



One-step sol-gel fabrication of $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ photocatalysts

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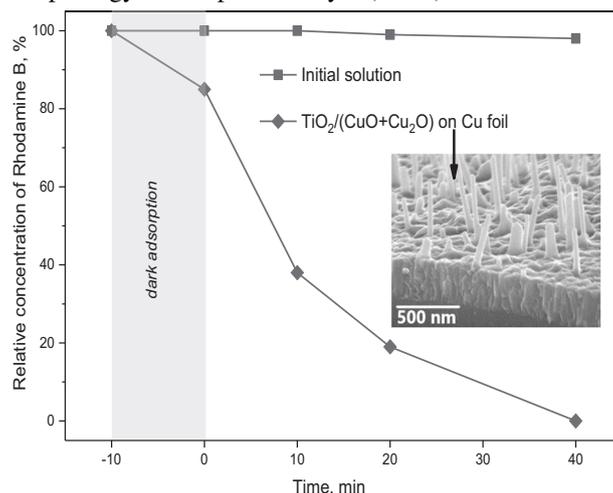
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Abstract

Photocatalytically active $\text{TiO}_2 + \text{CuO} + \text{Cu}_2\text{O}$ composite structures on copper foil and pre-oxidized copper grids were fabricated using a novel one-step sol-gel synthesis. The sol used included titanium tetraisopropoxide, ethylene glycol monomethyl ether, and nitric acid. Scanning electron microscopy of the composites synthesized upon calcination of the dip-in deposited sol at 400–500 °C demonstrated them to consist of a granular oxide surface layer with a thickness up to 200 nm penetrated by CuO whiskers as long as up to several micrometers. Copper oxides (CuO and Cu_2O), as well as titanium dioxide (TiO_2) in the anatase phase, were registered by X-ray diffraction analysis. High photocatalytic activity with respect to the test pollutant Rhodamine B in an aqueous solution under UV-activation was observed. The developed surface morphology combined with an efficient separation of photogenerated charge carriers at the $\text{TiO}_2/(\text{CuO}$ or $\text{Cu}_2\text{O})$ heterojunctions is considered to be responsible for the observed photocatalytic activity. The proposed one-step fabrication of catalytically active materials immobilized on a substrate is promising for improving existing water and air purification systems.

Graphical Abstract

Photocatalytic decomposition of Rhodamine B in water solution (10 mg/l) by a photocatalyst containing CuO, Cu_2O , and TiO_2 under UV irradiation, and morphology of the photocatalyst (insert)



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Highlights

- $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ photocatalysts were one-step synthesized on copper foils and grids by sol-gel method.
- Pre-oxidation of copper grids develops the morphology of the composite photocatalyst on their surfaces.
- $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ catalysts synthesized on copper foils completely reduce test pollutant Rhodamine B in water solution within 40 min under UV irradiation.

1 Introduction

The sol-gel method makes it possible to produce a wide range of photocatalytic materials due to its flexibility and formulation variability. An important advantage of this method is the possibility to fabricate free-standing powders and immobilized catalysts covering various substrates. One of the popular materials for photocatalysis obtained by the sol-gel method is titanium dioxide (TiO_2 , titania). It is considered as an almost perfect semiconductor for photocatalytic use due to its high stability, low cost, harmlessness to humans and environment, and high electronic conductivity [1]. Nanostructures based on TiO_2 exhibit high photocatalytic activity both in the decomposition of organic compounds and in water disinfection [2, 3]. One of the disadvantages of this material is a rather large bandgap (3.2 eV), which limits its photosensitivity to the ultraviolet radiation range.

TiO_2 -based photocatalysts can be sensitized to the visible wavelength range using semiconductor materials with a smaller bandgap, such as Cu_2O and CuO (2.0 and 1.2 eV, respectively). Such semiconductors make it possible to absorb visible radiation and are also promising for use in optoelectronics, photovoltaics, and sensors. To increase the photocatalytic activity, materials with a high specific surface area are also used. Various methods are employed to obtain materials with a developed surface, such as chemical etching, lithography, and template synthesis. Oxide layers containing arrays of nanosized CuO filaments can be easily formed by thermal oxidation of copper, as shown in [4]. Due to their high specific surface area, these structures are of interest for application in composite photocatalysts. Composites containing CuO and/or Cu_2O and TiO_2 deserve special attention due to the possibility of separation of photogenerated charge carriers at TiO_2/CuO , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{CuO}/\text{Cu}_2\text{O}$ heterojunctions accompanied by light absorption in the visible and ultraviolet ranges.

Usually, one performs some technological steps to fabricate a composite photocatalytic coating using a sol-gel method. For example, previously synthesized nanoparticles can be added to the sol [5, 6] with a subsequent sophisticated synthesis [7], or substrates with chemically or lithographically modified surfaces are used [8]. In this paper we

demonstrate a possibility to fabricate nanostructured photocatalytically active $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ composites on copper foil substrates employing a one-step sol-gel fabrication technique.

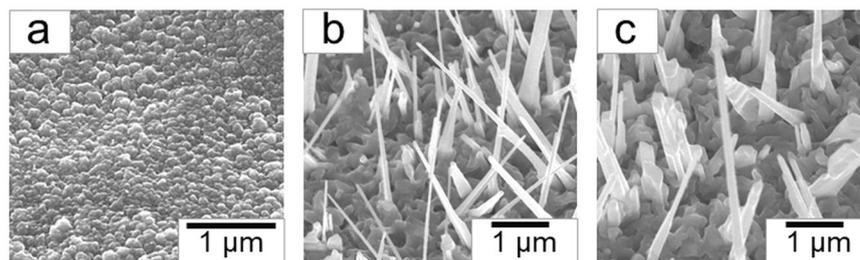
2 Experimental

The substrates used in the experiments were 3.5×3.5 cm in size cut from a copper (99.9%) foil with a thickness of $127 \mu\text{m}$ and copper grids (for comparison) with a wire diameter of $40 \mu\text{m}$ and a cell size of $100 \mu\text{m}$. Copper surface preparation included the following chemical treatment steps: removal of organic contaminants by boiling in isopropanol (90°C) for 2 min, removal of inorganic contaminants to improve wettability by etching in Na_3PO_4 (60 g/L) + Na_2CO_3 (40 g/L) for 10 s at 70°C , and removal of the surface oxide film by etching in 5% H_2SO_4 solution for 20 s at room temperature. All solutions were prepared using distilled water. In order to control CuO and Cu_2O growth on the virgin substrates, they were heat-treated in a muffle furnace at $350\text{--}500^\circ\text{C}$ for 20 min in air.

TiO_2 coatings were synthesized on both virgin and pre-oxidized substrates by their dipping in a solution containing 1.2 g of titanium tetraisopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) as a precursor, 8 ml of ethylene glycol monomethyl ether ($\text{C}_3\text{H}_8\text{O}_2$) as a solvent, and 0.5–0.7 ml concentrated HNO_3 for adjusting the solution pH to 1. After immersion the samples were dried in an airstream at 60°C and finally annealed in a muffle furnace at $400\text{--}500^\circ\text{C}$ for 10–20 min in air.

The morphology of the substrate surfaces was examined by scanning electron microscopy (SEM) on the Hitachi S-4800 microscope (Hitachi Ltd., Japan) by recording the secondary electron images with 15 kV of acceleration voltage. The phase composition of the synthesized covers was determined by X-ray diffraction (XRD) on the X-ray diffractometer RIGAKU ULTIMA IV (Rigaku, Japan) supported by the parallel beam optic and $\text{CuK}_{\alpha 1}$ radiation source. The photocatalytic activity of the composites was estimated by the degree of decomposition of the model pollutant Rhodamine B in an aqueous solution (10 mg/L) under UV irradiation (365 nm) within 1–60 min. To study photocatalytic activity, 3 g of the solution was poured into

Fig. 1 SEM images of the copper foil surfaces after annealing at 350 (a), 450 (b), and 500 °C (c) for 20 min in air



Petri dishes with a diameter of 30 mm with the experimental samples at the bottom. Light exposure was carried out with a 9 W mercury lamp placed at a distance of 10 cm from the surface of the solution. This experimental configuration makes it possible to neglect the attenuation of radiation before reaching the photocatalyst surface. Vibrational mixing of the solution was provided to ensure a uniform supply of contaminants to the catalyst. The change in the concentration of the analyte in the solution was determined by the peak intensity of optical absorption of Rhodamine B (at 553 nm). Absorption spectra of the solutions were registered by PROScan MC 122 (SOL Instruments, Belarus) spectrophotometer at room temperature with a scanning step of 1 nm. Before UV irradiation, experimental samples were kept in the test solution under dark conditions for 10 min to complete chemical adsorption of the analyte on the surface of the photocatalyst.

3 Results and discussion

Pre-oxidation of both copper foils and grids resulted in the formation of grained layers with whiskers at their surfaces, as illustrated for foils in Fig. 1. Whiskers appear after annealing at 400 °C and higher temperatures. Their size and density are increased with increasing temperature, reaching a few micrometers in length and 100–200 nm in thickness. With an increase of the temperature to 500 °C, the predominant growth of whiskers was replaced by bulk growth of the grained layer. Identical whiskers and their evolution with annealing temperature were observed for copper grids. Thus, copper oxidation at 450 °C appears the best for a balance between surface densities of whiskers and grains covering the copper surface.

XRD analysis of the oxidized samples showed them to contain mainly the CuO phase. This is illustrated in Fig. 2 for the grids, while qualitatively the same results were registered at foils. Some Cu₂O phase was also resolved.

To determine the volume ratio between identified phases, a quantitative analysis of the XRD patterns by the direct comparison method was undertaken, taking into account only statistically relevant peaks. The results are presented in Table 1.

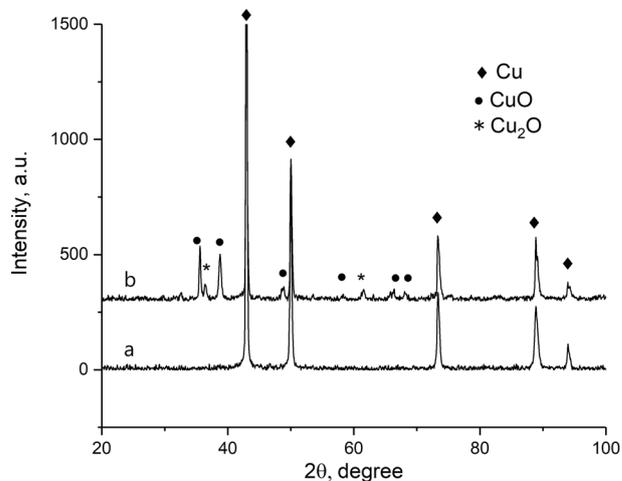


Fig. 2 XRD patterns of a virgin copper grid (a) and a copper grid annealed at 450 °C in air (b)

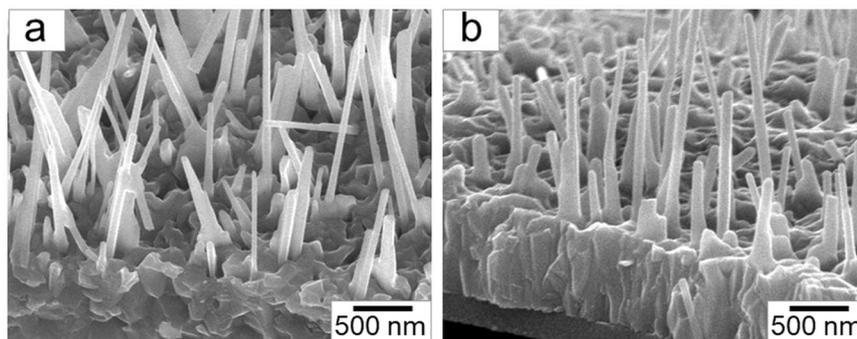
According to the calculation results, the phase relation of Cu:CuO:Cu₂O is about 81:15:4%. Summarizing the above SEM and XRD observations, one can suppose that the whiskers formed are composed of CuO and the surface grained layers consist of CuO and Cu₂O phases. The conclusion about CuO whiskers is supported by the fact that these whiskers are formed starting from the temperatures (above 400 °C) at which Cu₂O is not thermodynamically stable and transforms into CuO at a sufficient concentration of oxygen in the annealing ambient.

Experiments with the sol-gel formation of TiO₂/(CuO+Cu₂O) heterostructures on virgin and pre-oxidized copper surfaces showed some differences for foils and grids. In the case of the pre-oxidized substrates, TiO₂ (mainly anatase), CuO and Cu₂O phases were registered by XRD on both foils and grids upon calcination of the one-time dip-in deposited sol at 450 °C and higher temperatures. Meanwhile, no well-defined TiO₂ peaks were resolved in the XRD patterns of copper grids which were not pre-oxidized. In contrast, whiskers coming through a grained surface layer were formed on the unoxidized foils. It was noted that one dip-in deposition of the sol is not sufficient to obtain XRD intensity of the TiO₂ related peaks comparable with those on the pre-oxidized foils. In order to compensate for this difference, deposition and drying of the sol onto

Table 1 XRD data for grids

2 θ , degree	Intensity, a.u.	Phase	2 θ , degree	Intensity, a.u.	Phase
32.6	17	CuO	61.55	30	Cu ₂ O
35.6	198	CuO	65.8	21	CuO
36.0	22	Cu ₂ O	66.4	32	CuO
36.4	53	Cu ₂ O	68.05	22	CuO
36.55	45	Cu ₂ O	73.3	261	Cu
38.75	183	CuO	88.9	255	Cu
42.95	1460	Cu	89.15	174	Cu
48.9	42	CuO	93.95	62	Cu
50.05	595	Cu			

Fig. 3 SEM images of the pre-oxidized (a) and unoxidized (b) copper foils after dip-in deposition and calcination of the TiO₂ sol at 450 °C for 20 and 10 min, respectively, in air. The sol was deposited one time onto the pre-oxidized foil and 5 times onto the unoxidized one



the unoxidized foils were repeated five times. The typical morphology of the structure formed is shown in Fig. 3.

The thickness of the grained layer was found to increase with an increase of the calcination time. Different expansion coefficients of copper and oxide structures on its surface generate interface stresses inevitably relaxing with formation of cracks. We have found experimentally that at 450 °C calcination within 10 min can protect the synthesized coating from cracks, while a TiO₂/(CuO+Cu₂O) composite is formed. The thickness of the grained layer in this case is about 200 nm. The above regime was used for the fabrication of the samples for the photocatalytic tests. Both pre-oxidized grids and unoxidized foils were used as substrates.

Figure 4 compares the efficiency of photocatalytic decomposition of Rhodamine B by CuO+Cu₂O and TiO₂/(CuO+Cu₂O) on copper grids and TiO₂/(CuO+Cu₂O) on a copper foil.

The best result was demonstrated by TiO₂/(CuO+Cu₂O) composites formed on the copper foil. There are at least two reasons for this. First of all, at the same geometric size of the foil and grid substrates, the active surface of the foil substrate is larger. In addition, the TiO₂ content in the composite on the foils is also higher as can be estimated from the intensity of the corresponding XRD peaks. The efficient surface area ratios of copper oxides and titania were estimated within a model taking whiskers in the form of cylinders with an average length and thickness (in this case, the area of one whisker was taken as equal to the area

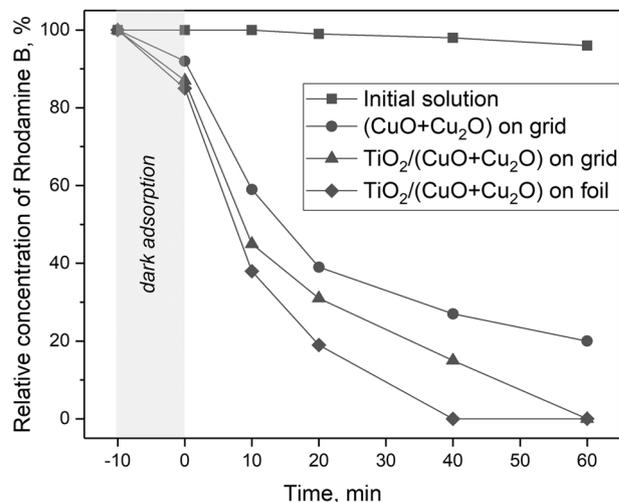


Fig. 4 Photocatalytic decomposition of Rhodamine B in water solution (10 mg/l) by CuO, Cu₂O, TiO₂ containing catalysts under UV irradiation

of an average cylinder without one base), uniformly distributed over the surface of titania film with an appropriate density. We estimated the density of whiskers, their average length, and thickness from SEM images, and presented the area ratio as the area corresponding to the surface of the whiskers and the area left unoccupied by the whiskers on TiO₂. The average thickness of whiskers is 0.10 μm, the height is 1.49 μm, and the density is 0.60 units/μm² for the

grid; and 0.11 μm , 1.22 μm , and 15.10 units/ μm^2 for the foil, respectively. Thus, 1 μm^2 area of the photocatalyst accounts for 0.995 μm^2 of TiO_2 and 0.296 μm^2 of $(\text{CuO}+\text{Cu}_2\text{O})$ for the grid, and 0.857 μm^2 of TiO_2 and 6.458 μm^2 of $(\text{CuO}+\text{Cu}_2\text{O})$ for the foil. The area ratio for Ti:Cu oxides is about 1:0.29 for the grid and 1:7.53 for the foil. This simple approximation compared with the results of photocatalysis shows that the combination of oxides plays a leading role in efficient photocatalysis.

The composites $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ on grids also showed antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* under visible light irradiation, as we previously reported in [9]. This suggests potential antibacterial applications for such composites synthesized on copper foils.

4 Conclusion

The proposed sol-gel synthesis of $\text{TiO}_2/(\text{CuO}+\text{Cu}_2\text{O})$ composites was shown to be efficient for the one-step fabrication of immobilized photocatalytically active coatings on copper foils and pre-oxidized copper grids. The foils allow for the creation of immobilized photocatalysts with large active surfaces and a variety of shapes. The grids appear more promising for applications requiring transparency for liquids and air elements. In any case, the one-step production of catalytically active materials is promising for improving existing water and air purification systems.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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