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**SECOND INTERNATIONAL CONFERENCE
ON ELECTRON MICROSCOPY OF
NANOSTRUCTURES**

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Carbon quantum dots-assisted CdS/TiO₂ heterojunction for photocatalytic reduction of hexavalent chromium under visible light

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In the field of photocatalysis, various semiconductor materials have been widely used, precisely because of their electronic structure, which allows them to operate under the different types of irradiations. Titanium dioxide, TiO₂, is the most widely used photocatalyst due to its biological and chemical inertness, non-toxicity, availability and affordability. Nevertheless, the inefficient utilization of visible light and high recombination rate of electrons and holes, limit its practical application. Two types of modifications have been used to improve certain properties of TiO₂ and take the advantages of the good ones: changing the phase structure, crystallinity, or morphology and combining with various ions, noble metals, semiconductors or other materials by doping, deposition, or sensitization [1,2]. In this work, sol-gel synthesized TiO₂ [3] was modified by depositing carbon quantum dots (CQD) and/or cadmium sulfide, CdS, in order to form heterojunctions and so-called "Z" scheme [4]. CQDs were deposited by decomposition of citric acid in hydrothermal conditions (sample CQD-TiO₂), and CdS by thermal decomposition of thiourea in the presence of cadmium acetate (samples CQD-TiO₂ and CQD-TiO₂-CdS).

FESEM showed that TiO₂ is formed from relatively spherical particles of different sizes, which are composed of spherical nanoparticles, whose sizes are < 50 nm (Fig. 1a). It was not possible to clearly distinguish CQD particles in the sample CQD-TiO₂ by FESEM, but the beige color of the sample indicated the presence of CQD. FESEM and EDS analyzes of the samples CQD-TiO₂ and CQD-TiO₂-CdS confirmed the presence of randomly dispersed CdS nanoparticles on the surface of TiO₂ (Fig. 1b). Diffusion reflection spectroscopy (DRS) showed that the deposition of CQD slightly increased the light absorption limit of TiO₂, but also led to additional absorption in the visible part of the spectrum (Fig. 2). CdS is considered responsible for shifting the absorption limit of TiO₂-CdS and CQD -TiO₂-CdS up to ~530 nm (Fig. 2).

The obtained photocatalysts were used for photocatalytic reduction of Cr(VI) under simulated visible irradiation, at pH = 3. As it was expected, pure TiO₂ was inactive due to the wide band gap. The photocatalytic activity of CQD-TiO₂ was improved compared to pure TiO₂, thanks to CQD that expand the range of light absorption. While studying the photocatalytic activity of TiO₂-CdS, the concentration of Cr(VI) decreased during equilibration in the dark. The presence of Cd²⁺ in the solution, determined by atomic absorption spectroscopy, indicated CdS corrosion due to low pH values, so it is possible for S²⁻ ions to reduce Cr(VI). When comparing the overall performance of the samples with CdS, CQD -TiO₂-CdS had a much smaller decrease in Cr(VI) concentration during equilibration in the dark and better photocatalytic efficiency compared to TiO₂-CdS, which can be attributed to the presence of carbon nanoparticles and probably the formation of "Z" scheme, which provides significantly higher efficiency of photocatalysts than heterojunction type II, which is formed in TiO₂-CdS. The CQD-TiO₂ and CQD-TiO₂-CdS photocatalysts represent a good basis for further research with the aim of removing harmful Cr(VI) from waste streams.

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