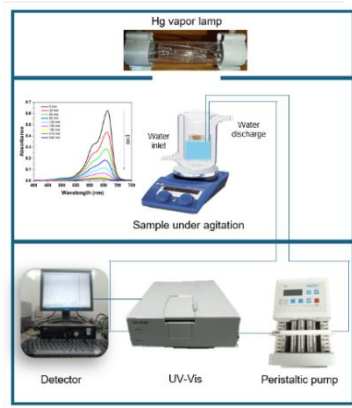


CuInS₂ Quantum Dots as Photocatalysts for Heterogeneous Photocatalysis of Organic Pollutants Assisted by Flow Injection Analysis

ORAL
Ph.D. Student: Y
Journal: ESPR

C. B. da Silva¹, L. R. C. Cunha¹, M. A. Schiavon¹. (1) Universidade Federal de São João del-Rei, São João del-Rei, Brazil, ceciliabaldino15@aluno.ufsj.edu.br / schiavon@ufsj.edu.br.



Degradation of organic pollutants represents a current problem. Heterogeneous photocatalysis using semiconductor oxides sensitized by quantum dots is a way to procedure this treatment. In this work, water-soluble CuInS₂ QDs obtained by one-pot method, was used to sensitize TiO₂ for the degradation of methylene blue (MB). Photolysis, photocatalysis (TiO₂) and photocatalysis (CIS QDs+TiO₂) were assisted by the Continuous Flow Injection Analysis (FIA) system. The best results obtained were from CIS QDs+TiO₂ photocatalysis, in which the MB degradation percentage was 95.7%, at 45 °C. The reaction rate of the photodegradation process increased with temperature and introduction of the the CIS QDs into the system, accelerated the percentage of the degraded dye. This study is promising for evaluating the photocatalytic performance of semiconductor heterojunction in removing organic pollutants.

Introduction

Contamination by organic pollutants poses a significant environmental challenge. A promising solution to mitigate this contamination is photocatalysis [1,2]. Titanium oxide (TiO₂) are considered an excellent photocatalysts, but it presents a wide bandgap (3.2 eV), requiring excitation mainly by ultraviolet light. Consequently, to improve its performance, an alternative is to modify the TiO₂ surface with quantum dots (QDs), providing the extension of the length of sunlight absorption [3]. QDs are semiconductor nanocrystals, that expansive absorption range spanning visible light wavelengths and short charge transport distances that facilitate the efficient separation and transfer of photogenerated carriers. CuInS₂ (CIS QDs) have low toxicity, absorption in practically the entire visible region and is relatively simple and cost-effective to manufacture [4]. Heterogeneous photocatalysis typically involves solid photocatalysts supported on inert substrates. During photocatalysis, photogenerated electrons in the conduction band (CB) are captured by dispersed O₂ molecules in the solution, while in the valence band (VB), OH⁻ or H₂O react with holes to generate ^{*}OH, accountable for the degradation of organic pollutants. In this study, a TiO₂ paste was deposited on Fluorine Tin Oxide-coated glass substrate (FTO), subsequently sensitized by CIS QDs to degradation of methylene blue (MB). The tests were assisted by a Continuous Flow Injection Analysis (FIA) system, to ensure process automation, reproducibility and real-time monitoring.

Material and Methods

CIS QDs were prepared by using indium chloride salts, copper chloride, N₂S₉H₂O and 10 mL of deionized water. The surface ligand was MPA, and the pH value was adjusted to 10. The solution was heated in a water bath at 100 °C for 2 h [6]. Titanium nanoparticle paste was produced with adaptations of the Grätzel method [7]. The films were deposited on an FTO substrate with active area of 1 cm² and annealed at different temperatures for 45 min. After sintering, the TiO₂ films were sensitized for 24 h in CIS QDs solution, resulting in photocatalyst substrates. Photocatalytic tests for MB degradation were carried out using a FIA system within a photocatalytic reactor. The system was illuminated by a 125 W mercury vapor lamp irradiation (60 mW/cm²). The substrates were immersed in a double-walled glass reactor with internal water circulation for temperature control, containing 80 mL of MB solution.

Results and Discussion

Fig. 1a shows representative absorption and photoluminescence (PL) spectra from the CIS QDs. The absorption spectrum showed maximum at 410 nm. The bandgap (E_g), calculated using the Tauc Plot method, was 1.48 eV. The emission peaks of the CIS were observed at about 712 nm. The calibration curve for MB was obtained as shown in Eq. 1 ($A = -0,00933 + 72060,606C$). The primary peak intensity at 664 nm has been monitored, every 20 min, in each temperature condition evaluated (5, 25 and 45 °C) Fig. 1b shows a plot of C/C₀ vs. time for the

photocatalytic degradation of dye. The degradation potential of photolysis was 14.13, 16.34 and 33.67%, for 5, 25 and 45 °C, respectively (Tab. 1 and Fig. 1.b). The results of reaction rate constant (k) in photolysis indicated an acceleration in the photodegradation process with the increase in temperature. Only TiO₂ on the substrate showed a dye degradation rate of 17.84, 19.83 and 38.28 %, for 5, 25 and 45 °C, respectively. Compared to photolysis, TiO₂ photocatalyst allowed an average increase of 3.97 % in degradation rate. A small decrease was inferred in the values of photolysis and TiO₂ photocatalyst activation energy (E_a), 18.92 and 16.53 KJ/mol, respectively, indicating that the reaction occurred a little faster with the introduction of TiO₂. The results of degradation rate from photocatalyst (CIS QDs+TiO₂) were 51.84, 93.98 and 95.70 %, for 5, 25 and 45 °C, respectively. When compared to the results of photolysis and TiO₂ photocatalysis, sensitization with CIS QDs demonstrates a considerable increase in the degradative capacity of the dye, as can be seen in Tab. 1 and Fig. 1.b. It is related to the formation of reactive species in CB and VB of the semiconductor heterojunction [5]. From Arrhenius equation, E_a is inversely proportional to k . However, the introduction of the CIS QDs+TiO₂ photocatalyst promoted an increase in the E_a of the reaction (Tab.

1), even with the k values increasing. A possible explanation is that CIS QDs can alter the mechanism of the degradation reaction. In general, evaluating the results obtained by the introduction of the CIS QDs+TiO₂ photocatalyst, it can be stated that it presented the best efficiency. Since, as expected, the CIS QDs provided greater energy use of the wavelength of the electromagnetic spectrum, which in conjunction with TiO₂, managed to absorb in the ultraviolet and visible wavelengths. During the photodegradation process, it was noticed that the photocatalyst did not detach from the substrate, indicating that the deposition of the paste and its subsequent sensitization by CIS QDs was successful. For this reason, there was no need to filter the photodegraded analyte, allowing the photocatalyst to be further reused and recycled.

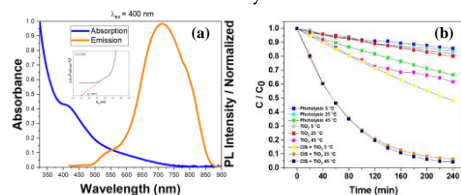


Figure 1. (a) UV-Vis and PL spectra of CIS QDs and (b) Comparison for photolysis and photocatalysis of TiO₂ and CIS QDs+TiO₂ at the temperatures studied.

Table 1. Comparison of rate constants, activation energy and efficiencies for various samples.

Sample	Reaction rate ($\text{min}^{-1} \cdot \text{cm}^{-2}$)			E_a (KJ/mol)	Degradation (%)		
	5 °C	25 °C	45 °C		5 °C	25 °C	45 °C
Photolysis	5.90×10^{-4}	7.37×10^{-4}	1.65×10^{-3}	18.92	14.13	16.34	33.67
TiO ₂	8.06×10^{-4}	9.18×10^{-4}	1.98×10^{-3}	16.53	17.84	19.93	38.28
CIS QDs + TiO ₂	3.03×10^{-3}	1.21×10^{-2}	1.39×10^{-2}	28.02	51.84	93.98	95.70

Conclusions

The results obtained demonstrated excellent photodegradation of MB under the incidence of light radiation, with a maximum efficiency of 95.7%, in 240 min and 45°C, using CIS QDs+TiO₂. The results acquired for the degradation rate of the reaction, with increasing temperature, within the same system (photolysis, TiO₂ and CIS QDs+TiO₂), corroborate their respective reaction rate values, showing that increasing temperature accelerates the photodegradation process. The activation energy, however, must be better evaluated later, since the sensitization of TiO₂ by CIS QDs may be degrading the dye through a different reaction mechanism than that presented for the other systems studied. The use of a system where the photocatalyst is fixed to the glass substrate has proven to be quite suitable, as its removal is easy compared to the use of powders. The FIA system allowed analyzing aliquots in a continuous flow, without the need to remove volumes from time to time, guaranteeing reproducibility and stability.

Acknowledgments

This work was supported by CNPq, FINEP, CAPES and FAPEMIG.

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