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Photocatalytic elimination of water pollutants using innovative titania thin film heterostructures embedding carbon quantum dots

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Abstract

Titanium dioxide based photocatalysis is a well-established advanced oxidation process (AOP) that recently has expanded its borders comprising advanced reduction processes (ARPs) as well. To enhance the photocatalytic activity, titania heterostructures embedding semiconductors, or clays, or plasmonic metals can be proposed as very promising solutions. In this study, carbon quantum dots (C-QDs) prepared hydrothermally, were successfully combined with titania (TiO_2). The photocatalytic activity of the C-QDs/TiO_2 heterostructures was successfully tested in the photocatalytic reduction of 4-nitrophenol (PNP) and hexavalent chromium (Cr^{+6}) pollutants. Moreover, the composite thin films were also effectively used in photocatalytic degradation of characteristic dye contaminants, thus confirming their high potential for photoinduced oxidation reactions. The mechanisms of the photocatalytic reactions were studied using appropriate scavengers and it was demonstrated that electrons (e^-) are at the origin of the photocatalytic reduction of Cr^{+6} and 4-NP, while holes (h^+) are the main active species for the photocatalytic oxidation reactions.

Keywords: Photocatalysis, carbon quantum dots/TiO_2 composites, Organic-inorganic pollutants degradation

1. Introduction

Photocatalysis is a broadly used technology for water purification via pollutants' degradation and is directly related to the "Advanced Oxidation Processes (AOP)". Recently, photocatalysis is also explored in advanced reduction processes (ARPs) and related technologies. Titania (TiO_2) is one of the most commonly used photocatalysts. Nevertheless, titania absorbs only a very small part of the visible electromagnetic radiation due to its large energy gap (3.2 eV) and shows a rapid recombination of electric charge carriers (electrons and holes). In addition, the morphological characteristics of the catalyst play a very important role. Titanium dioxide has a limited specific surface area, thus leading to limited adsorption capacity. For this reason, research focuses on the combination of titanium dioxide with other materials. Titania heterostructures have been proven to have a smaller energy gap, slower carrier recombination, better adsorption capacity of substances, and a larger specific surface area. In addition, it has been observed that the combination of titania with other materials (including semiconductors, clays, plasmonic metals), greatly improves its photocatalytic activity. A typical example, is the combination of titania with carbon-based nanomaterials, for application in the photocatalysis of emerging pollutants, whose presence in the aquatic environment needs be addressed urgently.

C-QDs were discovered back in 2004 when Xu *et al.* performed gel electrophoretic separation of single-walled carbon nanotubes (SWCNTs) synthesized by arc discharge methods. C-QDs have been lately used in photocatalysis, mostly in order to improve the activity of the main photocatalyst. When C-QDs are embedded in a semiconductor, they can suppress the recombination of holes with electrons, acting as electron receptors. Their addition raises the total surface area and at the same time C-QDs can help transfer the photo-generated electrons

from the surface of the semiconductor and thus prevent them from reconnecting to the holes.

In this work, carbon quantum dots were prepared via hydrothermal treatment and were combined with nanostructured TiO_2. The photocatalytic activity of the C-QDs/TiO_2 (TCD) composite was evaluated in the oxidation/degradation of Rhodamine B and methylene blue organic dyes as well as in the photocatalytic reduction of p-nitrophenol and hexavalent chromium water contaminants. Finally, trapping experiments were performed to elucidate the photocatalytic reactions' mechanism.

2. Experimental

2.1. Materials

No further purification was performed to the chemicals. Titanium (IV) n-butoxide ($C_{16}H_{40}O_4Ti$, ≥99%), potassium iodide (KI, ≥98%), benozoquinone ($C_6H_4O_2$, ≥98%), potassium bromate ($KBrO_3$, ≥98%), isopropyl alcohol (C_3H_8O, ≥98%), urea (CH_4N_2O, ≥98%) and absolute ethanol (C_2H_5OH, ≥99%) were purchased from Acros-Organics. Glacial acetic acid (CH_3COOH, ≥98%), and 1, 5- Di-phenylcarbazide ($C_{13}H_{14}N_4O$, ≥98%), Triton X-100 ($C_{16}H_{26}O_2$, ≥99%), terpineol ($C_{10}H_{18}O$, ≥98%), cellulose ethane ($C_{34}H_{66}O_{24}$, ≥99%) were all supplied from Sigma-Aldrich. Methylene blue ($C_{16}H_{18}ClN_3S$, ≥98%), sodium hydroxide (NaOH, ≥99%), and potassium dichromate ($K_2Cr_2O_7$, 98%) were obtained from Fluka, while Rhodamine B ($C_{28}H_{30}N_2O_3$, ≥98%), sodium sulfate (Na_2SO_4, ≥99%), and 4-nitrophenol ($C_6H_5NO_3$, ≥98%) from Merck. Hydrochloric acid (HCl, 37%), and absolute acetone (C_3H_6O, ≥99%) were supplied from Riedel-de Haen. Nafion perfluorinated ($C_7HF_{13}O_5S.C_2F_4$, ≥98%), Potassium hydroxide (KOH, ≥99%), and potassium chloride (KCl, ≥99%) were purchased from Chem-Lab.

2.2. Synthesis of the photocatalytic films

The reference titania photocatalytic films (short name: T) were developed onto conductive FTO glass substrates. Firstly, a compact layer of TiO_2 was prepared using sol-gel technique. 3.6 mL titanium (IV) isopropoxide, 6.8 mL CH_3COOH, 38.0 mL EtOH and 7.0 g of Triton X-100 were mixed and stirred for about 5 min. For the sol-gel deposition, the FTO substrates were immersed vertically into the sol solution for a few seconds and were then thermally treated calcinated at 550 ^oC for 30 min. The same procedure was repeated 4 times. For the mesoporous layers, 3.0 g of Degussa P25 powder was grinded by adding 0.5 mL of CH_3COOH and 1.5 mL of DI water. Afterwards, 17.5 mL of EtOH were progressively added with continuous grinding. The above mixture was transferred to a round-bottomed flask, with addition of 50 mL of EtOH, followed by stirring in an ultrasonic bath. After that, 10.0 g of terpineol and 2.8 g of 10% v/v ethyl cellulose ethane solution were added, followed by stirring in an ultrasonic bath. For the reference samples, the above mentioned solution was first dispersed in EtOH in a 1:1 ratio, and then the deposition was held performed on the compact layer TiO_2 by the doctor blade technique, followed by annealing at 550^{o}C for 30 min. This process was also repeated 4 times.

For preparing the composite TiO_2/C-QDs photocatalytic film (short name: TCD), firstly C-QDs were synthesized via a simple hydrothermal method. 3g of citric acid were mixed with 3g of urea and dissolved into 10 mL of DI water. The mixture was stirred and placed in a Teflon-lined autoclave inside a microwave radiation reactor system. The pressure was defined up to 40 bar, microwave radiation energy 800 Watt, temperature 200^{o}C and time interval 15 min. The C-QDs solution was purified via centrifugation at 6000 rpm and simple filtration. Thus, the precipitate was removed, while the supernatant solution of C-QDs was mixed with acetone. The obtained sediment was dissolved in EtOH and stored. The final C-QDs solution was mixed with the Degussa P25 solution in a 1:1 ratio, in order prepare mesoporous photocatalytic films of the composite TiO_2/C-QDs materials. The exact preparation process remained the same as the one of the reference film.

2.3. Photocatalytic oxidation/ reduction experiments

The photocatalytic activity of the reference (T) and composite films (TCD) was examined by the photocatalytic reduction of Cr^{6+} (5 mg/L) and p-nitrophenol (4-NP) (10 mg/L), and the photocatalytic oxidation of the organic dyes, methylene blue (MB) (5 mg/L) and Rhodamine B (RhB) (4 mg/L). The photocatalysts were placed in 10 mL aqueous solution of each of the pollutants, until adsorption-desorption was achieved after one hour. Next, UV-A illumination was employed for 2 hours by 4 UV-A Sylvania lamps (350-390 nm, 0.5 mW cm^{-1}). Every 30 minutes the pollutants' concentration was measured with a UV/Vis Hitachi 3010 spectrophotometer. In the case of Cr^{6+}, the colorimetric technique based on the diphenylcarbazide (DCP) metal ion indicator was applied.

In order to distinguish the photocatalytic oxidation-reduction mechanism of MB, Rh-B, Cr^{+6} and 4-NP pollutants under UV light illumination, trapping experiments were carried out. Thus, four different scavengers were selected and added into the pollutants' solutions: benzoquinone (BQ – 1 mM) as $O_2^{\cdot-}$ quencher, potassium bromate ($KBrO_3$ – 10 mM) as e^- quencher, potassium iodide (KI – 10 mM) as h^+ quencher and isopropyl alcohol (IPA – 10 mM) as $OH^{\cdot}$ quencher.

3. Results and discussion

The photocatalytic activity of the prepared photocatalytic films was examined through the reduction of the toxic Cr^{6+} and 4-NP to non-toxic Cr^{3+} and 4-AmP, respectively and through the oxidation of the azo-dye MB and the dye RhB.

The results of the pollutants' photocatalytic reduction, as well as those of the trapping experiments for reduction are presented in Figure 1. The removal efficiencies of pollutants with the utilization of the synthesized films (T

and TCD) are summarized in Table 1. It is obvious that the composite photocatalyst containing C-QDs demonstrated enhanced photocatalytic activity in comparison to the reference photocatalyst. Reasonably, the C-QDs assist in better charge carrier's separation. To determine which reactive species are responsible for the photocatalytic reduction, e^- or $O_2^{\bullet-}$, photocatalytic trap experiments (scavenger tests) were carried out for Cr^{6+} in the presence of BQ and $KBrO_3$. As shown in Figure 1c, chromium reduction efficiency remained unaffected in the presence of the BQ, while the photocatalytic reduction was prevented when the $KBrO_3$ was added in the solution. Based on the mentioned results, it is proved that the reactive species responsible for the Cr^{6+} photocatalytic reduction were the photogenerated electrons (e^-).

Additionally, the results of the photocatalytic oxidation of dyes and the trapping experiments are demonstrated in Figure 2. It is clear that in case of MB oxidation TCD demonstrated remarkably improved dye adsorption during the dark conditions, implying more available surface. As regards the degradation of RhB, the enhancement of the photocatalytic performance was obvious for TCD. Trap experiments in MB degradation revealed that the reactive species for the photocatalytic oxidation were the holes (h^+), as the photocatalytic activity was suppressed with the addition of KI scavenger.

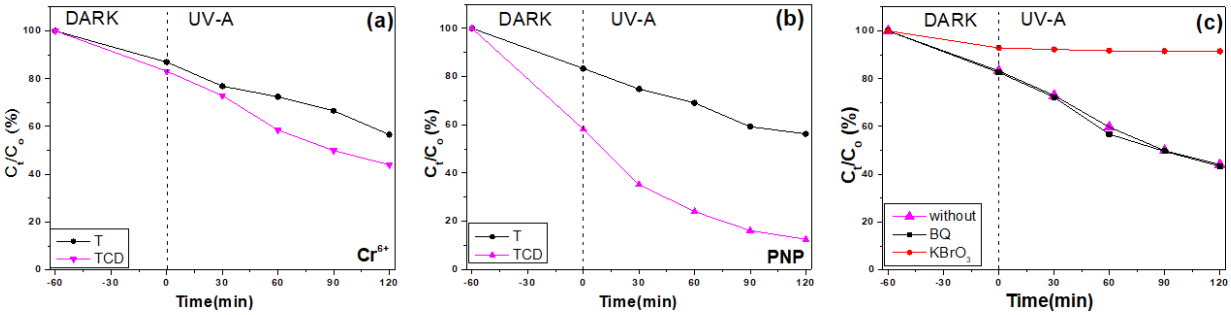

Figure 1. Photocatalytic degradation of Cr^{+6} (a) and 4-NP (b) under UV light irradiation using the developed photocatalysts; Effect of scavengers on photocatalytic reduction of Cr^{6+} during the trapping experiments of TCD (c).

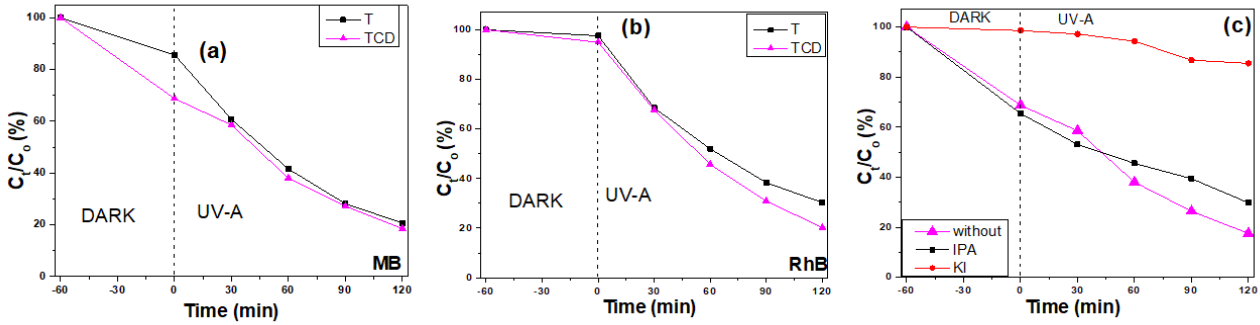

Figure 2. Photocatalytic degradation of MB (a) and RhB (b) under UV light irradiation using the developed photocatalysts; Effect of scavengers on photocatalytic oxidation of MB during the trapping experiments of TCD (c).

Table 1. Removal efficiency of pollutants with the utilization of the synthesized films

	Removal efficiency (%)			
Samples	**Cr^{6+}**	**4-NP**	**MB**	**RhB**
T	43.39	43.76	79.33	69.68
TCD	55.97	87.53	81.49	79.78

4. Conclusion

In this study, thin films of titania composites with carbon quantum dots (C-QDs) were synthesized. The photocatalytic activity of the composites was evaluated in the oxidation of MB and RhB dyes and in the reduction of hexavalent chromium and p-nitrophenol, respectively. The TCD photocalyst demonstrated enhanced adsorption and significant photocatalytic activity attributed to the C-QDs addition. Trapping experiments were carried out to elucidate the reactions' mechanism, proving that the photogenerated holes (h^+)

were responsible for oxidation reactions and the photoelectrons (e^-) for reduction reactions, respectively.

References

Han F., Kambala V.S.R., Srinivasan M., Rajarathnam D., Naidu R. (2009), Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review, Applied Catalysis a-General, **359**, 25-40.

Wang M.Y., Iocozzia J., Sun L., Lin C.J., Lin Z.Q. (2017), Inorganic-modified semiconductor TiO_2 nanotube arrays for photocatalysis, Energy & Environmental Science, **10**, 2041-2041.

Stylidi M., Kondarides D.I., Verykios X.E. (2004), Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO_2 suspensions, Applied Catalysis B-Environmental, **47**, 189-201.

Ibrahim I., Ali I.O., Salama T.M., Bahgat A.A., Mohamed M.M. (2016), Synthesis of magnetically recyclable spinel ferrite (MFe_2O_4, M = Zn, Co, Mn) nanocrystals engineered by sol gel-hydrothermal technology: High catalytic performances for nitroarenes reduction, Applied Catalysis B-Environmental, **181,** 389-402.

Athanasekou C.P., Likodimos V., Falaras P. (2018), Recent developments of TiO_2 photocatalysis involving advanced oxidation and reduction reactions in water, Journal of Environmental Chemical Engineering, **6** , 7386-7394.

Xu X., Ray R., Gu Y. (2004), Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments," Journal of the American Chemical Society, 126, **40**, 12736-12737.

Ibrahim I., Athanasekou C. P., Manolis G., Kaltzoglou A., Nasikas N.K., Katsaros F., Devlin E., Kontos A.G., Falaras P. (2019), Photocatalysis as an advanced reduction process (ARP): The reduction of 4-nitrophenol using titania nanotubes-ferrite nanocomposites, Journal of Hazardous Materials, **372**,37-44.

Ibrahim I., Belessiotis G.V., Arfanis M.K., Athanasekou C. P., Philippopoulos A.I., Mitsopoulou C.A., Romanos G.E., Falaras P. (2020) , Surfactant Effects on the Synthesis of Redox Bifunctional V_2O_5 Photocatalysts, Materials, **13**, 4665.

Zhou W., Pan K., Qu Y., Sun F.F., Tian C.G., Ren Z.Y., Tian G.H., Fu H.G. (2010), Photodegradation of organic contamination in wastewaters by bonding TiO_2/single-walled carbon nanotube composites with enhanced photocatalytic activity, Chemosphere, **81**, 555-561.

Martinez C., Canle M., Fernandez M.I., Santaballa J.A., Faria J. (2011), Kinetics and mechanism of aqueous degradation of carbamazepine by heterogeneous photocatalysis using nanocrystalline TiO_2, ZnO and multi-walled carbon nanotubes-anatase composites, Applied Catalysis B-Environmental, **102**, 563-571.

Li Y., Cui W.Q., Liu L., Zong R.L., Yao W.Q., Liang Y.H., Zhu Y.F. (2016), Removal of Cr(VI) by 3D TiO_2-graphene hydrogel via adsorption enriched with photocatalytic reduction, Applied Catalysis B-Environmental, **199**, 412-423.

Zhang H., Zhao L.X, Geng F.L., Guo L.H., Wan B., Yang Y (2016), Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation, Applied Catalysis B-Environmental, **180**, 656-662.

Ji H.D., Du P.H., Zhao D.Y., Li S., Sun F.B., Duin E.C., Liu W. (2020), 2D/1D graphitic carbon nitride/titanate nanotubes heterostructure for efficient photocatalysis of sulfamethazine under solar light: Catalytic "hot spots" at the rutile-anatase-titanate interfaces, Applied Catalysis B-Environmental, **263**.

Zhang J.J., Kuang M., Wang J., Liu R.R., Xie S., Ji Z.J. (2019), Fabrication of carbon quantum dots/TiO_2/Fe_2O_3 composites and enhancement of photocatalytic activity under visible light, Chemical Physics Letters, **730**, 391-398.

Arfanis M.K., Adamou P., Moustakas N.G., Triantis T.M., Kontos A.G., Falaras P. (2017), Photocatalytic degradation of salicylic acid and caffeine emerging contaminants using titania nanotubes, Chemical Engineering Journal, **310**, 525-536.

Papoulis D., Panagiotaras D., Tsigrou P., Christoforidis K.C., Petit C., Apostolopoulou A., Stathatos E., Komarneni S., Koukouvelas I. (2018), Halloysite and sepiolite -TiO_2 nanocomposites: Synthesis characterization and photocatalytic activity in three aquatic wastes, Materials Science in Semiconductor Processing, **85**, 1-8.

Ibrahim I., Kaltzoglou A., Athanasekou C., Katsaros F., Devlin E., Kontos A.G., Ioannidis N., Perraki M., Tsakiridis P., Sygellou L., Antoniadou M., Falaras P. (2020), Magnetically separable TiO_2/$CoFe_2O_4$/Ag nanocomposites for the photocatalytic reduction of hexavalent chromium pollutant under UV and artificial solar light, Chemical Engineering Journal, **381**.

Antoniadou M., Arfanis M.K., Ibrahim I., Falaras P. (2019), Bifunctional g-C_3N_4/WO_3 Thin Films for Photocatalytic Water Purification, Water, **11**.

Shammi Z.M., Kianfar A.H., Momeni M.M. (2020), Hydrothermal synthesis and characterization of CuO-CoO/TiO(2)for photocatalytic degradation of methylene blue under visible light and catalytic reduction of P-nitrophenol, Journal of Materials Science-Materials in Electronics, **31**, 14810-14822.

Mishra G., Mukhopadhyay M. (2019), TiO_2 decorated functionalized halloysite nanotubes (TiO2@HNTs) and photocatalytic PVC membranes synthesis, characterization and its application in water treatment, Scientific Reports, **9**.