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Quantum efficiency of photocatalytic water splitting by fractal nanostructures Ag–AgI

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Quantum efficiency of photocatalytic water splitting by fractal nanostructures was studied. It was shown that the layers of nanostructures, synthesis by chemical reaction of substitution and subsequent partial iodizing, consist of fractal dendrites. It has been established that quantum efficiency of water splitting depends on the thickness of silver layer of nanostructure in non-linear form and increases with the increase of semiconductor layer AgI.

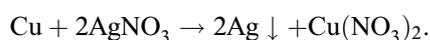
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Energy and environmental issues are becoming more and more important in the last decades due to global climate changes caused by the use of fossil fuels [1]. For applications in practice, solar energy needs to be converted into chemical fuel [2,3]. Hydrogen is considered to be an ideal fuel [4]. Photocatalytic water splitting is a promising method of application and conversion of solar energy. Materials for efficient production of hydrogen and oxygen from water and acid and alkaline solutions have already been developed [5–11]. The reaction of photocatalytic water splitting may be divided into the following stages: (1) absorption of photons with the production of electron–hole pairs; (2) separation of charges and their transport to capture sites on the catalyst surface, resulting in an increase in photocurrent; (3) water splitting with the release of H₂ and O₂ [12–14].

AgI-based catalysts attract considerable attention in the field of photocatalysis [15–17]. Ag–AgI nanocomposites are resistant to corrosion and have stable photocatalytic characteristics [16]. The aim of the present study is to examine the quantum efficiency of water splitting by a hybrid photocatalyst based on fractal Ag–AgI nanostructures under the influence of irradiation in the UV and visible ranges.

Nanoporous Ag films were synthesized by a substitution reaction from an aqueous solution of AgNO₃ on copper substrates [18]:



The duration of nanostructure synthesis was 5, 10, and 30 s. Nanostructures were iodized for 5, 10, and 20 min in iodine vapor at room temperature. The morphology of samples was studied using a JSM 7001F scanning electron microscope (SEM).

In photoelectrochemical catalysis experiments, the samples were introduced into an aqueous solution of NaNO₃ (8.71 mass%) and irradiated by an Exfo Novacure 2100 (Artisan) fiber source in the UV and visible spectral ranges with a voltage of 0.5–5 V applied to the photocatalytic cell via a 1 kΩ ballast resistor. The quantum efficiency was determined as [19]

$$\eta = \frac{N_e}{N_{ph}} = \frac{I_{ph}\hbar\omega}{P_{Abs}e},$$

where N_e is the number of photoelectrons, N_{ph} is the number of absorbed photons, I_{ph} is the photocurrent, P_{Abs} is the absorbed radiation power, and ω is the radiation frequency.

It was found that the synthesized nanoporous films consist of dendrites with a „trunk“ length up to 6 μm, „branches“ with a length up to 1 μm (Fig. 1, a), and hexagonal lamellar crystals up to 900 nm in size. Nanoneedles with a length up to 50 nm and a thickness of 10–15 nm are positioned at the tips of „branches.“ Figure 2 shows the EDX map of the SEM image of a part of the copper substrate after the substitution reaction. It confirms that the synthesized micro- and nanostructures consist of silver.

The mean dendrite layer thickness after the substitution reaction with a duration of 5 s is 3.5 μm. The layer thickness varies insignificantly in the process of iodizing. As was demonstrated in our earlier study [20], silver dendrites transform partially or completely in the process of iodizing into silver iodide with the β-AgI crystal hexagonal phase. The color of samples subjected to iodizing changes from grey to light yellow. The thickness of dendrite branches increases in the process (Fig. 1, b), since AgI has a lower density than Ag. A sharp current rise in the photocatalytic cell is coincident with the onset of irradiation.

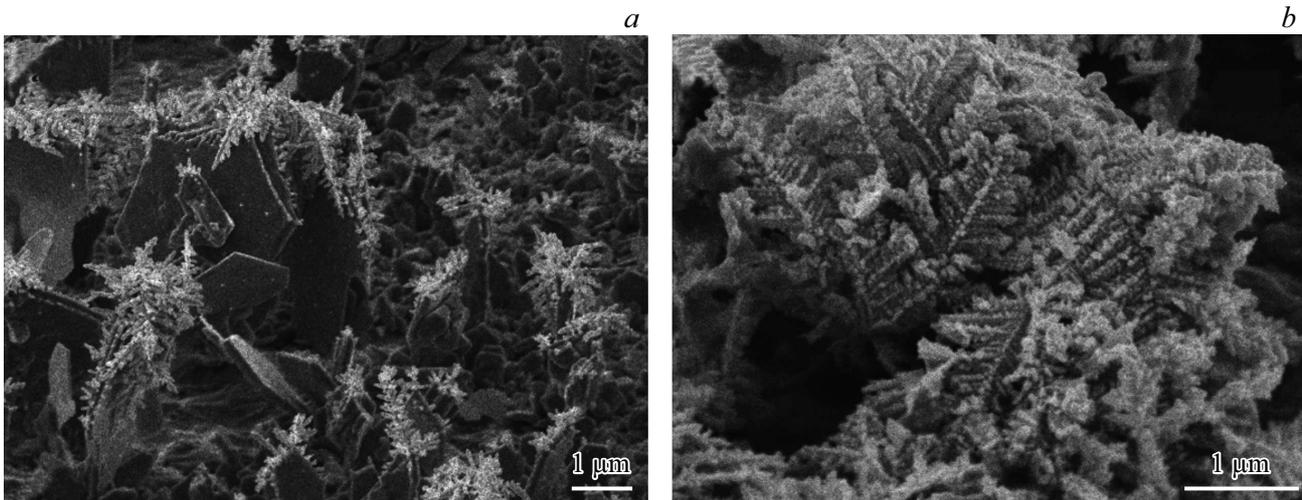


Figure 1. SEM images of silver dendrites on a copper substrate after the substitution reaction (a) and iodizing (b). The duration of the substitution reaction and iodizing is 5 s and 5 min, respectively.

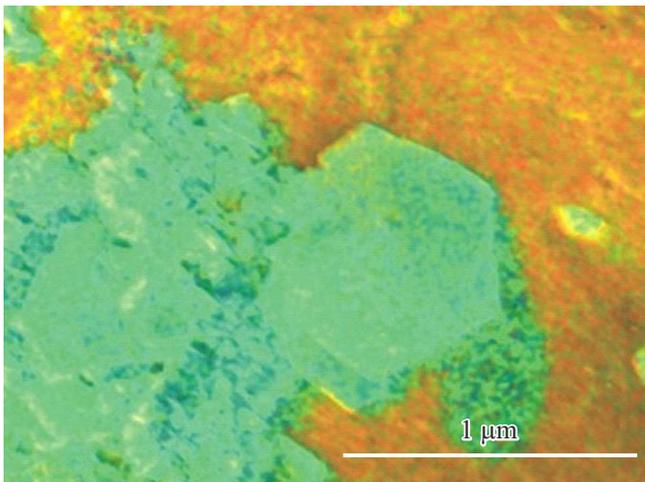


Figure 2. EDX map of the SEM image of a part of the copper substrate after the substitution reaction with a duration of 5 s.

The quantum efficiency of water splitting increases at higher applied voltages (Fig. 3). It also increases with increasing duration of the substitution reaction. At a substitution reaction duration greater than 5 s, the voltage dependence of the quantum efficiency changes radically, and the quantum efficiency at a voltage of 5 V reaches a level of 1% (Fig. 3, a). An increase in the duration of iodizing has only a weak effect on the quantum efficiency (Fig. 3, b); notably, iodized samples demonstrate a higher quantum efficiency of water splitting than non-iodized ones.

Microdendrites form larger agglomerates as the thickness of the nanoporous Ag layer increases. The photocathode surface area increases by a factor of $42 \cdot 10^3$ (relative to the substrate area) as a result. This leads to an increase in the number of hot electron production sites on the photocatalyst surface. As the duration of iodizing of

silver layers increases, the semiconductor AgI layer grows thicker. This has a significant effect on the band gap of the material. The distance traveled by carriers from the photogeneration site to the capture site increases in „thicker“ AgI layers, and the recombination of charges gets enhanced accordingly. This observation agrees well with the results of theoretical calculations for a heterojunction solar cell, where the recombination enhancement was attributed to the effect of space charges.

Electrons moving freely in an electrolyte, which leave the electrode–electrolyte interface with a certain probability, reduce H^+ ions in a solution. Therefore, the energy needed for this process corresponds to the energy barriers determined for photoemission in other metal/semiconductor–electrolyte systems. The potential barrier height decreases as the voltage applied to a photocatalytic cell increases. The number of photoexcited electrons, which are involved in the reduction of protons, grows as a result, and the quantum efficiency of water splitting increases accordingly.

Thus, fractal Ag–AgI nanostructures produced in a substitution reaction may be used as photocatalysts for water splitting. The quantum efficiency of water splitting increases with increasing duration of the substitution reaction. The quantum efficiency of water splitting is approximately 1% at an applied voltage of 5 V. When the duration of iodizing of nanoporous layers increases, the photocurrent varies uniformly with an increase in the applied voltage at different thicknesses of the AgI layer.

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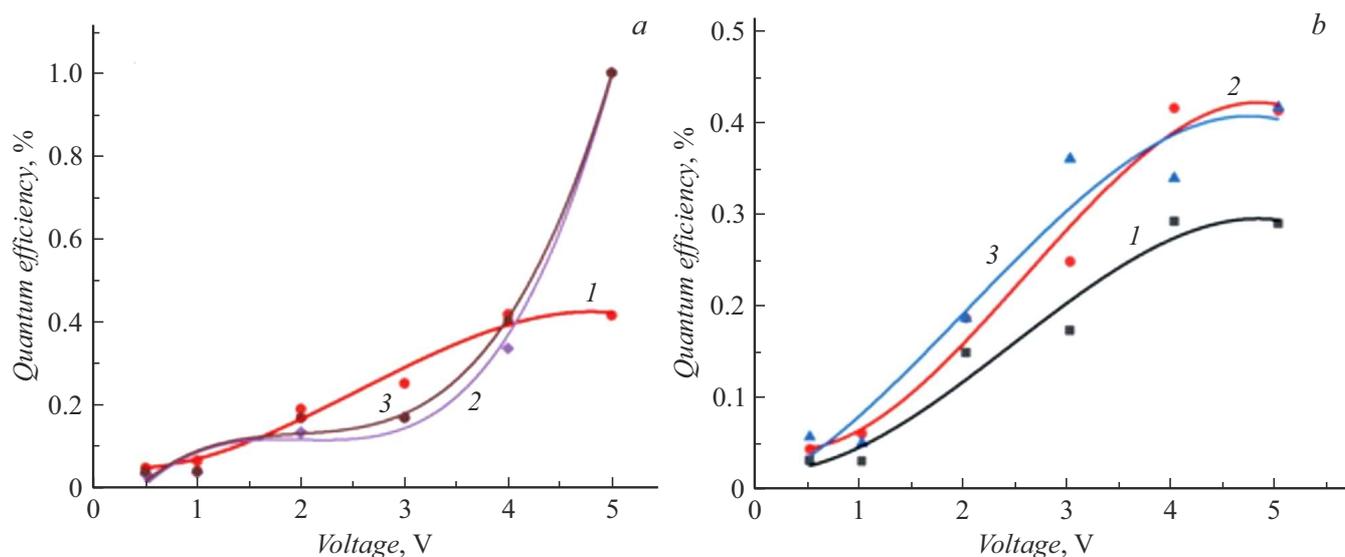


Figure 3. Dependences of the quantum efficiency on the applied voltage corresponding to different durations of the processes of production of nanoporous Ag (a) and iodizing (b). a — The duration of iodizing is 10 min, substitution reaction: 1 — 5 s, 2 — 10 s, and 3 — 30 s; b — the duration of the substitution reaction is 5 s, iodizing: 1 — 5 min, 2 — 10 min, and 3 — 20 min.

Conflict of interest

The authors declare that they have no conflict of interest.

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