Qdots towards Hg$^{2+}$ could be attributed to the high reactivity of Hg$^{2+}$ ions towards Qdots, forming metal-like products such as HgS, CdHg$\_x$S$_{1-x}$ etc. Unlike Hg$^{2+}$ ion, the luminescence intensity of QD1-8 measured at 584 nm increased first, reached a maximum at around 3 mM Cd$^{2+}$ ion concentration, and then decreased. The initial enhancement in luminescence intensity could be due to the formation of the Cd(OH)$_2$ layer over the CdS:Mn partially passivated core, which resulted in the reduction of the non-radiative recombination of charge carriers (electron-hole recombination without luminescence). Further, the decrease in the luminescence intensity with the increase in Cd$^{2+}$ ions could not be explained without further investigation.

Different analytes were found to provide characteristic luminescent signatures as shown in FIG. 8. Once cataloged, such signatures allow unambiguous identification of particular analytes. For example, when exposed to Pb$^{2+}$ ions, the luminescence spectral characteristics of QD1-8 (lower right) was quite different as compared to the spectral characteristics obtained from Cd$^{2+}$ and Hg$^{2+}$ ions (left). For exposure to Pb$^{2+}$, a decrease in emission intensity at 584 nm was noticed and a new emission (upper left) peak at 643 nm appeared as the Pb$^{2+}$ concentration increased from 0.166 mM to 14.28 mM (upper right). Several control spectral experiments were performed including emission spectra of pure methanol, methanol-water mixture, 14.28 mM PbCl$_2$ in methanol and emission spectra in the presence of room-light to confirm the unusually sharp peak (much like a scattering peak) in the emission spectra. With a 370 nm UV exposure, 643 nm deep emission from 14.28 mM PbCl$_2$ treated QD1-8 a sample was seen visually. The emission data obtained demonstrates that partially passivated Qdots can be used as environment sensitive probes which provide identification of specific analytes. To obtain improved selectivity in samples containing several analytes, the Qdot-based Heavy Metal Detection Probes (QHMDF) according to the present invention having Macro-Cyclic Crown based Ligands described above relative to FIGS. 2(b)-(d) can be used.

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.

We claim:

1. A core shell particle, comprising:
   a luminescent nanocrystal core, and
   a partially passivating semiconducting shell on a surface said nanocrystal, and
   an analyte selective shell covalently attached to said semiconductor shell.

2. The core shell particle of claim 1, wherein said nanocrystal comprises a metal chalcogenide and said semiconductor shell comprises a compositionally different metal chalcogenide.

3. The core shell particle of claim 2, wherein said nanocrystal comprises CdS and said semiconductor shell comprises ZnS or ZnSe.

4. The core shell particle of claim 1, wherein said nanocrystal includes a transition or lanthanide metal dopant.

5. The core shell particle of claim 1, wherein said semiconductor shell provides a band gap of at least 4 eV at 25° C.

6. The core shell particle of claim 1, wherein said analyte selective shell comprises a Macro-Cyclic Crown Ligand (MCCL).
7. A quantum dot-based sensing system, comprising:
at least one core shell particle including a luminescent
nanocrystal core, and
a partially passivating semiconducting shell on a surface
said nanocrystal,
an analyte selective shell covalently attached to said semi­
conductor shell;
a light source for irradiating said core shell particle, and a
light detector for receiving emissions from said core shell
particle, wherein said emissions change in response to
the presence of at least one analyte.

8. The system of claim 7, further comprising at least one
optical fiber including a transmitting leg and a receiving leg,
and a core portion located between said transmitting leg and
said receiving leg covered with at least one of said core shell
particles.

9. The system of claim 7, wherein said analyte selective
shell comprises a Macro-Cyclic Crown Ligand (MCCL).

10. The system of claim 7, wherein said nanocrystal com­
prises a metal chalcogenide and said semiconducting shell
comprises a compositionally different metal chalcogenide.

11. The system of claim 10, wherein said nanocrystal com­
prises CdS and said semiconducting shell comprises ZnS or
ZnSe.

12. A method of sensing analytes, comprising the steps of:
providing at least one core shell particle comprising a
luminescent nanocrystal core and a partially passivating
semiconducting shell on a surface said nanocrystal, and
an analyte selective shell covalently attached to said semi­
conductor shell;
exposing a fluid suspected of including at least one analyte
to said core shell particle, and
determining whether said analyte is present in said fluid
based on a change in luminescent response of said core
shell particle following exposure to said fluid.

13. The method of claim 12, wherein said fluid comprises
water.

14. The method of claim 12, wherein said analyte is
selected from the group of heavy metal cations.

15. The method of claim 14, wherein said heavy metal
cation comprises Hg, Cd or Pb.

16. The method of claim 12, wherein when said analyte is
present in said fluid said change in luminescent response of
said core shell particle following exposure to said fluid com­
prises an enhanced luminescent response.

17. The method of claim 12, wherein said analyte selective
shell comprises a Macro-Cyclic Crown Ligand (MCCL).

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