

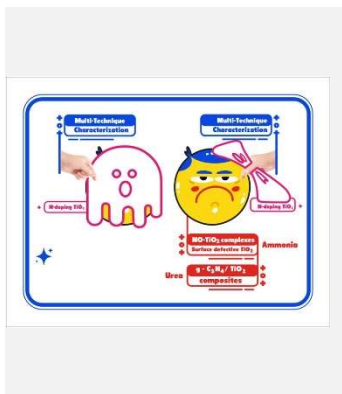
Wet synthesis of nitrogen modified TiO₂. Visible light absorption is not always related to N-doped TiO₂.

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It was found that urea modification of TiO₂ at 450 °C led to the generation of g-C₃N₄/TiO₂ 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 nitrogen-modified-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 tetraisopropoxide 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 μm), and evaluated by UV-vis spectroscopy at 617 nm.

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 nitron (4-POBN) as a probe for [•]OH radicals (Figure 4) showed the presence of POBN-OH adduct only under UVA irradiation.

