Nano-photocatalysts based on ZnS quantum dots/chitosan for the photodegradation of dye pollutants

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Abstract. In this work, nano-photocatalysts based on ZnS quantum dots (QD) functionalized by chitosan were developed using “green” colloidal chemical process in aqueous media at room temperature. The ZnS/chitosan nano-photocatalysts were extensively characterized and the results demonstrated that chitosan was an effective capping ligand for the direct production of water-soluble ZnS QDs with average nanocrystal sizes of approximately 3.5 nm. Methylene blue dye was used as “model organic pollutant”, which was effectively oxidized by the photocatalytic surface activity of the ZnS/chitosan nanostructured systems under UV irradiation. In summary, innovative “green” nano-photocatalyst nanomaterials were produced based on a fluorescent inorganic “core” of ZnS QDs and a biocompatible organic “shell” of chitosan for potential use on the photodegradation of hazardous dye pollutants present in industrial wastewater.

1. Introduction

Although international environmental standards are becoming more stringent, many industries, such as textile, plastics, paper and pulp, leather, cosmetics, and food, generate streams of waste effluents that contain high amounts of organic dyes, which exhibit carcinogenic and mutagenic properties towards living organisms and pose a serious threat to human life [1-3]. Despite several technological systems for the removal of organic pollutants have been developed, most of them are based on conventional processes for treatment of these effluents, which are unsatisfactory for purifying the wastewater from the industries. Therefore, traditional water treatment methods are now gradually being complemented by advanced oxidation processes (AOPs), such as photocatalysis methods that can provide quick and high efficiency on the oxidation of organic pollutants at low levels without the formation of polycyclic products [3,5]. Among the alternatives for “low-dimensional” materials for photocatalysis application, semiconductor nanocrystals (referred to as quantum dots, QDs) have recently emerged as a novel class of nanomaterials with unique physicochemical, electronic, magnetic and optical properties. Currently, the most commonly used QDs are made of Cd\(^{2+}\) core, which is highly toxic to humans and to the environment. Even though Cd\(^{2+}\) is incorporated into the nanocrystalline core as sulfides or selenides, surrounded by a “biocompatible shell” (e.g. polymers, proteins, polysaccharides), there is no definitive

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information regarding how these toxic ions will impact the use of QDs in environmental and biomedical applications. Thus, “cadmium-free” nanomaterials, such as zinc sulfides (ZnS), have been interesting choices for producing QDs eco-friendly photocatalyst, due to the higher surface area-to-volume ratio as compared to their bulk counterparts with superior photon absorption at the nano-interfaces. In addition, size confinement caused by the small dimension of the QDs leads to a significant increase in the band gap energy compared to the bulk material producing a higher redox potential in the system [6].

In this paper, we endeavor to develop a novel nano-photocatalyst based on semiconductor ZnS QDs conjugated with chitosan by using a single-step “green chemistry” aqueous colloidal process at room temperature. In addition, methylene blue (MB) dye was used as “model organic pollutant”, which was effectively oxidized by the photocatalytic surface activity of the ZnS/chitosan conjugates under UV irradiation. This new class of nanohybrids may offer countless opportunities to develop fluorescent and photocatalytic nanomaterials for environmental applications.

2. Experimental procedure
ZnS nanoparticles (QD-ZnS) were synthesized via an aqueous route at room temperature (RT) as previously reported by our group [7].

UV-Vis spectroscopy measurements were conducted using a Perkin-Elmer spectrometer (Lambda EZ-210) in transmission mode over a wavelength range of 600 nm to 190 nm. The absorption spectra were used to monitor the formation of ZnS QDs during the reaction as well as their relative colloidal stability in the medium.

Photoluminescence (PL) characterization of the QD-ZnS conjugate was conducted based on spectra acquired at RT using a Nanodrop 3300 fluoro-spectrometer (Thermo Scientific, UV Light Emitting Diode (LED) with \( \lambda_{\text{excitation}} = 365 \pm 10 \text{ nm} \)).

QD-ZnS conjugate and chitosan were analyzed using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Thermo Fischer, Nicolet 6700) over a range of 400 to 4000 cm\(^{-1}\) with 64 scans at a resolution of 2 cm\(^{-1}\). These samples were prepared by placing a droplet of the chitosan solution or QDs colloidal dispersions onto the KBr powder followed by drying at 60±2 °C for 24 h.

Morphological and structural features of the ZnS QDs were characterized using transmission electron microscopy (G2-20-PEI transmission electron microscope, TEM) coupled to an energy dispersive X-ray (EDX) microprobe and selected area electron diffraction (SAED) analysis at an accelerating voltage of 200 kV. In all of the TEM analyses, the samples were prepared by dropping the colloidal dispersion onto a holey carbon/copper grid.

The photocatalytic activity of the ZnS conjugates was evaluated via the photodegradation of MB (water-soluble dye that was used “model organic pollutant”) under UV light irradiation (UVC, \( \lambda=280-100 \text{ nm} \), 6 W, at \( \lambda=254 \text{ nm} \), Boitton Instruments, parallel to the surface of the suspension at a fixed distance of 20 cm). The experiments were performed at RT using 15 mL of a suspension containing 30 mg.L\(^{-1}\) of the QD-ZnS catalyst and 2.5 mg.L\(^{-1}\) (QD-ZnS/dye = 12) of the dye which was poured into a petri dish (10 cm in diameter). The mixed suspensions were first magnetically stirred in the dark for 1.5 h to achieve adsorption-desorption equilibrium. At certain time intervals, 3 mL of the mixed suspensions were collected and analyzed by UV-Vis spectroscopy (Lambda EZ-210, Perkin Elmer) to determine the dye concentration based on the Beer-Lambert curve to correlate the absorbance with the dye concentration at its characteristic maximum absorption wavelength (\( \lambda=664 \text{ nm} \)).

3. Results and Discussion
In figure 1(a), it is presented the UV-vis spectrum of ZnS semiconductor (ZnS QDs) conjugates using the carbohydrate chitosan as the stabilizing ligand during the synthesis. The spectrum exhibits a broad absorption band between 250 and 350 nm with the exciton absorption transition (\( \lambda_{\text{exc}} \)) at approximately 267 nm indicating that the ZnS QDs were produced and stabilized by chitosan as the capping-ligand within the quantum confinement regime.
The optical band gap (absorbance onset), the blue-shift values and QD size [8] were determined from the absorption coefficient data as a function of the wavelength using the Tauc relation (figure 1(b)) extracted from the UV-Vis spectra [9]. As summarized in figure 2, the results support the formation of ZnS-chitosan conjugates in aqueous media because the band gap energy of the semiconductor (3.92 eV, that corresponds to 316 nm) was significantly greater than the ZnS bulk (i.e., 3.61 eV, blue-shift = 0.42 eV) [10].

![Figure 1](image1.png)

**Figure 1.** (a) UV-Vis spectra and (b) optical band gap plot using Tauc equation of the ZnS-chitosan conjugates.

Figure 3A shows the photoluminescence spectrum collected at RT of the system under evaluation. The band edge recombination in UV range was not detected and other bands in violet-blue range were observed. According to the literature, ZnS quantum dots typically exhibit emission peaks in the 400-550 nm wavelength range, which is primarily associated with point defects, such as vacancies (V) and interstitial ions (I) and also surface defects [7].

![Figure 2](image2.png)

**Figure 2.** Schematically representation of size and band gap energy of ZnS QDs in comparison to ZnS bulk.

FTIR spectrum of chitosan (figure 3B(a)) presents absorption peaks at 1645 cm\(^{-1}\) and 1560 cm\(^{-1}\), which are assigned to the carbonyl stretching of the secondary amides (amide I band) and the N-H bending vibrations of the deacetylated primary amine (-NH\(_2\)) and amide II band, respectively. In addition, the absorptions at 1030-1040 cm\(^{-1}\) and 1080-1100 cm\(^{-1}\) indicate the C-O stretching vibration in chitosan, which are associated with the C6-OH primary alcohol and the C3-OH secondary alcohol respectively [7]. After conjugating the ZnS QDs dots with the capping chitosan (figure 3B(b)) all these bands of chitosan were “red-shifted”, i.e., shifted to lower wavenumber. These changes can be mainly
attributed to the interactions occurring between the functional groups of the chitosan ligand and the ZnS quantum dots, indicating that the primary and secondary alcohols, amine, and acetamide groups of the chitosan polymer have interacted with the ZnS nanocrystals at the surfaces [10].

**Figure 3.** (A) PL spectrum of ZnS-chitosan conjugates. (B) FTIR spectra of chitosan (a) and QD-ZnS conjugate (b).

Figure 4 shows representative TEM images of ZnS QDs with spherical-like shapes. The estimated nanoparticle size is in reasonable agreement with the values obtained from the UV-Vis optical absorbance (3.5±0.3 nm). In addition, the electron diffraction pattern of the QDs with a lattice parameter compatible with the ZnS cubic crystal (JCPDS 05-0566) is showed in figure 4(A). EDX spectrum shows the chemical analysis of the nanocrystals with Zn and S as the major elements (figure 4(B)), excluding the copper, oxygen and carbon peaks related to the TEM grid and the polymer stabilizer.

**Figure 4.** (A) TEM image with nanocrystal plane spacing and (B) EDX spectrum of QD-ZnS.

The ZnS-chitosan conjugates were tested as catalysts in the presence UV radiation and the results are presented in figure 5. The discoloration profile at 664 nm (figure 5(a)) for the solution containing
methylene blue dye indicated that the ZnS QDs removed the dye from the aqueous medium effectively: approximately 90% of the coloration after a 90 min reaction under UV light (figure 5(b)). This photocatalytic performance of the ZnS QDs conjugates was expected by considering: (i) ZnS QD band gap energy and relative position; (ii) the redox potential of $\text{H}_2\text{O}/\text{OH}^*$, $\text{OH}^-/\text{OH}^*•$ and $\text{O}_2^-/\text{O}_2•^-$ species that lies within the band gap of the ZnS QDs; and (iii) the intermediate energy states due to defects in crystal structure inhibiting or delaying the rapid carrier recombination processes [4,11].

![Figure 5](image.png)

Figure 5. (a) Absorption spectral changes of MB aqueous solution in the presence of ZnS QDs under UV light (ZnS QDs:MB = 12). (b) Schematic MB degradation by ZnS-chitosan nano-photocatalyst.

4. Conclusions
Nanoconjugates based on ZnS quantum dots stabilized by biocompatible chitosan ligands were effectively synthesized via a novel facile route based entirely on aqueous colloidal chemistry at room temperature. The ZnS-chitosan conjugates were fluorescent and exhibited photocatalytic activity for the degradation of organic pollutant compounds dyes (i.e., methylene blue) under UV irradiation.

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