Wet synthesis of nitrogen modified TiO₂. Visible light absorption is not always related to N-doped TiO₂.

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It was found that urea modification of TiO₂ at 450 °C led to the generation of $g-C_3N_4/TiO_2$ type II heterojunctions containing, in addition, single-electron trapped oxygen vacancies (SETOV, V_o) and Ti³⁺ species all responsible for visible light absorption. On the other hand, ammonia-modified TiO₂ may lead, at 450°C, to generating NO-TiO₂ surface complexes and V_o as responsible for visible light absorption. In contrast, at 550°C, a high content of V_o would exclusively be responsible for light harvesting. By ESR-spin trapping, it was found that all the synthesized materials exhibited photogeneration of 'OH radicals only under UV irradiation, and their photocatalytic activity was evaluated under UV- and blue-LED irradiation in the discoloration malachite green (MG) solutions.

Introduction

Even today, it continues to appear in the literature studies claiming the synthesis of N-doped TiO₂ by sol-gel method using urea and ammonia as precursors [1]. For this reason, the main objective of this study is to attempt to demonstrate the formation of heterojunctions, defective TiO2 surfaces, or surface complexes instead of N-doping in nitrogenmodified-TiO₂ when it is synthesized by the sol-gel method using ammonia and urea as precursors. For this purpose, deep characterization of materials through techniques such as DRS, XPS, HR-TEM, and low temperature (77 K) electron spin resonance spectroscopy (ESR) was achieved. The photocatalytic activity was evaluated using UV- and blue-LEDs in the discoloration of malachite green (MG) aqueous solutions. All these physicochemical features, photocatalytic activity, and ESR-spin trapping measurements offer strong insights into the advantages and limitations of these modified TiO2 materials in photocatalytic applications.

Material and Methods

Materials were synthesized using the hydrolysis of titanium tetraisoproxide in acidic media and adding urea and ammonia (30%wt.). Further annealing under air atmosphere was carried out at 450 and 550°C, respectively, obtaining materials called U-TiO₂-450, U-TiO₂-550, A-TiO₂-450, and A-TiO₂-550, Characterization was achieved using DRS, XPS, FTIR, HR-TEM, and EPR techniques. The photocatalytic activity was evaluated in the discoloration of MG (1x10⁻⁴ M) under UV-LED and blue-LED illumination for 2h under continuous magnetic stirring and controlled temperature (25°C).

Samples were withdrawn at different times, filtered by PTFE filters (0.22 μ m), and evaluated by UV-vis spectroscopy at 617 nm.

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Results and Discussion

Urea-modified TiO₂ exhibited visible light absorption and the presence of SETOV and Ti³⁺ species (EPR g-factors at 1.996 and 1.974, respectively). It was also found evidence of g-C₃N₄ by HR-TEM and EPR (signal at g-factor 2.004) (Figure 1).

The ammonia-modified materials showed visible light absorption. XPS N 1s signals were compatible with NO species in the surface (Figure 2b), while the Ti 2p spectrum of material A-TiO₂-550 showed a shoulder at BE of 457.8 eV due to Ti³⁺ species (Figure 2c). EPR spectra at 77 K (Figure 2d) confirmed the presence of these species (signals with a g-factor of 1.994).

Regarding the photocatalytic activity), under UV-LED irradiation (Figure 3), urea-modified materials negatively affected the photocatalytic activity since U-TiO₂-450 and U-TiO₂-550 showed an MG aqueous solution discoloration of around 50%. The A-TiO₂-450 material showed a similar photocatalytic behavior to unmodified TiO₂ calcined at 450 °C (TiO₂-450). On the other hand, a different behavior was observed under blue LED irradiation. The U-TiO₂-450 sample exhibits the highest MG solution discoloration.

ESR-spin trapping measurements using α -4-pyridyl 1-oxide N-tert-butyl nitrone (4-POBN) as a probe for 'OH radicals (Figure 4) showed the presence of POBN-OH adduct only under UVA irradiation.



Figure 1. (a) DRS and (b) FTIR spectra of urea-modified TiO₂. (c) HR-TEM micrograph of U-TiO₂-450 and (d) EPR spectrum of urea-modified TiO₂ taken at 77 K.



Figure 2. (a) DRS and (b) XPS N 1s spectra of ammoniamodified TiO₂. (c) Ti 2p XPS spectrum of A-TiO₂-550 sample and (d) EPR spectrum of ammonia-modified TiO₂ taken at 77 K.



Figure 3. Photocatalytic activity of urea- and ammonia- TiO_2 materials (1g L⁻¹) under (a) UV-LED irradiation (320 nm) (b) Blue-LED irradiation (420 nm). Initial pH 5.0.





We concluded that urea-modified TiO₂ nanopowders produced mainly g-C_3N_4/TiO_2 composites, which may generate type II heterojunctions. These negatively heterojunctions affect can the photocatalytic activity of the materials under UV irradiation since the photoinduced holes and electrons remain on the VB $(g-C_3N_4)$ and CB (TiO_2) , with the lowest oxidative and reductive potential, respectively. Oxygen vacancies in these materials would produce a detrimental effect on the photocatalytic activity of this type II heterojunction serving as recombination centers. Ammonia-modified TiO₂ nanopowders showed a

Animonia-induited TiO₂ handpowders showed a different behavior. At 450°C, the partial oxidation of ammonia may lead to the formation of surface NO-TiO₂ complexes [2] and color centers responsible for visible light absorption. In contrast, at 550°C, the generation of color centers (F, F⁺, and F⁺⁺) and Ti³⁺ species would be responsible for the visible light harvesting. The photogeneration of 'OH radicals in these materials may be exclusively due to the UV-photoinduced holes in the VB of TiO₂. The high amount of color centers in the ammonia-modified TiO₂ material annealed at 550°C caused a detrimental effect on its photocatalytic activity.

Conclusions

Urea- and ammonia-modified TiO_2 showed the formation of $g-C_3N_4/TiO_2$ heterojunction and surface modifications instead of nitrogen doping as responsible for visible light absorption and photocatalytic activity.

References

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