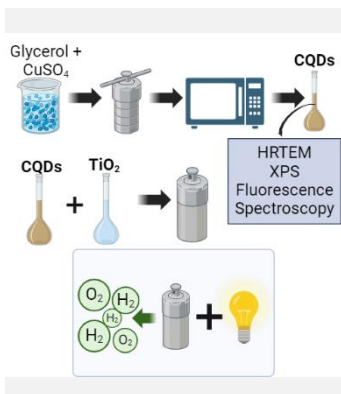


Metal-doped Synthesized Carbon Quantum Dots via microwave irradiation as TiO₂ sensitizers for hydrogen photocatalytic generation

POSTER
Ph.D. Student: Y
Journal: CEJ

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Carbon Quantum Dots (CQDs) have unique properties and recently they have attracted attention due to their small size, high conductivity, fluorescence emission, low toxicity, and other desirable characteristics. CQDs were synthesized by microwave (MW)-assisted chemical synthesis using several metals as reaction promoters, such as Fe³⁺, Cu²⁺, Zn²⁺, Na⁺, and H⁺. Glycerol with its high dielectric constant was used as solvent. The CQDs were characterized by HRTEM, XPS and fluorescence spectroscopy. The Cu-doped CQDs were stable in aqueous suspension and had a mean diameter of 3.7 nm. Finally, some of the prepared CQDs were impregnated in different proportions on TiO₂ nanoparticles and used for the production of H₂ under UV-visible irradiation. Visible light photodegradation ($\lambda \geq 400$ nm) of indigo carmine water solution was confirmed.

Introduction

Titanium dioxide (TiO₂) composite nanostructures have exhibited higher photocatalytic efficiency compared to bare TiO₂ for hydrogen evolution. In particular, the sensitization of TiO₂ with carbon structures,[1] such as carbon nanotubes, fullerenes, graphene, and notably carbon quantum dots (CQDs), has called the attention due to carbon abundance on Earth. CQDs have recently attracted increasing interest owing to their visible light absorption capacity, quantum confinement effects, multiple exciton generation, luminescent properties and efficient energy transfer.[2] Many CQDs syntheses exist, such as the top-down and bottom-up methodologies. The incorporation of ion metals in the CQDs preparation is interesting as a way of avoiding the use of any nonmetallic co-dopant. Heteroatom doped CQDs showed in general higher photoluminescence (PL) quantum yield in relation to un-doped ones. Excellent fluorescent properties of Cu-CQDs and their selectivity for fast detection of Fe³⁺(aq) for potential biomedical applications have been reported.[3] Other metals have been used for the synthesis of CQDs, for example, iron and nitrogen co-doped CQDs were synthesized through a solvothermal method assisted by microwave (MW) irradiation.[4]

MW irradiation is a green chemistry process and can be coupled to low-toxic chemicals and solvents, such as water. The absorption of MW energy depends on the polarity of the solvents that heats the reaction mixtures locally as a consequence of dipolar polarization and ionic conduction. In this context, glycerol and water have high dielectric constants of 46.5 and 80 at 20 °C respectively. In particular, glycerol is a by-product of the biodiesel and there is crude glycerol in surplus on the market which creates new challenges in terms of its uses. It is estimated that during the production of 100 kg of biodiesel 10 kg of glycerol is generated.[5]

In that context, here it is presented green preparation methods of CQDs that were impregnated onto commercial TiO₂ nanoparticles (NPs). The use of MW irradiation coupled to glycerol/water solutions containing metal as promoters leads to efficient CQDs synthesis. The prepared TiO₂@CQDs were used in the photocatalytic evolution of hydrogen, as well as photodegradation of dyes as model pollutants. The prepared photocatalysts have the potential to harvest the Sun's UV and also the visible light that reaches the Earth.

Material and Methods

Bi-distilled glycerol and methanol were purchased from Casa da Química, Brazil. Ethanol (95%), Glycerol (99%), CuSO₄·5H₂O (97%), FeSO₄ (99%), Na₂SO₄ (99%), and ZnSO₄ (99%) were obtained from Dinâmica, Brazil. Fe₂(SO₄)₃ (95%) and MgSO₄ (98%) were acquired from Synth and Êxodo, Brazil, respectively. Indigo Carmine (IC) (100%) was obtained from Merck, Brazil.

A typical synthesis consisted of the addition of 0.1 mL of the metal water solution to 15 mL of Glycerol. The solution was magnetic stirring for homogenization and then introduced into a homemade Teflon reactor for MW irradiation. The MW was carried out using a commercial Panasonic Microwave oven (1600 W) at high power for 130 s. After the synthesis, 1 g of the final solution was diluted with 50 mL of deionized water for fluorescence investigations.

Characterization was carried out by HRTEM, EDX, XPS, and UV-diffuse. The photocatalytic activity was evaluated by gas chromatography using a Shimadzu GC-2010 equipment with a molecular sieve 5 Å packed column. Methanol was used as hole scavenger. A high pressure Xe/Hg lamp (Sciencetech Inc. 140 W) was used for the photocatalytic experiments.[6] For the photodegradation experiments of IC aqueous solutions

(30 ppm) a quartz photochemical reactor were irradiated using a Long Wave Pass CUT-ON Filter, 400 ± 5 nm from Newport Corporation. The changes in concentrations of the dye were monitored by measuring the absorbance at 610 nm.

Results and Discussion

Figure 1 shows that the fluorescence intensity was strongly dependent on the cation type. Among the other tested cations, the PL emission was maxima when Cu^{2+} ions were used and minima for the Zn^{2+} ions. Optimization of the experimental conditions using Cu^{2+} as promoter between 0.5 mmol/L and 10 mmol/L (CuSO_4) showed a maximum PL at 2.5 mol/L. The as-prepared CQDs showed a stable PL up to 30 days that was the maximum time measured.

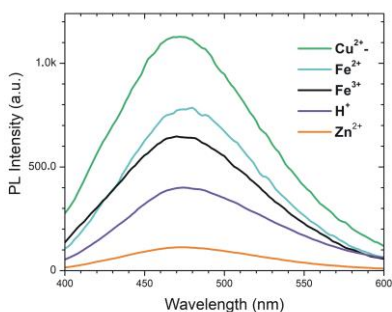


Figure 1. Fluorescence emission spectra of the CQDs solutions prepared with several cation promoters. The counterion was SO_4^{2-} in all the cases. MW irradiation time: 130 s. λ_{exc} : 390 nm.

The Cu-CQDs were characterized using HRTEM for the morphology and size distributions. The size distribution has an average diameter of 3.7 nm with nearly 50% of the CQDs with diameter equal or smaller than 2.7 nm. From the HRTEM image, the lattice fringes of CQDs represented an interplanar distance of 0.31 nm, which agrees with the (002) spacing of graphitic carbon.[7]

The EDX data show that the Cu signals are mainly originated from the CQDs suggesting that the present simple green methodology using MW can produce doped Cu-CQDs in a similar way that previous works using traditional heating methods.

UV-diffuse results show an intense absorption band at 3.2 eV that is indicative of crystalline semiconducting TiO_2 with a typical band gap of the anatase phase (3.2 eV). The TiO_2 @CQDs nanocomposite shows an additional intense absorption band in the visible light region (410 - 600 nm). The band gap energy was determined to be 1.96 eV according to Kubelka-Munk function.

Figure 2 shows the results of H_2 photogeneration on pristine TiO_2 NPs and impregnated with the Cu-doped CQDs. The H_2 evolution for TiO_2 @CQDs is about 1.5 times higher than pristine TiO_2 NPs. The inset of Figure 2 confirms the photocatalytic visible light activity ($\lambda \geq 400$ nm) of the as prepared TiO_2 @CQDs through photodegradation of the IC dye solution under only visible light irradiation.

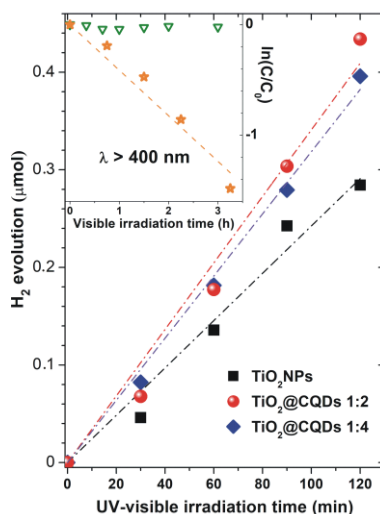


Figure 2. H_2 evolutions using TiO_2 @CQDs nanocomposites under UV-Vis irradiation. TiO_2 NPs were impregnated with Cu-doped CQDs. Inset: Photodegradation of an IC solution in the presence of TiO_2 @CQDs photocatalyst under only visible light irradiation (stars). $[\text{IC}] = 30$ ppm. The IC solution was also irradiated with only visible light in the absence of the photocatalyst (triangles).

Conclusions

Here it was demonstrated a rapid, environmentally friendly method for producing CQDs using MW irradiation with a standard commercial microwave oven. A high dielectric solvent glycerol, a by-product of the biodiesel, was used as an efficient medium for absorption of the MW radiation. The resulting CQDs exhibited a size distribution, with an average diameter of 3.7 nm. The prepared TiO_2 @CQDs nanocomposites showed photocatalytic activity for H_2 evolution and photodegradation of IC under UV-visible and only visible light irradiation, respectively. Further characterization and optimization of the CQDs using different cation promoters are currently in progress.

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-CAPES (finance code 001).

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