

CdS nanocomposites assembled in porous phosphate heterostructures for fingerprint detection

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ABSTRACT

A fluorescent hybrid cadmium sulfide quantum dots (QDs) nanocomposites assembled in a porous phosphate heterostructures (PPH) functionalized with mercaptopropyl (PPH-SH) and propionitrile (PPH-CN) where synthesised in water and show high stability. Both materials, show fluorescence in the 450–700 nm wavelength range but the PPH-SH-CdS is about five times more fluorescent than PPH-CN-CdS. The maximum emission wavelengths of the resulting materials are 576 nm (PPH-SH-CdS) and 616 nm (PPH-CN-CdS) and show Stokes shifts higher than 300 nm. The nanocomposites were characterized by TEM, EDS, FT-IR, XRD and fluorescence. These materials are suitable for fingerprint analysis.

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1. Introduction

The study of novel materials based on semiconductor nanocrystals is becoming an attractive area of research. Quantum dots (QDs) are colloidal semiconductors nanocrystals that due to their electronic excitations confined in all three spatial dimensions have properties between bulk semiconductors and discrete molecules that make them a more adaptable alternative to conventional semiconductor [1,2]. Their unique size-dependent optical properties have various prospective applications in optoelectronic devices, nonlinear optical devices and biological labels because their optical emission can be tuned simply by controlling the size of the nanocrystals [3–5]. These nanomaterials are of easy fabrication using colloidal chemistry approaches either through organometallic routes [6,7] or by aqueous synthesis [8,9]. However, their uniform incorporation into solid-state matrices to enhance their stability and luminescence, creating nanostructural materials with unique physical and chemistry proprieties [10,11], is difficult due the aggregation of the nanocrystals that adversely affect their light emission properties [12]. This problem can be minimized by QDs encapsulation in chemically inert matrix with an accurately control dispersion and aggregation of the nanoparticles [13]. Also, this immobilization may reduce the hazards of these inorganic nano-systems, preventing the release of such particles, especially those in which the nanoparticles are inherently dispersive, as those

applications will inevitably lead to the exposure of nanoparticles to organisms [14].

Cadmium sulfide (CdS) QDs are one of the most studied semiconductors because of their unique chemical, physical and optical properties that make them potentially useful in a great variety of applications [15–18]. The extension of the dispersion of nanoparticles on a solid material depends on the uniformity of the pores of the matrix. Matrices with uniform pore structure and controlled diameter are preferable as host materials for nanoparticles. The nanolevel uniformity of the pore structures of mesoporous materials, such as porous phosphate heterostructure (PPH) [19], seems a challenge system to build nanocomposites systems, owing to the possibility to obtain materials with different pore size (2–50 nm) and structures.

Latent fingerprints are the physical evidence in identification and generalized proof of identity despite the increasingly use of DNA test. Forensic investigators often use special optical equipment and/or chemical substances to make latent fingerprints visible. The conventional powdering technique involves preferential adherence of powder particles to fingerprint residues to provide contrast between the fingerprint profile and the background surface [20]. The detection of latent fingerprints includes optical, physical and chemical or a combination of them, exploiting the differences in characteristics of the fingerprints and the substrates on which they are found [21]. Powder dusting is the simplest and most commonly used procedure for developing latent fingerprint. It is also the oldest technique to be used and dates back to the last decade of the XIX century when mercury and graphite based

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powders were used for developing fingerprints in non-porous absorbent surfaces [22,23]. On the basis of chemical constitution the powders can be classified into different types: regular, metallic and luminescent. Regular powders consist in a resinous polymer for adhesion and a colorant for contrast containing for example ferric oxide and rosin, manganese dioxide and rosin or titanium dioxide and kaolin [24]. A very simple method to develop fingermarks involves the use of iodine fuming coupled to an organic dye as colorant such as fluorescein, rhodamine B and xanthene dyes [25–28]. Metallic powders containing meshed metals have been used, for example lead, aluminum, gold and silver [29–32]. Also metal oxide particles such as titanium dioxide, iron oxide or zinc oxide are used as developing fingerprints powders [33–37].

Recently, the integration of nanotechnology with latent fingerprint detection has broadened the implications in a variety of areas including enhancing contrast and increasing selectivity, particularly due to development of luminescent powders [38–43]. The incorporation of QDs in selected materials has opened a new window in the fingerprint science. In the present work, PPH materials conjugated with CdS quantum dots were design and synthesised for latent fingerprint analysis. Namely, PPH with mercaptopropyl (PPH-SH) and propionitrile (PPH-CN) organic groups functionalization where synthesised and used as hosts for CdS QDs rendering them stable luminescent optical materials. This work focused on PPH as host materials because it is a new material with the surface functionalities easily modified accordingly with the required properties [19]. The objective is to provide a more versatile and innovative material both in the luminescent properties and its applicability.

2. Experimental

2.1. Synthesis of PPH-SH and PPH-CN

Preparation of hybrid porous phosphate heterostructure functionalized with mercaptopropyl and propionitrile organic groups were carried out analogously to porous phosphate heterostructure synthesis [19]. Briefly, cetyltrimethylammonium (CTMA)-expanded zirconium phosphate was prepared from a solution of (CTMA)Br (Aldrich) in 1-propanol, to which H_3PO_4 (85%, BDH) and zirconium(IV) propoxide (70%, Aldrich) were loaded according to previously reported procedures [44]. The solid obtained (CTMAZrP) was suspended in water (10 g/l), and a solution of hexadecylamine (Aldrich) in 1-propanol (35 g/l) was added as a co-surfactant (10 ml/100 ml CTMAZrP water suspension). After 1 day under stirring, a solution (50%, v/v) of tetraethylorthosilicate (TEOS) (Aldrich) and the corresponding organo-silyl derivate (3-mercaptopropyl)trimethoxysilane (95% Aldrich) and 3-(triethoxysilyl)propionitrile (98% Aldrich) in molar ratio 5 in 1-propanol was added. After 3 days under stirring at room temperature the suspension was centrifuged and the solid obtained washed with ethanol (3×25 ml), and dried at 333 K in air. In this case, the surfactant molecules used as template of silica galleries of interlayer space cannot be removed by calcinations to liberate the inner of galleries because the organic groups would be destroyed. For this, acid extraction is used with a solution HCl:Ethanol (1:10 v/v). This extraction was made three times to assure the correct extraction of surfactant molecules. After this acid extraction, the solid was washed with ethanol and dried at 333 K in air. The solids obtained were named, PPH-SH and PPH-CN respectively.

2.2. PPH-S-CdS and PPH-CN-CdS preparations

PPH-SH (100 mg) was suspended in H_2O and stirred for 4 h at room temperature, then the pH was adjusted at 7.0 with NaOH (1 M) and, after that period of time, an excess of cadmium chloride

Table 1

Textural parameters of the different materials synthesised.

Material	R/P ¹ (molar ratio)	d_{001} (Å)	S_{BET} ² ($m^2 g^{-1}$)	Vp ³ ($cm^3 g^{-1}$)	Dp ³ (Å)
PPH		40	620	0.543	30.9
PPH-SH	1.193	40	472	0.513	37.9
PPH-CN	5.230	38	516	0.607	42.9

¹ Molar ratio organic propyl groups to PPH.

² Surface obtained by Brunauer-Emmett-Teller method.

³ Volume and diameter pore size by means Cranston and Inkley method.

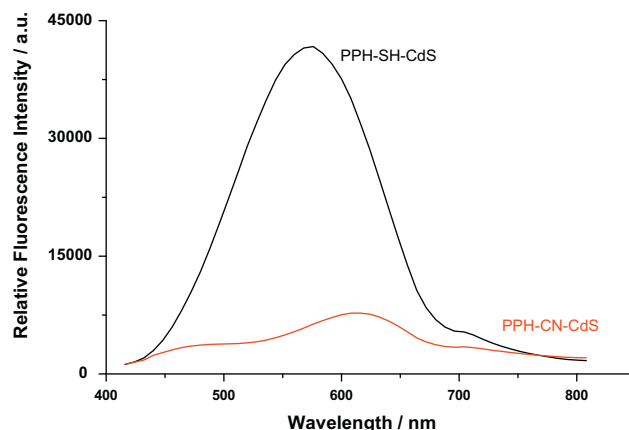


Fig. 1. Emission spectra of PPH-SH-CdS and PPH-CN-CdS.

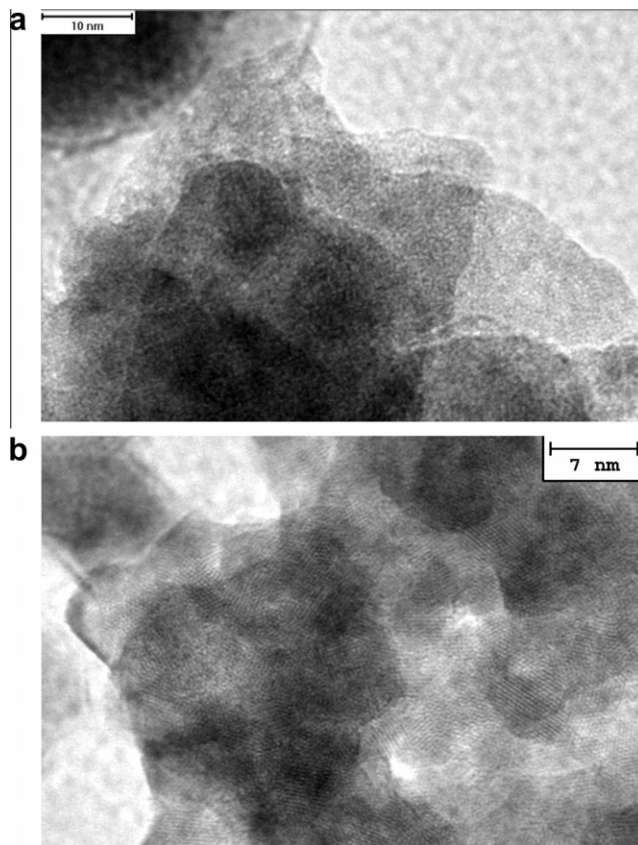


Fig. 2. TEM images of CdS QDs nanocomposites (dark bits) confined in the pristine (a) PPH-SH and (b) PPH-CN.

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