11TH INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
OTEH 2024
Serbia, Tara, 9-11 October 2024

Cu -DECORATED TIO_2 NANOPARTICLES AS THE PHOTOCATALYTIC MATERIAL FOR CIPROFLOXACIN DEGRADATION

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Abstract: *Efficient removal of antibiotic residues from the water using environmentally friendly and zero-waste technologies represents an emerging challenge. The increasing development of photocatalytic materials needs a comprehensive and systematic approach to understand the principles behind their performance. In this contribution, the Cu-decorated TiO_2 nanoparticles were prepared using various input amounts of Cu (0.5 – 2%), employed for photocatalytic degradation of ciprofloxacin solution (30 mg photocatalyst per 50 mL of solution), and compared to bare TiO_2 at the same concentration. The observed performance improvement of investigated photocatalytic material compared to bare TiO_2 upon decoration with Cu was discussed from various aspects. Some of them include: morpho-structural changes (increase of active surface for photocatalysis upon reduced agglomeration), chemical effects (the improved generation and reactivity of active oxygen species upon modification of their adsorption properties), and modification of photochemical properties of the semiconductor material itself (impact of metal decoration on the band gap structure).*

Keywords: *Rutile TiO_2; Photocatalysts; Degradation.*

1. INTRODUCTION

Environmental water pollution by antibiotics from households, farms, and hospitals represents an emerging concern worldwide. Ciprofloxacin (CIP), a synthetic fluoroquinolone derivative, is among the most frequently used medication for human treatment, which is stable, difficult to decompose and resistant to common water treatments [1,2]. There are many articles that include oxidation of ciprofloxacin by ozonation, electrochemical oxidation, Fenton reagent, and photocatalytic degradation with UV light using a different semiconducting- and nanomaterials [3,4]. Main disadvantages of current photocatalytic degradation include: limitations to laboratory-size use fast charge recombination, limited ability of photo-generated electrons and holes to migrate, and potential toxicity of byproducts [5]. On the other hand, the rapid progress in developing novel materials is expected to help overcoming these difficulties.

The correlation between fundamental material properties and its catalytic performance has been of persisting interests in investigation of the photocatalyzed processes. The simultaneous use of experimental and theoretical approach contributes to the multi-level understanding of the materials performace, from the chemical and electronic properties to the application level and the possibility to predict catalytic performance of the materials that are not synthesized yet.

This contribution deals with TiO_2 decorated by Cu deposition onto its surface, which was applied to degrade ciprofloxacin photocatalytically in an aqueous solution. The prepared photocatalysts was characterized by XRPD and SEM analysis, and the ciprofloxacin degradation was monitored by UV-Vis spectrometry. The DFT analysis of OH radical binding on photocatalyst model surfaces has revealed the correlation between catalytic improvement and the chemical properties of the photocatalyst materials.

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DOI: 10.5937/OTEH24100K

2. METHODS

2.1. TiO_2 nanoparticles preparation

Titanium (IV)-isopropoxide (Sigma-Aldrich, St. Louis, MO, USA, 97%) was dissolved in isopropanol and stirred on a magnetic stirrer at room temperature, after 10 minutes deionized water (pH = 6) was added dropwise during 3h. The molar ratio of titanium (IV)-isopropoxide: isopropanol:water was fixed at 5:3:10. The as-prepared precipitate was filtrated and washed using ethanol, dried overnight in the drying oven at 100 ºC, then it was calcined at 700 ºC for 5 hours and left in the oven to cool down.

2.2. Structural and morphological characterisation of the TiO_2 nanoparticles

The X-ray powder diffraction (XRPD) measurements were conducted on Philips PW 1050 X-ray diffractometer using Ni-filtered Cu radiation and Bragg-Brentano focusing geometry. The diffraction intensities have been recorded in the 5–70° 2θ range with a step size of 0.02° and acounting time of 6 s per step. Scanning electron microscopy (SEM) was performed with a PhenomProX electron microscope (Phenom, Thermo Fisher Scientific, Waltham, MA, USA).

2.3. Photodegradation experiments

The procedure of photodegradation was carried out with 30 mg of catalyst for the ciprofloxacin commercial solution for infusion, diluted by distilled water up to the concentration 4.75×10^{-4} M. The reaction mixture was stirred for 30 minutes in the dark, alongside blank (solution ciprofloxacin without catalyst). Next, the blank and the reaction mixture were irradiated under UV light (Philips TUV 15W UVC Disinfection, Poland) for 4 hours. The photodegradation process was monitored by recording the UV-Vis spectra (LLG Labware, Detroit, MI, USA) in the wavelength range from 190 to 500 nm. The 3 mL aliquots were drawn in time interval 25 min and filtrated prior to the recording of UV-Vis spectra.

2.4. Theoretical calculations

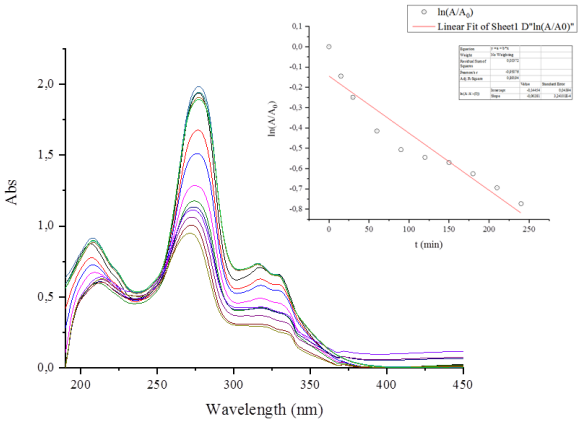
For DFT calculations, a *pwscf* code of the Quantum ESPRESSO package (version 7.2) was used [6]. Ultrasoft pseudopotentials based on GGA-PBE approximation with a plane wave kinetic energy cutoff of 50 eV were implemented. Optimized rutile bulk parameters were a = 4.639 Å and c = 2.968 Å. The TiO_2 surface was modelled as a (110) slab in a 4-layer 1×1 (17-atom) cell. There was at least a 25 Å vacuum between slabs, and the dipole correction was employed to avoidinteraction between periodic images. All calculations were spin polarized. Hubbard correction (GGA+U) was used in a simplified version of Cococcioni and de Gironcoli's work [7]. An effective U value of 3.0 eV for the Ti-d states was used. The k-point grid was sampled through a Monkhorst—Pack scheme, using 4×4×1 k-points. Electronic and ionic force convergence criteria were 10^{-6} Ry and 10^{-4} Ry/Bohr, respectively.

3. RESULTS AND DISCUSSION

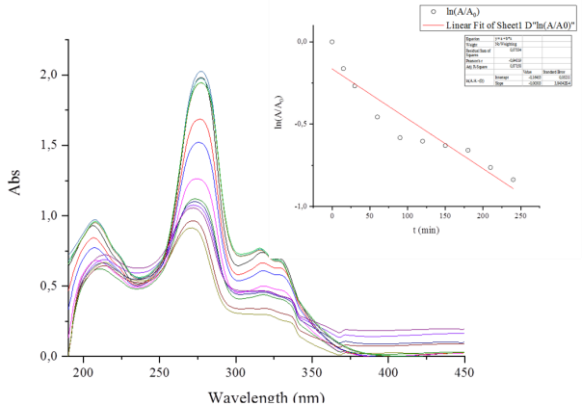
Ciprofloxacin degradation efficiency was measured as the relative depletion of absorbance of the characteristic peak at 277 nm. Degradation rate constants were calculated from the decrease in absorbance at 277 nm, assuming the pseudo-first-order kinetics (Equation (1)):

$$A = A_0 e^{-kt} \quad (1)$$

where A_0 is the absorbance at time at zero minute, and k (min^{-1}) is a pseudo-first-order rate constant.



(a)



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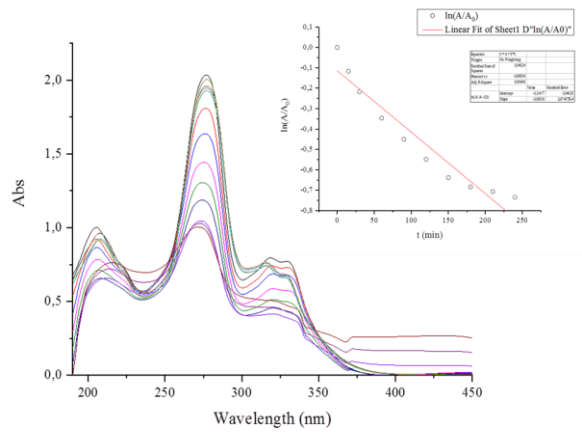


(c)

Figure 1. UV-Vis spectra of the ciprofloxacin solution of the initial concentration 4.75×10^{-4} M during 240 min of photodegradation with 30 mg 0.5% TiO_2(Cu) (a), 1% TiO_2(Cu) (b) and 2% TiO_2(Cu) (c). Corresponding linear forms used to calculate rate constants are given as inserts

The linearization of Equation (1) was applied to obtain the rate constant k from the slope of the graph (Equation (2)):

$$\ln\frac{A}{A_0} = -kt \quad (2)$$

The UV-Vis spectra of ciprofloxacin degradation using TiO_2 with Cu input concentrations 0.5%, 1%, and 2% are represented in Figure 1, and the corresponding linearized forms (2) are given as insert.

Calculated pseudo-first order rate constants are represented in Table 1. The pseudo-first order rate constants exhibit similar values in all three Cu input concentrations. The efficiency of CIP degradation achieves 51% within 240 minutes. However, the degradation efficiency is in average increased compared to bare TiO_2, which achieves no more than 44% at the same experimental conditions [8].

Table 1. Pseudo-first order rate constants and efficiencies of CIP degradation for different Cu input concentrations

Catalyst material	k (min^{-1})	Degradation of CIP (%)
0.5% TiO_2(Cu)	0.0028	48
1% TiO_2(Cu)	0.0030	46
2% TiO_2(Cu)	0.0030	51

XRD patterns of TiO_2 with input Cu amounts 0.5-2% are represented in Figure 2. Regarding the phase composition of the TIO_2(Cu) samples, it is the same as the bare TiO_2 powder. However, the absolute intensities of the peaks decrease over the entire range upon increase of input Cu amount. Possibly, metal deposition changes the relative intensity of individual planes due to a change in surface energy.

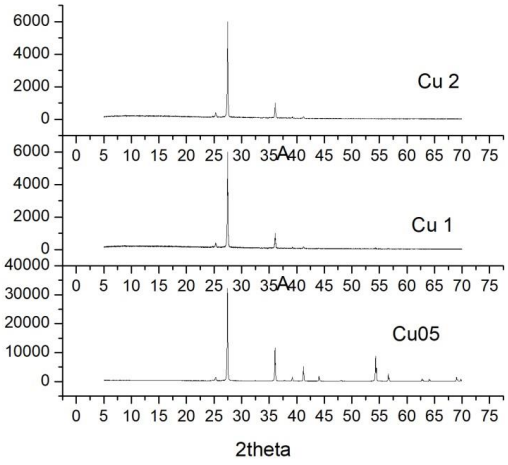
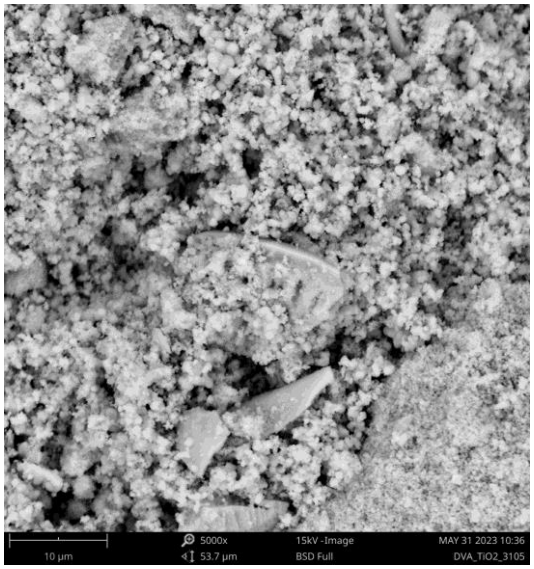
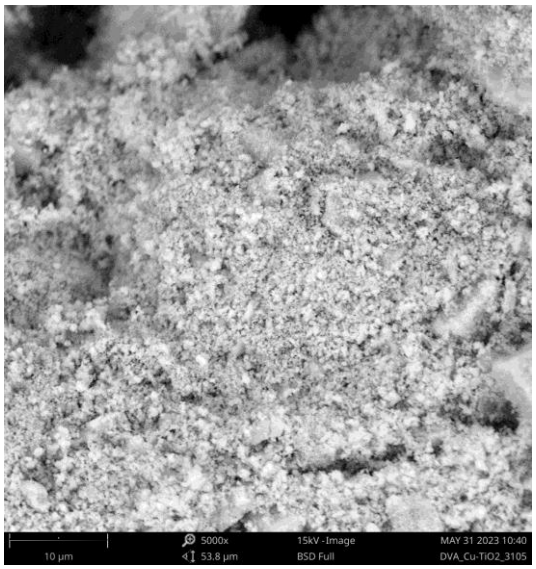


Figure 2. XRD patterns of TiO_2 with at three input concentrations of Cu (2%, 1% and 0,5%)

SEM images comparing bare TiO_2 and TiO_2(Cu) with 0.5% input Cu are represented in Figure 3.



(a)



(b)

Figure 3. SEM images of bare TiO_2 (a), and TiO_2(Cu) (b) at magnification 5000.

As obvious from Figure 3, addition of Cu results in a remarkable reduction of average particle size of TiO_2, possibly due to the significant reduction of agglomeration of smaller 20-30 nm TiO_2 particles upon deposition of Cu onto the TiO_2 surface.

Chemical effect of deposited Cu at coverage 0.25 ML on the photocatalytic performance is evaluated through DFT calculations of OH binding energy on metal top site of TiO_2(110) surface model (Table 2). Decrease of OH-radical binding energy in TiO_2(Cu) compared to bare TiO_2 potentially implies that the OH-radical is more reactive towards organic compounds because it is more efficiently desorbed.

Table 2. DFT calculated binding energies of OH radical on selected sites of model surfaces TiO_2, and TiO_2(Cu)

Surface model	Binding site	E_{ads}, OH
Bare TiO_2	Ti-top	-3.95 eV
TiO_2(Cu)	Cu-top	- 3.39 eV

Corresponding PDOS for TiO_2(110) surface with deposited Cu is represented in Figure 4. The PDOS features originating from Cu d-orbitals appear in the bandgap suggesting the modification of semiconductor properties of TiO_2 surface upon Cu deposition.

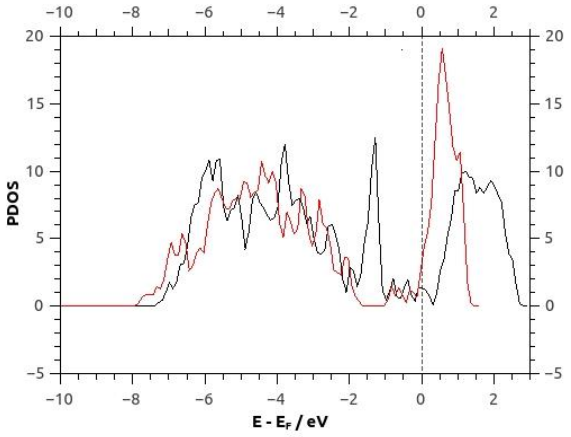


Figure 4. PDOS structure of TiO_2(Cu) (coverage 0.25 ML) vs bare TiO_2

4. CONCLUSION

The provided approach in investigation of TiO_2(Cu) systems for photocatalytic degradation of ciprofloxacin contributes to the understanding of performance on experimental and theoretical level. Variations of input Cu concentration do not have significant impact on the degradation kinetics and efficiency. However, the degradation reaction is in average more efficient on TiO_2(Cu) compared to bare TiO_2. Morphological changes upon Cu deposition on TiO_2 result in the change of surface energy and the decrease of particle size upon reduced agglomeration. DFT calculations of OH binding energy predict that the photogenerated OH-radicals bound on Cu-top site could be more reactive towards organic compounds compared to these on bare TiO_2, while PDOS confirm appearance of Cu d-states in the TiO_2 bandgap.

Acknowledgements

The authors would like to thank the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia [grant number 451-03-66/2024-03/200017 and 451-03-66/2024-03/200175].

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