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Synthesis and self-assembly of hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures and their photoluminescence applications for fingerprint detecting and cell imaging

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Abstract

Hierarchical SiO$_2$-QDs@SiO$_2$ (QDs=CdTe, PbTe or PbS) nanostructures have been prepared by an integrated synthesis and self-assembly strategy using 3-mercaptopropionic acid (MPA) to stabilize the QDs and NaOH to control the self-assembly of QDs on the SiO$_2$ nanobead carriers. 3-10 nm QDs covered with a 1-2 nm SiO$_2$ shells were embedded on the surface of 50 nm SiO$_2$ nanobead carriers separately, resulting in hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures. MPA and NaOH played important roles in the nucleation and growth of QDs, etching the SiO$_2$ nanobead carriers to colloidal surface, and self-assembly of the QDs on viscous SiO$_2$ nanobead carriers. The hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures possess various advantages: (I) the growth of QDs and self-assembly of QDs on SiO$_2$ nanobead carriers were performed in a one-pot reaction by a facile aqueous phase refluxing approach; (II) the SiO$_2$ shell with 1-2 nm in thickness can prevent the leakage of toxic Cd$^{2+}$ or Pb$^{2+}$ and avoid photobleaching or environmental pollution; (III) the surface of hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures can be functionalized easily through silane-coupling chemistry. Due to the excellent photoluminescence and biocompatibility, the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures modified by carboxyl (-COOH) active group can be available for covalent coupling to various biomolecules, which have shown potential applications in fingerprint detecting and in vivo cell imaging.

Keywords: SiO$_2$-QDs@SiO$_2$, hierarchical nanostructures, fingerprint detecting, cell imaging

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1. Introduction

Due to the unique size-tunable, narrow emission and high photostability properties, semiconductor quantum dots (QDs) have been attracting extensive attention [1-3], such as light-emitting diode [4-5], vivo imaging [6-7], optoelectronic and photovoltaic devices [8-10]. However, QDs were susceptible to external environment and easy to lose their fluorescence due to the optical and chemical instability in harsh environment. On the other hand, QDs generally contain highly toxic heavy metal ions such as Cd$^{2+}$, Pb$^{2+}$, which are easy to cause environmental pollution [11-12]. Up to now, a series of stable coating such as polymer and silica have been developed to improve the chemical stability and biocompatibility of the QDs. Silica coating, as a popular inert material, can provide chemical/physical shielding from the direct environment and possess good water dispensability [13-15]. Moreover, the surface of QDs with silica coating can be easily modified by various functional groups through silane-coupling method [16]. For example, Rogach et al encapsulated luminescent QDs into the SiO$_2$ particles by the Stöber method, and the QDs@SiO$_2$ core-shell nanocomposites showed good biocompatibility and photostability for fluorescence imaging [17]. Emilio et al encapsulated QDs in SiO$_2$ nanoparticles via the reverse microemulsion methodology, and the obtained multiplexed colored silica-QDs nanohybrids could avoid quenching of the photoluminescence (PL) of QDs [18]. These coating methods for preparing QDs involved complicated steps and non-environmental solvent, so exploring a simple green method to prepare QDs with high photostability still remains as a challenge.

In this paper, an integrated synthesis and self-assembly strategy for preparing the hierarchical SiO$_2$-QDs@SiO$_2$ (QDs=CdTe, PbTe or PbS) nanostructures in aqueous solution has been developed. The growth of QDs and self-assembly process were involved in this one-pot synthesis. The fabrication of hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures, which was include the synthesis of 3-10 nm QDs and self-assembly of QDs on the SiO$_2$ nanobead carriers in a
one-pot reaction. Fortunately, the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures can be successfully modified by -COOH or -NH$_2$ active group by the silane-coupling agent, and then the functionalized hierarchical nanostructures (SiO$_2$-QDs@SiO$_2$-COOH or SiO$_2$-QDs@SiO$_2$-NH$_2$) can be obtained. The as-prepared multicolored hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures have strong binding affinity for amino acids of the fingerprint by cross-coupling reaction, which can be available for making the fingerprint images visualized without background influence [19]. On the other hand, the as-obtained multicolored hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures show high PL fluorescence and good biocompatibility which could be effective for the enhancement of cell bioimaging. The synthetic process of the SiO$_2$-QDs@SiO$_2$ nanostructure is schematic representation in Scheme 1.

![Scheme 1. Synthetic procedures of the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructure.](image)

2. Experimental details

All chemicals used in this work were of analytical grade without further purification, and the reactions were carried out under open-air conditions. Tetrabutyl titanate, cadmium chloride hydrate (CdCl$_2$·2.5H$_2$O, 99%), tetraethoxysilane(TEOS), triton X-100, succinic anhydride (95%), 1-hexanol (98%), ammonia, sodium tellurite (97%), hydrazine hydrate, toluene, N,N-Dimethylformamide (DMF), (3-Aminopropyl)-triethoxysilane AMEO (KH550), 3-mercaptopropionic acid (MPA, C$_3$H$_6$O$_2$S, 99%), sodium sulphide, lead acetate and cyclohexane (98%) were purchased from Aladdin Chemistry Co., Shanghai, China.

The morphology of the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and transmission
electron microscopy (TEM, JEM-2100, Japan). The elemental compositions of the SiO$_2$-QDs@SiO$_2$ were confirmed via spatially energy dispersive X-ray spectroscopy (EDS, Falcon, EDAX). The X-ray diffraction (XRD) pattern of the SiO$_2$-CdTe@SiO$_2$ was recorded on a Bruker AXS D8 Discover diffraction system with a Cu Kα-radiation source (λ=1.5406 Å) at a scanning rate of 0.02°/s in the 2θ range of 10°-60°. FT-IR spectra of the surface functionalization of SiO$_2$-CdTe@SiO$_2$ were carried out using KBr tablets (1% w/w of product in KBr) with a resolution of 4 cm$^{-1}$ and 100 scans per sample.

**Synthesis of hierarchical SiO$_2$-QDs@SiO$_2$ (QDs=CdTe, PbTe or PbS) nanostructures**

1. (i) Synthesis of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures with the PL emission from yellow to red. In a typical procedure, 0.1 g of the SiO$_2$ nanobead carriers (prepared as the reference [20]) were added into a flask containing 48.0 mL of deionized water, 40 µL of MPA and 1.6 mL of 0.1M CdCl$_2$ solution. The pH value of the solution was adjusted to 10.0 by 0.1M of NaOH solution, and 8.0 mg of Na$_2$TeO$_3$ were added into the solution and stirred for 6 h at 80 °C. Subsequently 1.0 mL of 80% hydrazine hydrate was added into the solution. Series of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures with different colors from yellow to dark red could be obtained by adjusting the period of the refluxing time.

(ii) Synthesis of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures with green PL emission. The NaHTe, an intermediate product for preparation of CdTe QDs, was firstly synthesized by the reduction of tellurium powder with NaBH$_4$ [21]. In a typical procedure, 45 mg of NaBH$_4$, 16 mg of Te powder and 2 mL of deionized water were added into a flask, and then kept the flask in 60 °C water bath for several minutes until the black Te powder was disappeared. Then, the white sodium tetraborate (Na$_2$B$_4$O$_7$) precipitate appeared on the bottom of the flask and cooled the flask by ice. The synthesis process of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures was as following: 30 mL of solution containing 84.5 mg of CdCl$_2$, 60 µL of MPA and 0.1 g of SiO$_2$ nanobead carriers were transferred into a flask, and the pH value of the solution was adjusted to
10.0 by 0.1 M of NaOH solution and purged with N₂ for 1 h. Subsequently, 1.2 mL of oxygen-free NaHTe aqueous solution was injected into the solution, and refluxed at 100 °C for 1 h. The orange products were centrifuged at 5000 rp for 5 min and washed with ethanol and deionized water for three times, respectively. Then the hierarchical SiO₂-CdTe@SiO₂ nanostructures were obtained.

2. Synthesis of hierarchical SiO₂-PbTe (PbS)@SiO₂ nanostructures with the Near-IR PL emission. The hierarchical SiO₂-PbTe@SiO₂ or SiO₂-PbS@SiO₂ nanostructures could be synthesized with similar recipe by using (CH₃COO)₂Pb as Pb source and NaTeO₃ or Na₂SO₃ as Te or S source. 0.1 g of the SiO₂ nanobead carriers were added into a flask containing 48.0 mL of deionized water, 40 µL of MPA and 1.6 mL of 0.1M (CH₃COO)₂Pb solution. The pH value of the solution was adjusted to 10.0 by 0.1M of NaOH solution, and 8.0 mg of Na₂TeO₃ were added into the solution and stirred for 6 h at 80 °C. Subsequently 1.0 mL of 80% hydrazine hydrate was added into the solution. Series of hierarchical SiO₂-PbTe (PbS)@SiO₂ nanostructures with different sizes with the Near-IR PL emission could be obtained by adjusting the period of the refluxing time.

Modification of the hierarchical SiO₂-CdTe@SiO₂ nanostructures by -COOH or -NH₂ groups. As we know, the -OH group of Si-OH on the surface of SiO₂-CdTe@SiO₂ nanostructures can conjugated to other active groups through the silane-coupling reaction, and then -COOH or -NH₂ functional group modified SiO₂-CdTe@SiO₂ nanostructures can be obtained.

(i) Modification of the hierarchical SiO₂-CdTe@SiO₂ nanostructures by -COOH group: Typically, 0.1 g of succinic anhydride, 25 mL of N,N-Dimethylformamide (DMF) and 235 µL of KH550 were transferred into a flask, and kept at 70 °C for 3 h to obtain the -COOH group conjugated KH550 (KH550-COOH). Subsequently, 0.1 g of the hierarchical SiO₂-CdTe@SiO₂ nanostructures was added into the KH550-COOH solution to obtain the hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures. Finally, the resulting products were centrifuged at
5000rp for 5 min and washed with ethanol and water for three times, respectively. The samples were redispersed in deionized water as a stock solution.

(ii) Modification of the hierarchical SiO2-CdTe@SiO2 nanostructures by -NH2 group: Typically, 0.1 g of the hierarchical SiO2-CdTe@SiO2 nanostructures, 10.0 mL of toluene and 700 µL of KH550 were transferred into a flask, and refluxed at 80 °C for 12 h to obtain the hierarchical SiO2-CdTe@SiO2-NH2 nanostructures. Finally, the resulting products were centrifuged at 5000rp for 5 min and washed with ethanol and deionized water for three times, respectively. The samples were redispersed in deionized water as a stock solution.

**Fingerprint detecting test.** Fingerprinted on a clean glass substrate, and then painted the solution of SiO2-CdTe@SiO2 that containing carboxyl on the glass uniformly and air drying for two hours. After washing with deionized water, place the glass substrate under the UV light.

**Cell imaging experiment.** The potential bioimaging application of hierarchical SiO2-CdTe@SiO2-COOH nanostructures were carried out on the HeLa cells. First, the HeLa cells were grown in Dulbecco’s Modified Eagle Medium supplemented with 5% fetal bovine serum and 1% antibiotics at 37°C and 5% CO2, then seeded in 96-well tissue culture plates and allowed to adhere for 5 h. Subsequently, after washing with phosphate-buffered saline solution, the HeLa cells were incubated in a serum-free medium that contained hierarchical SiO2-CdTe@SiO2-COOH nanostructures at 37 °C for 3 h under 5% CO2.

**MTT assay.** Hela cells were cultured in Dulbecco’s Modified Eagles Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and antibiotics (100 U/ml penicillin, 100 mg/ml streptomycin). The SiO2, SiO2-QDs@SiO2 and QDs solutions with culture medium containing Hela cells were cultured in an humidified incubator with 5% CO2 at 37 °C. Cell viability was evaluated by using a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT; Sigma) reduction conversion assay and cell survival was expressed as
absorbance at 570 nm in a spectrophotometric microplate reader (Bio-RAD Model 680, USA).

3. Results and discussion

3.1. Morphology and structures

Fig.1 shows the SEM images of the as-prepared SiO₂ nanobead carriers, hierarchical SiO₂-CdTe@SiO₂, SiO₂-PbTe@SiO₂, SiO₂-PbS@SiO₂, SiO₂-CdTe@SiO₂-COOH and SiO₂-CdTe@SiO₂-NH₂ nanostructures. The as-prepared SiO₂ nanobead carriers are generally spherical shape and uniform (as shown in Fig.1a). The morphology of hierarchical SiO₂-CdTe@SiO₂ nanostructures shows that the small CdTe QDs are coated onto the surface of SiO₂ nanobead carriers (as shown in Fig.1b). The corresponding EDAX spectrum demonstrates the presence of Cd, Te, Si and O element in the final products (as shown in the inset one of Fig.1b). Hierarchical SiO₂-PbTe@SiO₂ and SiO₂-PbS@SiO₂ nanostructures can be successfully synthesized when (CH₃COO)₂Pb as Pb source and Na₂TeO₃ (Na₂SO₃) as Te (S) source. The hierarchical SiO₂-PbTe@SiO₂ and SiO₂-PbS@SiO₂ nanostructures show similar morphology as that of SiO₂-CdTe@SiO₂ nanostructures (as shown in Fig.1 c and d). The chemical properties of the surface of nanostructures can be modified through conjugation of the active groups, and the SEM images confirmed that the morphology of hierarchical SiO₂-CdTe@SiO₂-COOH and SiO₂-CdTe@SiO₂-NH₂ still remains as the original (as shown in Fig. 1e and f).
HRTEM characterization was applied to investigate the structure and morphology of the QDs of the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures. TEM images of QDs depicts that 3-10 nm QDs covered by a 1-2 nm SiO$_2$ shells were embedded onto the surface of the SiO$_2$ nanobead carriers (as shown in Fig.2). The uniform CdTe QDs about 5 nm in diameter deposited onto the surface of SiO$_2$ nanobead carriers with approximately 50 nm in diameter were separated well (as shown in Fig.2a). The HRTEM image of a CdTe QDs shows that the QDs is well-crystallized, and the lattice fringe with spacing of approximately 0.34 nm is corresponded to the interplanar distance of the (200) plane in the cubic CdTe (JCPDS Card No. 65-1046) (as shown in Fig.2b). The PbTe QDs with 7 nm in diameter were separated well onto the surface of SiO$_2$ nanobead carriers (as shown in Fig.2c). The PbTe QDs covered by a 2 nm of SiO$_2$ shell was embedded on the surface of SiO$_2$ nanobead carriers (as shown in Fig.2d). In addition, the HRTEM image of PbTe QDs shows that $d$ value of a PbTe QDs is about 0.33 nm, which can be assigned to the (200) reflection of cubic PbTe (as shown in Fig.2d). Similarly, the PbS QDs with a diameter of about 6
nm are deposited onto the surface of SiO$_2$ nanobead carriers separately (as shown in Fig.2e). HRTEM image of the hierarchical SiO$_2$-PbS@SiO$_2$ nanostructures shows that $d$ value of the PbS QDs is approximately 0.32 nm, which is corresponded to the (111) plane of cubic PbS (as shown in Fig.2f).

**Figure 2** TEM images of hierarchical SiO$_2$-CdTe@SiO$_2$ (a, b), SiO$_2$-PbTe@SiO$_2$ (c, d), and SiO$_2$-PbS@SiO$_2$ (e, f) nanostructures. The inserts of Fig.2b, d and f show the representative HRTEM image.

The growth of QDs and self-assembly of QDs and SiO$_2$ nanobead carriers are two important steps towards generating the advanced hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures. In the synthesis process, MPA and NaOH have played important roles in the synthesis and self-assembly strategy and then the formation of the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures. MPA, acting as the stabilizer, is a superior capping molecule for producing stable QDs and the carboxylic groups of MPA may coordinate with the Cd or Pb site of monomers or
clusters for fast growth of QDs nanocrystal. On the other hand, NaOH is another agent influencing the formation of hierarchical \( \text{SiO}_2\)-QDs@\( \text{SiO}_2 \) nanostructures [22]. NaOH can favor the PL enhancement in the colloid solution by decreasing the defects attributed to the formation of Cd-thiol (Cd(SR)) complexes on CdTe QDs surfaces. Furthermore, NaOH can assist the self-assembly of QDs on the surface of \( \text{SiO}_2 \) nanobead carriers, which include the following sequence: from (i) etching the surface of \( \text{SiO}_2 \) nanobead carriers by NaOH solution to obtain the colloidal surface to; (ii) adhering QDs on the viscous surface of \( \text{SiO}_2 \) nanobead carriers to; (iii) covering the QDs by a colloidal \( \text{SiO}_2 \) shell and then (iv) forming the hierarchical \( \text{SiO}_2\)-QDs@\( \text{SiO}_2 \) nanostructures.

![XRD patterns of the hierarchical SiO2-CdTe@SiO2 nanostructures](image)

**Figure 3** XRD patterns of the hierarchical SiO2-CdTe@SiO2 nanostructures

X-ray diffraction analysis was applied to investigate the CdTe crystalline of hierarchical \( \text{SiO}_2\)-CdTe@\( \text{SiO}_2 \) nanostructures. Three broad peaks at about 24.5\(^\circ\), 40.5\(^\circ\) and 48\(^\circ\) are correspond to the (111), (220), and (311) planes, which are matched with the cubic zinc blende structure of CdTe crystal (as shown in Fig.3). According to the XRD data, the average QDs size can be quantitatively evaluated using the Debye-Scherrer formula relates, which gives the relationship between peak broadening in the XRD and particle size:

\[
D = 0.89\lambda / (B \cdot \cos \theta_B)
\]

Where 0.89 is the Debye-Scherrer constant, \( \lambda \) represents the X-ray wavelength (\( \lambda = 1.5406\) Å),
where $B_{size}$ is the full width at half-maximum and $\theta_B$ is the Bragg diffraction angle [23]. The nanoparticle size of CdTe QDs determined by the Debye-Scherrer equation is about 4.5 nm, which is corresponded to the information obtained from the HRTEM image of CdTe QDs (as shown in Fig.2a).

3.2. Characterization of surface functionalization

![FT-IR spectra](image)

**Figure 4** FT-IR spectra of (a) SiO$_2$, (b) SiO$_2$-CdTe@SiO$_2$, (c) SiO$_2$-CdTe@SiO$_2$-COOH and (d) SiO$_2$-CdTe@SiO$_2$-NH$_2$ (samples a-d)

As we know, most applications of QDs are directly dependent on the chemistries that make them hydrophilic and biofunctional. The hierarchical SiO$_2$-CdTe@SiO$_2$-COOH or SiO$_2$-CdTe@SiO$_2$-NH$_2$ nanostructures give a chemical link with various functional molecules for promising applications. In this paper, the hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures can pave the way for applying them in the fields of imaging vivo cells and detecting fingerprint. FT-IR spectra are applied to confirm the surface binding of capping groups. The IR spectra of the samples confirmed -COOH or -NH$_2$ group were successfully connected to the hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures. The FT-IR spectra of hierarchical SiO$_2$-CdTe@SiO$_2$-COOH confirms that the successful functionalization of hierarchical SiO$_2$-CdTe@SiO$_2$ by the presence of carbonyl group (-CO-, $\nu_{C=O}$≈1565 cm$^{-1}$) and hydroxyl group (-OH, $\nu_{O-H}$≈3448 cm$^{-1}$) [24], as shown in Fig.4c. In addition, FT-IR spectra confirms the
amino group (-NH$_2$) is also successfully connected to the hierarchical SiO$_2$-CdTe@SiO$_2$ by the presence of peaks at about 1470, 2580 and 2924 cm$^{-1}$[25] (as shown in Fig.4d). Two distinct peaks for the SiO$_2$ nanobead carriers at about 800 and 1100 cm$^{-1}$ are attributed to the symmetric contraction vibration peak at horizontal and vertical of the bond of Si-O-Si. The presence of 1385 cm$^{-1}$ is due to the interaction of the samples with the KBr in the tablets, and the band around 1635 cm$^{-1}$ is assigned to the bending mode of the interlayer water molecule [26].

3.3. Optical properties of the hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures

![Figure 5](image)

**Figure 5** Emission (a) and absorption (b) spectra of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures in aqueous solution (excitation wave length: 380 nm), colloidal solutions of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures (left to right, inserts of Fig. 4b) consisting of samples 1-6 obtained by the aforementioned methods under normal and UV light (352 nm, 6 W)

It is well known that the PL wavelength range of QDs can be finely tuned by changing the size of the QDs particles [27-28]. In this paper, hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures show excellent luminescence properties and the PL colors can be tuned from green to red in the visible spectrum. Figure 5 shows the PL spectra, normalized UV-vis absorption spectra and corresponding photographs of the solution of hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures. The PL emission peaks of CdTe QDs range from 535 nm to 640 nm, which reveals the tunable emission spectrum is in the visible range (as shown in Fig.5a). The size-dependent quantum
confinement effects are apparent during the CdTe QDs growth process as solutions in vials shift across the visible spectrum from green to red emission (as shown in inset of Fig.5b). The corresponding peak position in UV-vis spectra ranges from 460 nm to 610 nm attributed to the increase in the non-radiative recombination of electrons and holes on the surface of the CdTe QDs as the size increases [29]. During the growth of CdTe QDs, smaller particles will dissolve and become the constituents of larger QDs, a process known as Ostwald ripening. The tunable colors of the hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures implies that our facile method can control the size of CdTe QDs from 2.6 nm to 5.0 nm, as a result that the PL emission from green to red region of the visible spectrum. Interestingly, the hierarchical SiO$_2$-CdTe@SiO$_2$ nanostructures still remains its PL properties after the modification by -COOH or -NH$_2$ group. The SiO$_2$ coating prevents the oxidative and photothermal degradation of the QDs and increases the stability of QDs@SiO$_2$ nanostructures. The spectra of SiO$_2$-CdTe@SiO$_2$ nanostructures exhibit only a slight red shift (~25 meV) over 30 days of water soaking and almost zero peak broadening for 60 days in air.

4. Fingerprint detecting

The pattern of friction ridge skin on the finger of the hands is unique to each individual, which can provide significantly information about one person [30-32]. Usually, ninhydrin solution, iodine/benzoflavone spray [33] and vacuum metal deposition [34] techniques have been developed to detect the fingerprint. However, these methods suffered from being influenced by the complex background. QDs can luminesce with great intensity and high photostability than commercially available organic fluorescence dyes, and so the QDs are the potentially ideal reagents for detecting the latent fingerprint deposited on polychrome substance. For instance,
Sametband et al. have shown that CdSe/ZnS QDs stabilized with n-alkaneamines in the organic solution can be used for the direct visualization of latent fingerprint on wet nonporous surfaces [35]. CdS/dendrimer in organic solvent has also been used for the detection of fingerprint [36-37]. However, the toxicity of QDs without protecting shell may hinder their applications in the fields of fingerprint detecting. Fortunately, the hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures demonstrate forensic work on the fingerprint detecting.

![Image](image_url)

**Figure 6** Photographs of the detection of a fingerprint deposited the glass under UV light (352 nm, 6 W)

Hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures can interact with the amino acid of a fingerprint, especially the sebum-rich fingerprint, and so acts as a dusting powder to locate and visualize fingerprints under the UV light [38]. Because the emission of the multicolored CdTe QDs in aqueous solution under UV light covers almost the visible region from green to red, the fingerprint deposited on objects can be readily detected without being influenced by the background colors. A fingerprint on the glass substrate was detected by the hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures, and the fluorescence photographs were shown in the figure 6. The -COOH groups modified on the hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures has a strong affinity for the amino acid or grease in the substances of the fingerprint, thereby enabling the visualization of the fingerprint, even the prints are faint.

5. Cells imaging

The free carboxyl (-COOH) group conjugated on the surface of hierarchical SiO$_2$-CdTe@SiO$_2$-COOH nanostructures is available for covalent coupling to various
biomolecules (such as proteins, peptides and nucleic acids) by cross-linking to reactive amine (-NH₂) groups of the vivo cells. The luminescence images of HeLa cells were shown in Figure 7. The bright spots are attributed to the CdTe QDs of the hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures, which can illuminate the entire image of the cell (as shown in Fig.7a and c). The cell image could also demonstrate by the dark frame (Fig.7b). These bright spots are mainly distributed in the membrane of HeLa cells. The shape and position of HeLa cells (as shown in Fig.7a and c) indicate the strong interaction between HeLa cells and hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures by forming the covalent bonds. It is obvious that the hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures did not permeate the cytomembrane, rendering the hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures suitable for cell-labeling markers.

![Figure 7](image)

**Figure 7** Fluorescence imaging of HeLa cells after incubated with hierarchical SiO₂-CdTe@SiO₂-COOH nanostructures (green-emitting nanocrystals). The acquisition was performed using the continuous-wave laser source emitting at 380 nm.

The quantity of the living cells was reflected by MTT assays (Figure 8). The MTT results reveal that SiO₂ shell increased cellular proliferation without any evidence of cytotoxicity and the viability of Hela cells were similar to the results of the SiO₂ control test, while the QDs without SiO₂ shell had obvious cytotoxicity. After 7 days cultured, the number of living cells decline dramatically.
6. Conclusion

In general, an integrated synthesis and self-assembly strategy for preparing the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures (QDs=CdTe, PbTe or PbS) has been developed. In the synthesis, 3-10 nm QDs covered by 1-2 nm SiO$_2$ shells were deposited onto the surface of SiO$_2$ nanobead carriers, resulting in the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures. The color-tunable hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures perform excellent optical property with PL emission from green (CdTe) to Near-IR (PbS and PbTe) of the region. Moreover, the hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures can be readily introduced to -COOH or -NH$_2$ active group. The hierarchical SiO$_2$-QDs@SiO$_2$-COOH nanostructures is available for covalent coupling to various bimolecular by cross-linking reaction, with the result that the SiO$_2$-QDs@SiO$_2$ nanostructures show promising potential applications in detecting fingerprint and imaging cells. This work sheds new light on the preparation of hierarchical SiO$_2$-QDs@SiO$_2$ nanostructures (QDs=CdTe, PbTe or PbS) and important applications in cell imaging and fingerprint detecting without being influenced by the multicolored environment.

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