

SUPPORTING INFORMATION:

**Sodium-Alginate Biopolymer as a Template for the Synthesis of
Nontoxic Red Emitting Mn²⁺-Doped CdS Nanoparticles**

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Abstract

Manganese-doped cadmium sulfide (CdS:Mn) nanoparticles were prepared by chemical synthesis using sodium-alginate as template. The preparation of the nanocomposites involved ionic crosslinking of the biopolymer by dimerization of its α -L-guluronic monomers with Cd²⁺ and subsequent formation of the semiconductor nanoparticles upon addition of sulfide ions in the presence of Mn²⁺. The crystalline phase of CdS in the material was confirmed by XRD. Surface morphology of the nanocomposites was investigated by SEM. The observation by TEM showed that the CdS:Mn particles were spherical in shape with diameters of approximately 4 nm. EPR measurements of the CdS:Mn-alginate nanocomposite showed that the Mn²⁺ ions were incorporated in cationic sites of CdS with lower symmetry. Due to a distorted crystal field induced by the Mn²⁺ ions, photoluminescence spectra of the CdS:Mn-alginate showed red fluorescence between 650 nm and 750 nm falling into the optical window for bioimaging in which the light has its maximum tissue penetration depth. It was demonstrated that the interaction between the nanoparticles and the matrix prevents release of CdS into the environment, leading to low acute toxicity of the nanocomposites.

Keywords: alginate; polysaccharide; CdS; Mn; quantum dot; diluted magnetic semiconductor

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Influence of CdS nanostructures on the alginate matrix

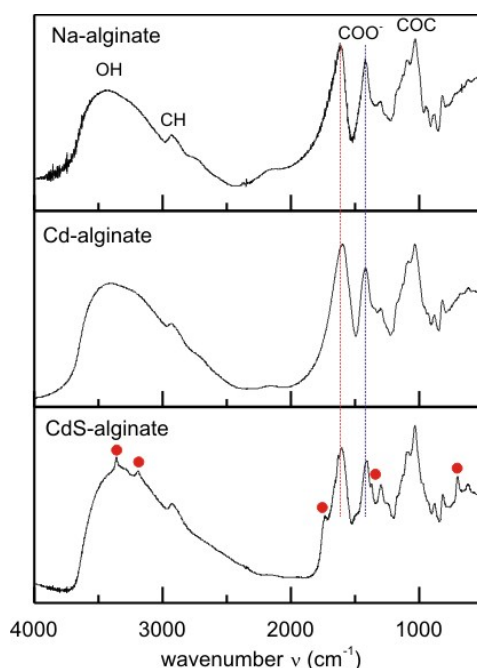


Figure S1. FTIR spectra of Na-alginate, Cd-alginate and CdS-alginate powders dispersed in KBr.

Infrared spectroscopy was employed to investigate the interaction between the CdS nanoparticles and the biopolymer matrix. FTIR spectra of Na-alginate, Cd²⁺ cross-linked alginate, and CdS-alginate nanocomposite powders dispersed in KBr are presented in Figure S1. The characteristic spectrum of the Na-alginate biopolymer is composed of a broad band centered at approximately 3500 cm⁻¹ that arises from the stretching of hydroxyl groups, low-intensity bands at about 2900 cm⁻¹ attributed to -CH₂ groups, two peaks at 1610 cm⁻¹ and 1417 cm⁻¹ that come from the asymmetric and symmetric stretching modes, respectively, of carboxylate salt groups (-COONa), and a number of vibrations in the range 1100–1000 cm⁻¹ assigned to the glycoside bonds in the polysaccharide (C-O-C stretching) (Sundarrajan, 2012). The spectrum of Cd²⁺ cross-linked alginate shows similar features as the spectrum of Na-alginate. As a consequence of the ion exchange of Na⁺ in the biopolymer by Cd²⁺ ions, a 10 cm⁻¹ shift towards lower wavenumbers was observed for the peak assigned to asymmetric stretching of carboxylate salt groups (red vertical line in Figure S1.).

Concerning the CdS-alginate nanocomposite, in addition to the shift of the asymmetric stretching mode of carboxylate salt groups the FTIR spectrum showed a small shift of the corresponding symmetric mode as well (blue line in Figure S1). A similar shift was observed

previously in alginate stabilized CdS and PbS nanoparticles (Sundarrajan, 2012) and supports the interaction of the nanostructures *via* carboxylate groups of the biopolymer. The spectrum of the nanocomposite showed additional bands at 3350 cm^{-1} , 3185 cm^{-1} , 1740 cm^{-1} , 1371 cm^{-1} and 700 cm^{-1} (marked by red circles in Figure S1). The lines at 3350 cm^{-1} and 3185 cm^{-1} are in the region pertaining to the vibrations of the hydroxyl groups from the carboxylic acids, while the bands at 1740 cm^{-1} and 1371 cm^{-1} belong to the carboxylic acid's C-O vibration modes. Finally, the presence of the band at 700 cm^{-1} can be attributed to C-S stretching vibration. Since the COO- stretching modes often show multiple bands due to coupling, the appearance of these new peaks can be explained by the interaction between the nanoparticle (and/or the excess of sulfide ions) and the biopolymer. Additionally, the bands at 1740 cm^{-1} and 1371 cm^{-1} also suggest the elimination of the interactions between the carboxylate groups and Cd^{2+} ions upon their interaction with sulfur.

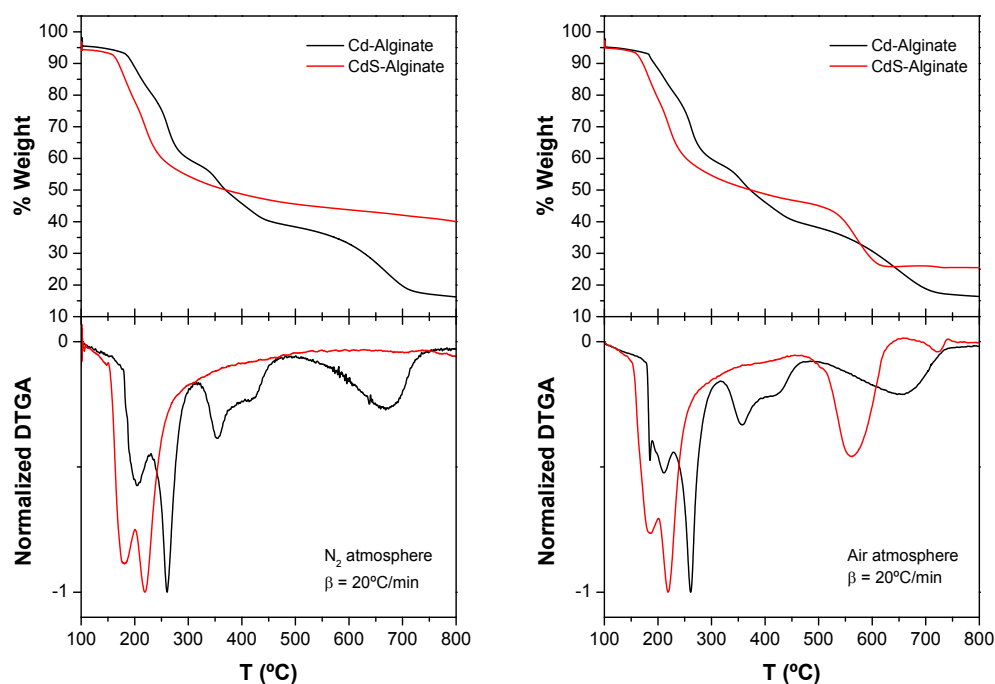


Figure S2. Thermal degradation curves of Cd-alginate powder and CdS-alginate nanocomposite in (left) N_2 and (right) air flow.

Thermogravimetric analysis of CdS-alginate nanocomposite was performed to investigate the influence of the nanoparticles on the thermal and thermo-oxidative degradation of the biopolymer, as well as to determine the weight percentage of the nanostructured phase in the nanocomposite. The TGA results for the nanocomposite were compared to the data

obtained for Cd-alginate since the thermal and thermo-oxidative degradation of the sodium-alginate was extensively studied for various pyrolysis conditions.

The TGA and DTGA curves of Cd-alginate powders and CdS-alginate nanocomposites, obtained in the inert (N₂) and oxidative (air) atmosphere are presented in Figure S2. Thermal degradation of the investigated material involved several steps of pyrolysis. In the case of Cd-alginate powder, it can be seen that the cross-linked polymer exhibits five degradation processes in both nitrogen and air atmospheres, similar to that of a pure sodium alginate. However, distinct degradation steps are clearly observed due to coordination of Cd²⁺ ions with COO⁻ ions in α -L-guluronic monomers. On the other hand, the thermal degradation of the CdS-alginate nanocomposite shows only two large degradation steps between 150 °C and 280 °C. These processes, which are approximately 50 °C shifted in comparison to the Cd-alginate, can be attributed to the first stages of the degradation of sodium-alginate, or more specifically, to the decomposition of pure alginate monomers without any coordination. This conclusion is in accordance with the FTIR result that showed lack of interactions between Cd²⁺ and COO⁻ upon addition of sulfur (Figure S1.) In the case of the thermo-oxidative degradation of CdS-alginate, an additional degradation step can be observed between 500 °C and 630 °C that corresponds to an oxidation process. This process is associated with approximately 20% of the mass loss. Also, the difference between the residues between CdS-alginate and Cd-alginate after the degradation in N₂ atmosphere was also about 20 %. These values indicate that the weight percentage of the semiconducting phase was higher than the one assumed from the synthesis conditions (between 10 and 20 wt% of CdS in alginate).