One-step hydrothermal surface oxidation of copper foil for photocatalytic water splitting

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Abstract. In this work a hydrothermal treatment of copper foil in alkaline solution without addition of other oxidizing agents was suggested for surface copper oxidation producing \( \text{Cu}_2\text{O} \) layer. Obtained \( \text{Cu}_2\text{O}/\text{Cu} \) heterostructures absorb light in a visible range and demonstrate a photocatalytic activity in a process of water splitting. Maximum value of photocurrent density was reached up to \(-0.7 \text{ mA/cm}^2 \) \((-0.6 \text{ V vs Ag/AgCl})\), which corresponds to quantum efficiency of \( \eta = 0.9\% \).

1. Introduction
Photocatalytic water splitting on semiconductor photocatalyst is a method for the hydrogen production under light irradiation. This technique is environmentally friendly, cheap and doesn’t require complex equipment.

Photodegradation of water occurs in the presence of photocatalyst, which can be used in a form of powder or as a part of photoelectrochemical cells. In photocatalyst electron-hole pairs are generated under light irradiation (if energy of incident photon is higher than band gap of semiconductor). After that, charges are separated and transferred to surface of photocatalyst where they are involved in the reduction and oxidation reactions with water (Figure 3, right part).

\[
\text{H}_2\text{O} + 2h^+ \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2
\]

\[
2\text{H}^+ + 2\overline{\text{e}} \rightarrow \text{H}_2
\]

At this moment a lot of photocatalysts has been developed (\( \text{TiO}_2 \), \( \text{Fe}_2\text{O}_3 \), \( \text{BiVO}_4 \), \( \text{TaON} \), \( \text{g-C}_3\text{N}_4 \), etc.), but none of them meets all the requirements for photocatalysts: optimal band gap, as well as the position of the valence and conduction bands, stability in aqueous solutions, low cost and non-toxicity [1, 2].

Copper (I) oxide corresponds to most of the parameters imposed on semiconductor photocatalysts and can absorb light in a visible range of the solar spectrum. It is a p-type semiconductor with band gap of \( 2.0 – 2.2 \text{ eV} \). Theoretically calculated value of photocurrent density for \( \text{Cu}_2\text{O} \) photoelectrodes is \(-15 \text{ mA/cm}^2 \), which corresponds to a quantum efficiency of \( 18\% \) [3, 4].

Hydrothermal method has many advantages in comparison with other approaches. It is a relatively simple method for synthesis of copper (I) oxide, which does not require high-purity reagents. This method allows, by varying pressure, temperature, time and pH of the solution, to obtain a well-crystallized product with a given composition and morphology [5-7].
The purpose of this work is to develop an approach for obtaining Cu$_2$O/Cu heterostructures via hydrothermal method and also to study their photocatalytic properties in the process of water splitting.

2. Experimental

2.1. Materials
Cu$_2$O copper foils with (10x15x0.5 mm sizes, grade M1, purity 99.9%) were used as the substrate. The plates were previously cleaned in an ultrasonic bath for 5 minutes in a mixture of isopropyl alcohol and acetone (1:1), then in 10% solution of hydrochloric acid, and finally in distilled water. The cleaned plates were fixed between PTFE supports (Figure 3, left part).

2.2. Synthesis
Hydrothermal synthesis was carried out at 180°C temperature for 1 hour in a NaOH solutions (analytical-grade) with concentrations from 0.05 to 1 mol/l, cell volume was 35 ml, the filling degree of the cell was 70% (Figure 3, upper part).

2.3. Characterization
The phase composition of the samples was determined by X-ray diffraction (Rigaku D/MAX 2500 diffractometer $\lambda$CuK$\alpha$ = 1.54178Å) and Raman spectroscopy (Renishaw InVia Raman microscope, laser wavelength - 514 nm, 20 mW, power output – 50%). The morphology of the samples was examined by scanning electron microscopy (SEM) (LEO Supra 50 VP).

The absorption spectra of the samples were recorded with Perkin Elmer Lambda 950 spectrophotometer in the wavelength range from 350 to 800 nm in the diffuse reflection mode. A sample of Labsphere's BaSO$_4$ WS-1-SL with known diffuse scattering characteristics was used as a standard.

The photocatalytic properties of the samples were examined using a three-electrode cell. The working electrode was Cu$_2$O/Cu sample, the counter electrode was a platinum coated titanium plate, the reference electrode was an Ag/AgCl electrode (3.5 mol/l KCl). The electrodes were immersed in a solution of 0.5M Na$_2$SO$_4$ (previously purged with a nitrogen for 30 minutes). A 20 W white LED 6300 K with a collimator lens was used as the light source. The measurement was performed with a potential sweep from 0 to -0.6 V at a speed of 10 mV/s in the chop-light mode (2 seconds light on, 2 seconds off, etc.). Intensity of the illumination at the sample position was determined at a level of 100 mW/cm$^2$ (Oriel PV Reference Cell System model 91150V).

3. Results and discussion
The SEM images show copper plates after hydrothermal treatment in 0.05 mol/l, 0.3 mol/l, 0.5 mol/l and 1 mol/l NaOH (Figure 1a-d). The surface of the substrate is coated with Cu$_2$O crystals, the size of which increases from 1 (0.05 mol/l) to 4 $\mu$m (1 mol/l) as a result of the recrystallization process (Figure 3 lower part) [8].

![Figure 1. SEM images of the Cu$_2$O crystals on the surface of copper foil after hydrothermal treatment in 0.05 mol/l (a); 0.3 mol/l (b); 0.5 mol/l (c); 1 mol/l NaOH (d).]
In accordance with XRD patterns (Figure 2), the intensities of the Cu$_2$O phase peaks increase with an increase of NaOH concentration from 0.05 mol/l to 0.3 mol/l, reaching a maximum value and, further, decrease at concentrations from 0.5 mol/l to 1 mol/l. The results obtained by X-ray diffraction are consistent with data obtained by Raman spectroscopy. The presence of CuO phase was not detected by XRD or Raman spectroscopy.

![Figure 2. XRD patterns of Cu$_2$O/Cu samples obtained after hydrothermal treatment of copper foils in NaOH solutions with various concentrations.](image)

According to [9, 10], two parallel processes take place during hydrothermal treatment of copper: 1a – oxidation of copper foil by oxygen, 1b – oxidation by hydroxide anions (Figure 3).

![Figure 3. Scheme of the hydrothermal synthesis of the Cu$_2$O/Cu heterostructure and following photocatalysis of water.](image)

During the synthesis of samples in NaOH solutions with different concentrations, a nonlinear dependence of the amount of copper (I) oxide on the alkali concentration takes place, which is caused by two competing processes: growth and dissolution of the copper (I) oxide layer. The amount of the Cu$_2$O phase increases with the increase of NaOH concentration to 0.3 mol/l. A further increase of the NaOH concentration leads to a decrease in the amount of oxide, due to the large impact of dissolution of the Cu$_2$O phase due to formation of a soluble complex Cu(OH)$_4$$^+$. [11].
In accordance with the data obtained, the optimal conditions for the synthesis of the Cu$_2$O/Cu heterostructure are hydrothermal treatment of the copper foil in a 0.3 mol/l NaOH solution at 180°C within 1 hour. Samples synthesized under these conditions were used for further studies.

To determine the light absorption for the Cu$_2$O/Cu heterostructure, diffuse reflectance spectrum was obtained (Figure 4).

![Figure 4](image.png)

**Figure 4.** The diffuse reflectance spectrum of a sample obtained by hydrothermal treatment of a copper foil in a 0.3 mol/l NaOH solution at 180°C within 1 hour. The inset shows a graph of the dependence of the Kubelka-Munk function on photon energies.

According to the spectrum, a sample obtained absorbs light over the entire range from 800 to 350 nm. A sharp increase in absorption transition starts at 640 nm and reaches a maximum near bandgap at 500 nm.

To determine the band gap of the material, the absorption on the wavelength was rearranged in coordinates $(\alpha h\nu)^m$ from hv (inset in Figure 4), where $\alpha$ is the absorption coefficient, hv is the quantum energy, $m = 2$ (Cu$_2$O is a direct band gap semiconductor).

The optical absorption coefficient $\alpha$ was calculated by the Kubelka-Munk equation [12]:

$$\alpha = \frac{(1-R)^2}{2R}$$

(1)

where $R$ is the diffuse reflectance of the sample.

In accordance with the dependence of the Kubelka-Munk function on photons energy, the value of the band gap of copper (I) oxide was determined as 1.982 ± 0.001 eV, which corresponds to the literature data [13].

To estimate the photocatalytic activity of the heterostructure, the dependence of the photocurrent density on the applied potential was measured (Figure 5).
Figure 5. Dependence of the photocurrent density on the applied potential for a sample obtained by hydrothermal treatment of a copper foil in 0.3 mol/l NaOH solution at 180°C within 1 hour.

According to figure 5, heterostructure demonstrates photocatalytic activity: the maximum value of the current density corresponds to -0.7 mA/cm² at a potential of -0.6V. The quantum efficiency of the process of photocatalytic water splitting was estimated as η = 0.9% by the equation 2 [12]:

\[
\eta(\%) = \left( \frac{1.23 - E_{RHE}}{E_{RHE}} \right) I \cdot 100\%
\]

where \( I \) – current density (mA/cm²), \( E_{RHE} \) – applied potential (V vs RHE), \( P \) – power of the illumination (mW/cm²). \( E_{RHE} = E_{AgCl} + E_{AgCl}^0 + 0.059pH \) \( (E_{AgCl}^0 = 0.197V \ (25^\circ C)) \).

The lower value of the photocurrent density than the theoretical (-15 mA/cm²) could be explained by the low electron mobility in copper (I) oxide and relatively low specific surface area (the oxide film consists of large crystallites with an average size of 2 μm).

4. Conclusions
The method for obtaining Cu₂O/Cu heterostructures by hydrothermal oxidation of copper foil in an alkaline solution without the addition of oxidizing agents is proposed. The optimal conditions for the synthesis of the Cu₂O/Cu heterostructure (0.3 mol/l NaOH at 180°C within 1 hour) were determined. This material absorbs in the visible range of the solar spectrum and is active in the process of photocatalytic water splitting: the maximum value of the photocurrent density is -0.7 mA/cm² at an applied potential of -0.6V (Ag/AgCl), which corresponds to a quantum efficiency η = 0.9%.

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