Conference Paper

Copper-doped quasi-one-dimensional ZnO for effective photooxidation of As (III) to As (V) in visible light

Olga I. Gyrdasova, Vladimir N. Krasil'nikov, and Natalya S. Sycheva

Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation

Abstract

By temolysis of the $Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2}$ complexes in one step $Zn_{1-x}Cu_xO$ solid solutions were obtained. Copper in these materials is a regulator of the photoactivity and morphology of aggregates. According to TEM, XPS, optical spectroscopy, and voltammetry, all samples studied contain monovalent copper. It was shown that the maximum photoactivity in the reactions of photooxidation of As (III) in UV and blue light has $Zn_{1-x}Cu_xO$ ($0<x<0.1$) solid solutions with tubular particle morphology. With an increase in concentration up to 10 at.%, copper manifests itself as an electron acceptor, which reduces the efficiency of the catalyst in both light ranges.

Keywords: photocatalyst, Cu-doped ZnO, heterostructures, wide-band-gap semiconductors, precursor synthesis

Corresponding Author:
Olga I. Gyrdasova
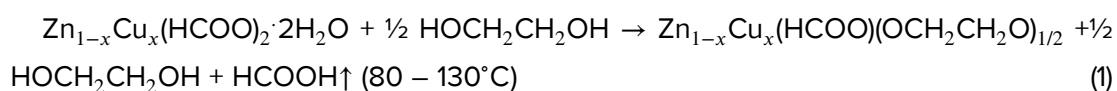Gyrdasova@ihim.uran.ru

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The use of ZnO as a photocatalyst for the oxidation of organic substances is due to its high photosensitivity, chemical stability, relatively low cost, availability and non-toxicity [1, 2]. All this allows us to consider this oxide as an alternative to existing commercial catalysts based on TiO_2 (Degussa P25) [3]. At the same time, the high rate of recombination of electron – hole pairs, exceeding the rate of surface red/ox processes, as well as photoactivity predominantly in the ultraviolet range with a low quantum yield, impose certain restrictions on the use of ZnO in catalysis [4, 5]. An increase in the photoactivity of such materials and its shift to the visible spectrum is possible by doping ZnO with transition metal ions, as well as by changing the size of the accessible surface and the morphology of the aggregates, and by increasing the degree of intrinsic defectiveness [5, 6]. Copper as an alloying agent manifests itself as an effective acceptor impurity, affecting the electronic band structure and its own defectiveness of ZnO, for example, the concentration of oxygen vacancies [7]. The method of synthesis of materials plays an important role in the formation of the composition, specific surface area and morphology of the aggregates, its intrinsic imperfection and, as a result, photocatalytic properties. The most promising way to synthesize doped

ZnO, in our opinion, is the precursor technology based on the thermolysis of individual complex zinc compounds with organic ligands. Previously, $Zn_{1-x}Cu_xO$ solid solutions and $Zn_{1-x}Cu_xO:CuO$ composite materials with different morphology and microstructure of aggregates were synthesized using zinc/copper mixed carboxylates as precursors. All of them showed photocatalytic activity in the oxidation of hydroquinone in blue light. [8–10]. There is information in the literature regarding the use of ZnO-based catalysts for the photocatalytic oxidation of As (III) to As (V) when exposed to visible light. [11]. However, there are very few of them. Basically, the photoactivity of such catalysts is studied by the example of discoloration of colored organic substances.

The aim of the present work was to synthesize and study the photocatalytic properties of copper-doped quasi-one-dimensional ZnO during the oxidation of As (III) to As (V) in aqueous solutions.

The precursor for the preparation of $Zn_{1-x}Cu_xO$ solid solutions (0≤x≤0.1) was the mixed formate-glycolate $Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2}$, obtained under solvothermal conditions according to the reaction:

$$Zn_{1-x}Cu_x(HCOO)_2 \cdot 2H_2O + ½\ HOCH_2CH_2OH \rightarrow Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2} + ½$$
$$HOCH_2CH_2OH + HCOOH\uparrow (80 – 130°C) \tag{1}$$

$Zn_{1-x}Cu_x(HCOO)_2 \cdot 2H_2O$ was produced by the interaction of formic acid HCOOH (ultra-high purity grade) with a stoichiometric mixture of ZnO (ultra-high purity grade) and $Cu_2(OH)_2CO_3$ (reagent grade) [12]. Ethylene glycol $HOCH_2CH_2OH$ (reagent grade) and acetone (high grade) were used for the synthesis of alcoholates and their washing. $Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2}$ (0≤x≤0.1) crystals are formed from the reaction solution in the form of thin needles prone to longitudinal intergrowth. Precursor crystals with x> 0.1 are spherical in shape. The chemical formula of the formate glycolate complex was established using methods IR spectroscopy, TGA/DTA and Powder X-Ray Diffraction Analysis. $Zn_{1-x}Cu_xO$ solid solutions (0≤x≤0.1) were obtained by annealing $Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2}$ in air at 500 ° C for 3 hours.

According to SEM data, the thermolysis products of the complexes preserve the morphology of the precursor crystals (**Figure 1**). According to the XRD data, performed using a STADI-P X-ray autodiffractometer (STOE) in CuKa1 radiation and a PDF-2 data library (Release 2009), solid solutions in the homogeneity region have a wurtzite structure (space group P63m). In addition to the lines of the wurtzite phase of ZnO, the diffraction pattern of $Zn_{1-x}Cu_xO$ samples with x≥ 0.1 contains impurity lines belonging to copper oxide (**Figure 2b**). According to TEM data, copper oxides in the impurity phase exist in two structural modifications — the cubic phase Cu_2O (Pn3n) and the monoclinic phase CuO (C2/c).
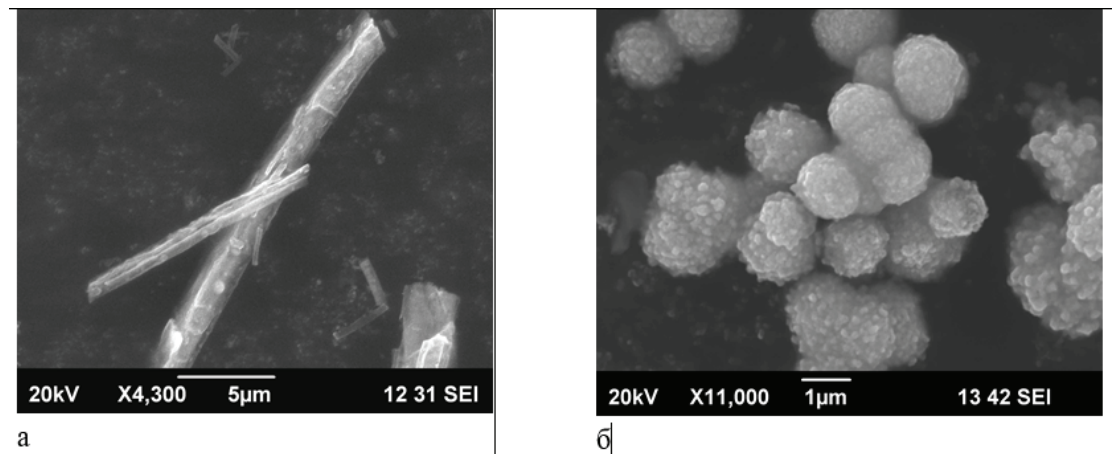
Figure 1: SEM image of $Zn_{1-x}Cu_xO$: x = 0.075 (a); x = 0.12 (b)

The photocatalytic activity of $Zn_{1-x}Cu_xO$ solid solutions (x = 0.025; 0.05) with quasi-one-dimensional particle morphology was tested in the photooxidation of trivalent arsenic. For experiments on the oxidation of arsenic (III), a 0.001 M solution of sodium mata arsenate (III) $NaAsO_2.3H_2O$ was selected. These solid solutions were selected based on the maximum photoactivity in the oxidation reaction of benzene-1,4-diol (hydroquinone) when exposed to blue light [12]. The change in the concentration of As (III) was controlled iodometrically according to the reaction [13]:
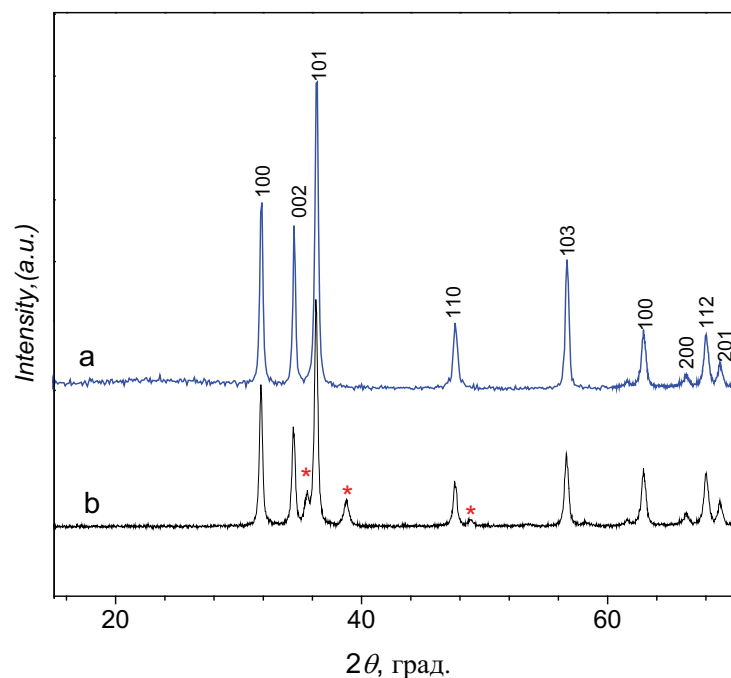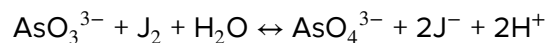
$$AsO_3^{3-} + J_2 + H_2O \leftrightarrow AsO_4^{3-} + 2J^- + 2H^+$$

Figure 2: X-ray diffraction patterns of $Zn_{1-x}Cu_xO$ samples: a - x = 0.05; b - x = 0.2; CuO - (*)

UV irradiation was carried out in a 50 ml glass photoreactor cell. 30 ml of an As (III) solution with an initial concentration of 30 mg / L was added to the reactor. Then, 0.25 g of catalyst was added to a solution with pH ~ 7. The reactor was placed on a magnetic stirrer; Irradiation was carried out using a BUF-15 lamp (max. = 253 nm). The suspension was stirred in the dark for 30 minutes to ensure adsorption equilibrium before lighting.
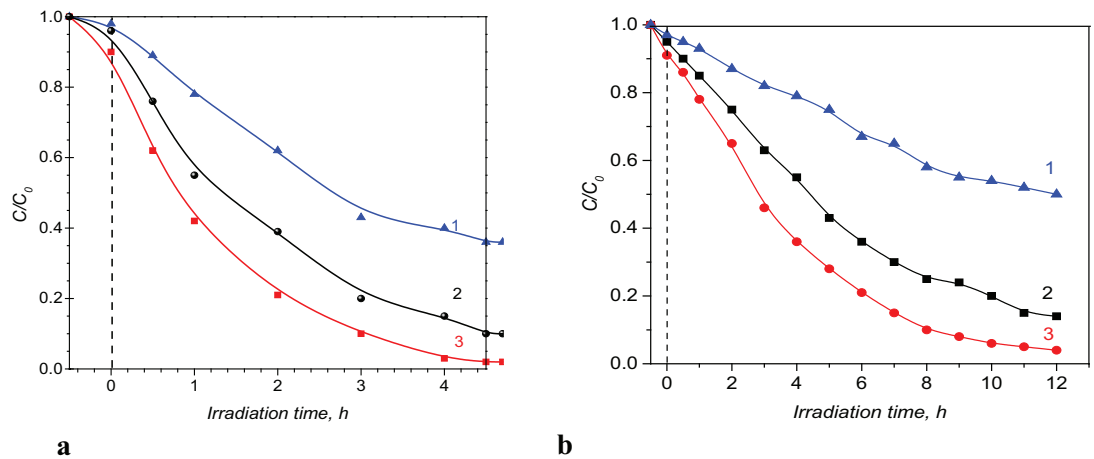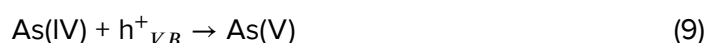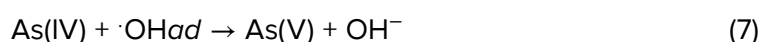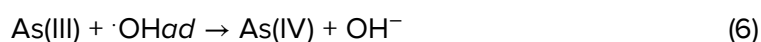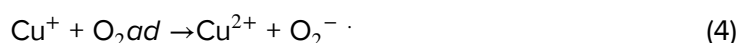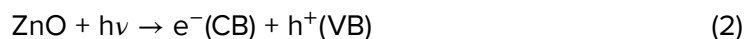

Figure 3: Photooxidation of As (III) on $Zn_{1-x}Cu_xO$: x = 0 (1), x = 0.025 (2), x = 0.05(3) when irradiated with UV light (a); blue light (b)

At certain intervals, samples were taken of the solution for analysis. After completion of the process, the catalyst was separated from the solution by filtration through an Advantec membrane filter (0.20 mm thick). **Figure 3** shows the kinetic oxidation curves of As (III) using catalysts $Zn_{1-x}Cu_xO$ with different copper contents. From the obtained data it is seen that the efficiency of the catalyst increases with increasing concentration of Cu in its composition. Similar dependences were obtained when the photocell was irradiated with light of the visible spectral range (λmax = 440–460 nm). It should be noted an increase in reaction time up to 12 hours (**Fig.3**).

For undoped ZnO, the photocatalytic characteristics are low due to its narrow range of light absorption and the fast recombination of electron-hole pairs. In $Zn_{1-x}Cu_xO$ solid solutions, copper ions not only create an effective acceptor level in the ZnO band gap, which hinders the recombination process during photodegradation, but also contribute to the formation of defects in the ZnO structure. Using the EPR method, we have established the existence of singly charged oxygen vacancies V_O^+ that contribute to the band structure of zinc oxide and thus affect the shift of its optical range [12].

When light acts on the surface of a $Zn_{1-x}Cu_xO$ particle, photoinduced electrons migrate to the conduction band (CB), and photoinduced holes remain in the valence band (VB). An electron is captured by the acceptor level of the Cu^{2+} ion, turning it into Cu^+. As a result, the lifetime of photoinduced holes increases, and electron – hole pairs (e^-/h^+) are effectively separated [7–10]. Hydroxyl groups from the surface of the catalyst

particle at turn react with holes in the valence band of $Zn_{1-x}Cu_xO$. This leads to the formation of reactive hydroxyl radicals (OH), extremely active oxidizing agents. Thus, the recombination of photogenerated electrons and holes is one of the most important factors determining the photoactivity of the catalyst upon irradiation in both light ranges. The photocatalysis process on $Zn_{1-x}Cu_xO$ can be represented schematically (**Figure 4**) and at the form of a sequence (2)-(10):

$$ZnO + h\nu \rightarrow e^-(CB) + h^+(VB) \tag{2}$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{3}$$

$$Cu^+ + O_2 ad \rightarrow Cu^{2+} + O_2^- \cdot \tag{4}$$

$$OH_{ad}^- + h^+ \rightarrow \cdot OHad \tag{5}$$

$$As(III) + \cdot OHad \rightarrow As(IV) + OH^- \tag{6}$$

$$As(IV) + \cdot OHad \rightarrow As(V) + OH^- \tag{7}$$

$$As(III) + h^+_{VB} \rightarrow As(IV) \tag{8}$$

$$As(IV) + h^+_{VB} \rightarrow As(V) \tag{9}$$

$$As(IV) + O_2 \rightarrow As(V) + \cdot O^{2-} \tag{10}$$

The obtained values of the oxidation rate constants of the As^{3+}/As^{5+} pair (I order reaction) depending on the catalysts composition under UV and blue light irradiation are collected in **Table 1**. It is seen that the introduction of even small copper amounts into the ZnO structure increases its photocatalytic efficiency in both light intervals more than 2 times.

TABLE 1: The hydroquinone oxidation reaction rate constants and half-reaction time on $Zn_{1-x}Cu_xO$ catalysts

Sample	UV		Blue light	
	$k_s \times 10^5$, s^{-1}	т, h	$k_s \times 10^5$, s^{-1}	т, h
ZnO	4.54	4.2	1.58	12.2
$Zn_{0.975}Cu_{0.025}O$	9.65	2.0	3.88	4.8
$Zn_{0.95}Cu_{0.05}O$	17.6	1.1	6.3	3.1
$Zn_{0.9}Cu_{0.1}O$	10.1	2.1	4.2	5.2

It should also be noted that with an increase in copper concentration in the composition of Zn1-xCuxO to 10 at.% a decrease in its photoactivity is observed (table 1). Copper in this case plays the role of electronic traps [7–11].
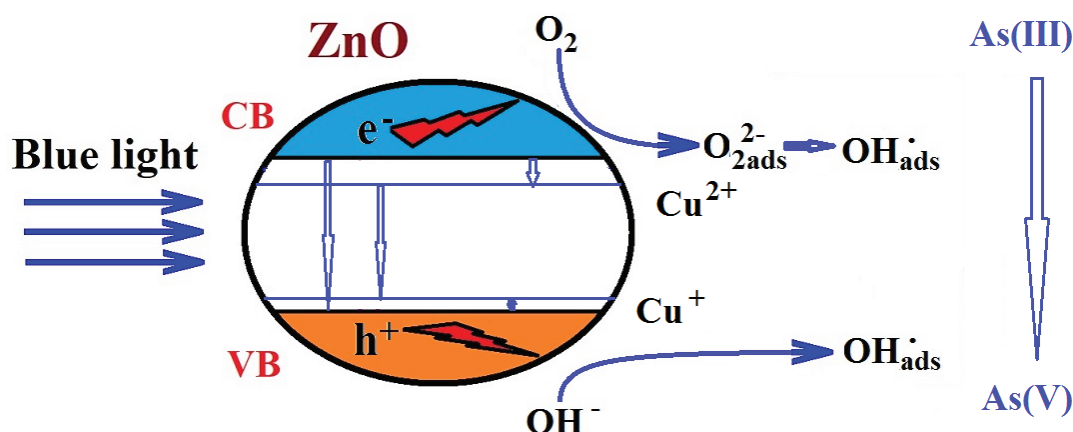
Figure 4: Schematic representation of processes occurring on a particle $Zn_{1-x}Cu_xO$

1. Conclusion

By thermolysis of $Zn_{1-x}Cu_x(HCOO)(OCH_2CH_2O)_{1/2}$ complexes $Zn_{1-x}Cu_xO$ solid solutions with a quasi-one-dimensional structure of aggregates were obtained. It was shown that the introduction of small amounts of copper ions in ZnO leads to a significant growth its photoactivity. The expansion of the spectral range of $Zn_{1-x}Cu_xO$ can be explained by the formation of an acceptor level $(Cu^{2+} + e^- \rightarrow Cu^+)$ in the ZnO band gap. This increases the separation efficiency of photogenerated e^-/h^+ pairs. $Zn_{1-x}Cu_xO$ (x = 0.025 and x = 0.05) showed maximum photoactivity in the oxidation reactions of As(III). With increasing concentration to 10 at.% copper manifests itself in the role of an electron acceptor. It also affects the formation of intrinsic defects, which are additional charge carrier recombination centers.

Acknowledgements

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