

Enhanced Photocatalytic Degradation of Emerging Contaminants on Copper–Nitrogen Modified Titania

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Abstract Current economic growth is based on intensive industrial activity which is inevitably producing high quantities of wastes that also affect the water reservoirs. In order to reduce the consequences of this contamination, scientific efforts are focused on advanced water purification processes, including photocatalytic treatment based on titanium dioxide nanostructures. Herein, the development of innovative photocatalysts consisting of titania modified by both copper and nitrogen (N–Cu/TiO₂) was investigated. These mixed (anion–cation) modified TiO₂ nanostructures prepared using a combustion sol–gel synthesis, were first characterized with XRD, EDX, UV/vis, Raman, and FTIR techniques. The analysis confirmed that N–Cu/TiO₂ is well crystalized in the anatase phase, while the non-detection of copper compounds in XRD spectra is attributed to the existence of well dispersed copper oxide nanoparticles onto the surface of the catalyst. The evaluation of the photocatalytic properties was performed under UV light irradiation using two emerging contaminants, caffeine and salicylic acid, frequently detected in municipal wastewaters. Based on the experimental results, copper loading influences the photocatalytic process and enhances the final degradation efficiency, compared to the reference material (N/TiO₂). An optimum copper loading value was determined and the results are compatible with a photocatalytic mechanism implying more efficient light absorption and/or reduced recombination of the photogenerated carriers.

Keywords: Titanium dioxide photocatalysis; copper–nitrogen modification; caffeine; salicylic acid; water treatment.

1. Introduction

The current industrial development is accompanied by rapid increase of environmental pollution (water, air, soil). In an attempt to face the acute problem of emerging water contaminants and its negative consequences to ecosystem (human beings, animals, plants, etc.), a number of innovative scientific strategies have been adopted, including, homogenous and heterogeneous catalysis and/or ozonation. Among the developed treatment technologies, heterogeneous photocatalysis using various semi-conductive metal oxides is an effective and promising approach for the environmental purification of

water and air. The main mechanism of this advanced oxidation process (AOP) is based on the illumination of the semi-conductive metal oxide with light of appropriate wavelength. When the light energy matches the energy gap of the semiconductor, electron/hole (e^-/h^+) pairs are created under illumination at the conduction (CB) and valence bands (VB), respectively. The photogenerated charge carries can react with the adsorbed H₂O (or OH⁻) and O₂ molecules on the semiconductor's surface to form OH[•] and O₂^{•-} radicals. These short-lived but highly reactive radicals are responsible for the pollutants degradation (Banerjee *et al.*, 2015).

The most widely studied photocatalyst is titanium dioxide semiconductor (TiO₂), because of its unique properties: high photo-activity, low cost, low toxicity and good chemical and thermal stability. Nevertheless, the practical application of titania is limited mainly due to charge carries recombination and restricted absorption (only in the UV region) of solar light. In order to overcome these drawbacks and improve the photocatalytic performance, many modification and doping techniques with anions (non-metal elements) and/or cations (metal elements) during the synthetic procedure are developed (Pelaez *et al.*, 2012). Nitrogen, fluorine, carbon or sulphur precursors are the most usual non-metal reagents for the modification of titania nanostructures. It is generally accepted that modification with nitrogen is producing the most efficient TiO₂ photocatalysts with visible light activated (VLA) properties. In case of metal modification, many transition metals have been examined. The exact choice of metal is based not only on the desired structural and optical properties of the final material, but also on the examined application. For example, modification of TiO₂ with copper significantly enhances the photo-conversion efficiency of CO₂ (reduction) to hydrocarbons (Olivo *et al.*, 2015). Last, the co-modification of titania materials with both anion and cation is expected to be even more effective due to synergistic effects, as both foreign ions might narrow the TiO₂ band gap. Furthermore, metal ions could improve the charge carrier separation, resulting to an improved generation of reactive oxygen species (Su *et al.*, 2016).

2. Objectives

In this work the co-modification of titania materials with copper and nitrogen during the synthetic process was investigated, so as the evaluation of their photocatalytic properties. During synthesis the copper content was varied from 0.01% to 3.0% wt. among the synthesized materials, while the quantities of nitrogen were kept constant. After structural and morphological characterization, the photocatalytic degradation against two frequently detected emerging contaminants in wastewaters, caffeine and salicylic acid, was evaluated. The growth conditions were tuned in order to prepare co-modified materials with improved photocatalytic performance compared to the reference materials, TiO_2 and N/TiO_2 .

3. Experimental

The synthesis of innovative N-Cu/TiO_2 semiconductors was performed by a facile combustion sol-gel technique, based on previous study of our group (Kontos *et al.*, 2008). First 7.5 ml of Titanium (IV) butoxide (TBOT – Aldrich 97%) were added dropwise into 50 mL of HNO_3 acidified aquatic solution. When TBOT was completely dissolved, appropriate quantities of copper nitrate ($\text{Cu(NO}_3)_2 \bullet 3\text{H}_2\text{O}$ – Scharlau 99.5%) were added. After 4 hours of vigorously stirring, this emulsion was turned to transparent solution with the addition of n-propanol and left overnight under stirring to become homogenized. Subsequently, 15 g of urea (Acros –99.5%) were added as the nitrogen source. Finally the solution was gradually dried at 100 °C and calcined at 400 °C for 2 hours. After calcination, TiO_2 was first pulverized to fine powder and then the excess organic species were removed from the surface under consecutive washings with deionized water. The color of the catalysts was yellowish for the samples with less copper addition, and turned dark green for samples with higher copper content. The modified samples are denoted as N-Cu/TiO_2-x , where x is equal to the mass percentage (% wt.) of copper to TBOT. A similar procedure was followed for the preparation of the reference materials: TiO_2 without addition of copper nitrate and urea, and N-TiO_2 without the addition of copper nitrate.

The absorbance spectra of the samples were obtained by a UV-Vis Hitachi 3010 spectrophotometer, equipped with an integrating sphere accessory and BaSO_4 as reference.

In order to evaluate the crystallinity of the formed samples, XRD analysis was conducted, using a Siemens D-500 diffractometer, which operates with $\text{Cu K}_{\alpha 1}$ ($\lambda = 1.5406 \text{ \AA}$) and $\text{Cu K}_{\alpha 2}$ ($\lambda = 1.5444 \text{ \AA}$) radiation, and a Micro-Raman analysis, using a Renishaw inVia Reflex microscope equipped with a solid state laser excitation source emitting at 514.4 nm.

Additional FTIR and EDX measurements were performed using a Thermo Scientific Nicolet 6700 FTIR with N_2 purging system and a FEI Quanta-Inspect scanning electron microscope coupled with energy-dispersive X-ray spectrometer (SEM/EDAX), respectively.

The photocatalytic activity of the synthesized materials was evaluated by monitoring the degradation of two emerging contaminants, caffeine (CA –15 ppm) and salicylic acid (SA – 17 ppm) under UV-A illumination. In

a typical photocatalytic experiment 10 mg of photocatalyst was stirred in 10 ml of pollutant under dark until adsorption – desorption equilibrium, into a lab-made photoreactor. UV irradiation was provided by four UV-A lamps (Sylvania 15W/BLB, $\sim 0.5 \text{ mW cm}^{-2}$), placed at a distance of 15cm from the samples.. After certain periods, the catalyst was separated from the suspension by centrifugation and the supernatant solution was measured with the UV-vis spectrophotometer in order to determine the pollutants' decomposition rate by the intensity of their characteristic absorption peak (273 nm for CA and 296 nm for SA). Each experimental point in the respective graphs corresponds to a new photocatalytic run.

4. Results and Discussion

The structural characterization with X-rays diffraction revealed that the main crystal phase was anatase (101) for all the synthesized materials. Compared to the reference TiO_2 , the addition of urea suppressed the formation of brookite phase. Small quantities of Rutile (110) were remained, but the weight fraction was less than 6%. Copper and/or copper oxides were not detected in the XRD patterns. Calculations of the unit cell dimensions showed no distortions, so copper is not expected to occupy any interstitial lattice sites in the TiO_2 crystal structure. Results from Raman characterization were in agreement with the XRD results, as anatase was the main phase of TiO_2 , with no characteristic peaks of any copper related compounds. The existence of copper into the samples was confirmed by the EDX technique. The calculated atomic ratio of copper (at%) was in accordance to the inserted quantities of copper nitrate into the precursor solutions, indicating dispersed copper formations in the internal and external crystal matrix of the catalyst. For example the atomic ratio for $\text{N-Cu/TiO}_2-0.3$ was equal to 0.31%. Furthermore, the non-detection of any copper compounds with XRD and Raman techniques, even if for the highest precursor concentrations, suggests that the copper additives probably formed well dispersed nanosized particles.

The study of optical properties revealed significant differences among the modified samples with different copper content. Based on previous studies, urea's incomplete combustion from TBOT oxidizer during calcination forms a nitrogen-rich carbonaceous shell layer onto the TiO_2 surface (Mitoraj *et al.*, 2010), which acts as a visible light active photosensitizer up to $\sim 500 \text{ nm}$. Samples with copper content below 0.15% wt. present identical optical properties (fig.1a). However further increment of copper content up to 3% wt. resulted in decrease of visible light absorption in the blue range and emergence of a copper oxide absorbance band above 600 nm (Colon *et al.*, 2006), as is depicted in fig.1b. High amounts of copper might act as extra oxidizer of urea during calcination, so the combustion leaves less carbonic residuals onto TiO_2 surface. Indeed, indicative FTIR spectra support this hypothesis, as the characteristic C-C, C-N and C-O vibrational modes of the organic layer bonded on TiO_2 which are observed in the 2100 to 2000 cm^{-1} range for N/TiO_2 (Moustakas *et al.*, 2013) tend to be diminished for the N-Cu/TiO_2-x samples. It is worth noting that these

reduced intensities are inversely proportional with the increment of copper content.

Before carrying out the UV photocatalytic experiments, we first verified the contaminants photostability under the tested conditions in absence of the photocatalyst (Arfanis *et al.*, 2017). Additional preliminary experiments were performed in the absence of light in order to validate any adsorption phenomena of CA or SA on the surface of the catalysts.

In order to examine the photocatalytic degradation kinetics of CA for each sample, four photocatalytic runs were performed, corresponding to every thirty minutes for a total period of two hours (fig 2a). The reference materials TiO_2 and modified N/TiO_2 degraded almost 30% and 65% of CA, respectively, so the addition of nitrogen established the enhanced photocatalytic properties of TiO_2 . The photocatalytic performance of the co-modified samples with copper and nitrogen showed remarkable variations with the amount of copper precursor. The photocatalysts with copper content up to 0.15% wt. were more efficient than the reference N/TiO_2 , whereas the $\text{N}-\text{Cu}/\text{TiO}_2-0.06$ showed the best performance (equal to 77% removal). The photocatalysts remained active up to $\text{N}-\text{Cu}/\text{TiO}_2-0.6$, even though they were less efficient than the reference N/TiO_2 . Further increase of the mass percentage of copper resulted in materials becoming photocatalytically inactive.

The photocatalytic degradation rates of SA were also examined by performing four one-hour photocatalytic

experiments (fig 2b). The efficiencies showed similar tendencies, as in the case CA. The modification of TiO_2 , either with nitrogen, or with nitrogen and copper, leads to enhanced degradation rates, up to an optimum concentration level. The best performance was observed for copper loading equal to 0.09% wt. Above this mass content percentage the photocatalytic performance was gradually decreased and the materials were practically inefficient for the degradation of SA compared to $\text{N}-\text{Cu}/\text{TiO}_2-0.09$.

5. Conclusions

Innovative photocatalysts of $\text{N}-\text{Cu}/\text{TiO}_2$ with different copper content (from 0.01 wt. till 3.0 wt.) were prepared by a simple combustion sol-gel method. The synthesized nanostructures were mainly consisted by the anatase crystal phase, with no evidence of impurities incorporated into the titania lattice. Through co-modification, absorption of light expanded in the visible range of the solar spectrum, mostly evident for samples with copper content from 0 to 0.15% wt. The optimized materials were evaluated for their photocatalytic activity against two frequently detected contaminants in wastewater, caffeine and salicylic acid. $\text{N}-\text{Cu}/\text{TiO}_2-0.06$ was found the most efficient catalyst against caffeine and $\text{N}-\text{Cu}/\text{TiO}_2-0.09$, against salicylic acid. Copper content above 0.3% wt. deteriorated the photocatalytic performance in both cases.

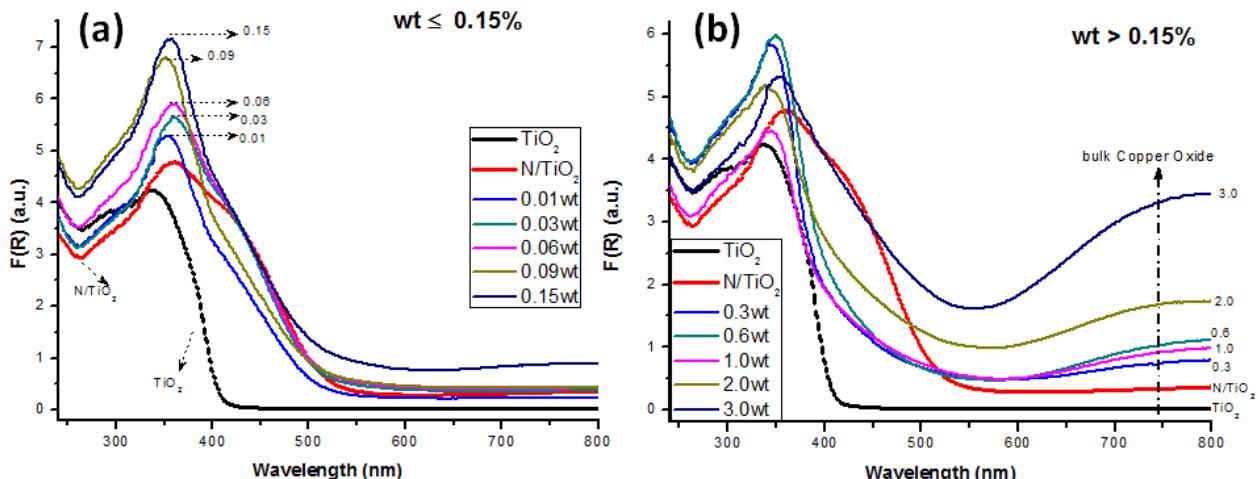


Figure 1. Absorption spectra of $\text{N}-\text{Cu}/\text{TiO}_2-\text{x}$, where $\text{x} \leq 0.15\%$ wt. (a) or $\text{x} > 0.15\%$ wt. (b).

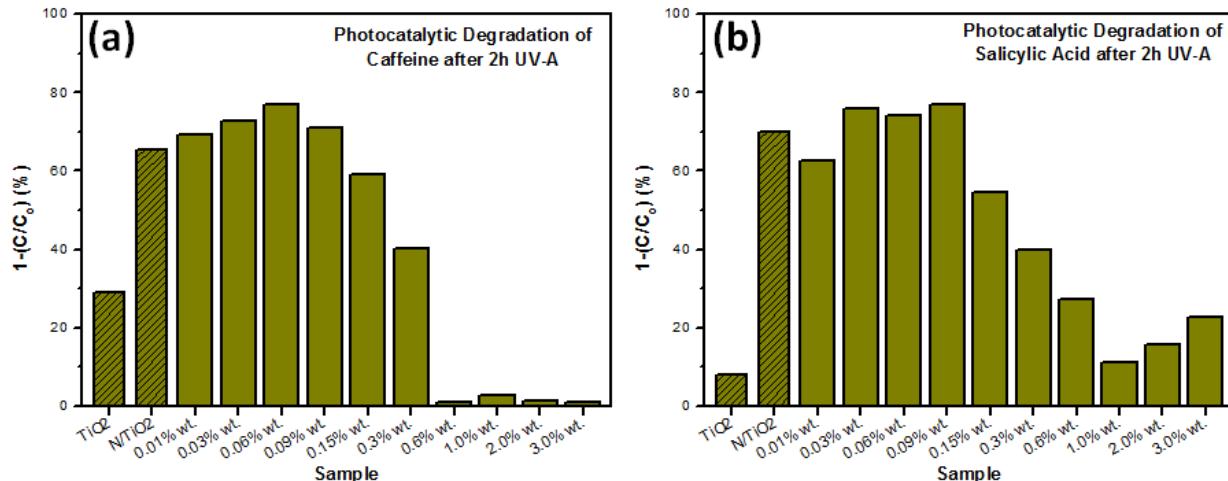


Figure 2. Photocatalytic removal efficiency of caffeine (a) and salicylic acid (b).

Based on these results, it is assumed that the co-modification approach enhances the efficiency of the photocatalysis process due to synergistic effects between the cationic and anionic additives. Both copper and nitrogen contributed to the decrement of TiO₂ band gap. Moreover introduction of copper, until an optimum amount, enhanced the separation of the photogenerated charge carriers. Above that level, photocatalysis was hindered because copper might act as center for recombination of the charge carriers.

The N–Cu/TiO₂ materials could be suitable candidates for various applications, including visible light photocatalysis, CO₂ photocatalytic conversion to hydrocarbons or the development of hybrid photocatalytic – filtration technologies. For this reason, the materials must be further characterized with more sophisticated spectroscopic techniques, such as XPS, EPR, TEM etc., in an effort to fully understand the synergistic effects between the anionic/cationic additives and how this relates to the enhancement of their photocatalytic activity.

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