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NANOSIZED IMPLANTS OF Ag^+, Cu^+ AND Cu^{2+} IONS INTO THE SURFACE LAYER OF POLYCRYSTALLINE CdS PHOTOCATALYST FOR THE OXIDATION REACTION OF IODIDE IONS

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Abstract: *The process of construction of the nanosized photoactive systems based on cadmium sulfide has been developed. Additional ions Ag^+, Cu^+, Cu^{2+} can be implanted into the surface layer of CdS microcrystals leading to the formation of nanosized particles of corresponding sulfides. High redox photocatalytic efficiency was determined in the model reaction of potassium iodide oxidation for the low-doped samples of CdS containing silver and copper ions and the composite nanostructured CdS-based sulfides containing nanoparticles of Ag_2S, Cu_2S i CuS. This effect is caused by the depression of electron-hole recombination because of reduction of the dope agent ions by free electrons, which results in the formation of reactive neutral atoms. Alternatively, this effect can also be caused by the transfer of photogenerated charges between likely charged clusters in nano- and microcomponents of the composite material.*

Keywords: *cadmium sulfide, potassium iodide, photocatalytic activity, nanostructured composite material, implantation.*

1. Introduction

Photocatalytic decontamination of some environment pollution agents through the reaction of oxidative destruction is quite a topical issue discussed widely in some articles [1, 2] and reviews [3, 4]. As seen from analysis of the recent publications, the processes of photocatalytic decontamination (by oxidation or reduction) of various inorganic and organic pollution agents by highly effective semiconducting photocatalysts is interesting for many scientific groups worldwide and the problem of development of such photoactive materials seems very topical [5-8].

The process of electron-hole recombination is naturally inherent for any photoexcited semiconductor and this is the key limiting factor that put obstacles on the catalyst's efficiency. Therefore, the decrease in the photocatalytic efficiency of the composite materials containing two different semiconductors can be caused by spontaneous electrons transfer between the conductivity bands or the analogous process of the holes transfer between the valence bands [9, 10]. The above mentioned transfer processes can take place only if they are allowed thermodynamically. Moreover, since the back transfer of the charges is prohibited thermodynamically, the excited semiconducting particles with divided charges can exist during the period of time that is required for interaction between the reaction components causing rise in the quantum yield.

Various model systems were used in investigations of the photogenerated charges separation [11] but the entire photocatalytic process has been thoroughly investigated for the two model systems only – photodecomposition of water and some alcohols, which produces molecular hydrogen [12] and reduction of methylene blue to its leucoform [13, 14]. It should be emphasized that the photoefficiency of both process is quite high. That is why it seems important to understand if the similar approach can be widened on some other redox systems, for instance, photocatalytic oxidation of iodides.

2. Experimental

The following source materials were used to build the nanostructured composites Ag_2S/CdS, Cu_2S/CdS and CuS/CdS: cadmium sulfide with specific surface area S_{BET} = 4.0 m^2/g, $AgNO_3$, Cu_2Cl_2, $CuSO_4 \cdot 5H_2O$. The solubility product of Ag_2S, Cu_2S and CuS is much lower than that of CdS (these values are $1{,}0 \cdot 10^{-51}$, $2{,}5 \cdot 10^{-50}$, $4{,}0 \cdot 10^{-38}$ and $4{,}0 \cdot 10^{-29}$ simultaneously [15]). Therefore, the former ions can substitute the latter one in the materials. The reaction of substitution has been carried out by stirring of CdS suspension in the solution containing the ions of the above mentioned less soluble sulfides. Reaction dynamics has been controlled by periodic sampling of the solution followed by the atom-absorption determination of concentrations of the free ions Ag^+, Cu^+, Cu^{2+} and Cd^{2+} in the samples. The substituted suspension was centrifuged and the sediment was washed by warm water in order to separate the unreacted components and then dried at the room temperature. Redox photocatalytic activity of the composite sulfides was evaluated through amount of the free iodine formed in the reaction of potassium iodide oxidation according to the method described in [16, 17]. Efficiency of the free iodine formation (r, %) was calculated by the methods reported in [18]. Oxidation of potassium is a suitable model reaction because it is comparatively simple and can be widely applied in the solar cells production technologies [19, 20]. It was considered that the specific surface area of the source cadmium sulfide remained unchanged throughout all chemical modifications.

3. Results and discussion

Similarly to syntheses of Bi_2S_3/CdS composites [13], the above mentioned method ensured obtaining of the CdS-based materials with exact preplanned values of the surface ions substitution ratio. It was considered that the distance between the surface ions of cadmium and sulfur was equal to the sum of their ionic radiuses while the total surface area of all nanocrystals was equal to the sum of all their ionic radiuses. The former parameter of the 1 g sample makes its specific surface area. This relation was used to calculate the total number of ions Cd^{2+} in the surface monomolecular layer.

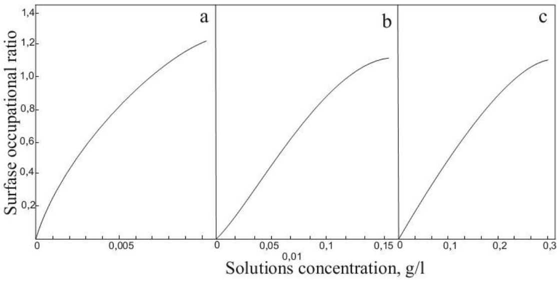

Fig. 1. Dependence of the surface occupational ratio for CdS and the following substitute ions: Ag^+ (a), Cu^+ (b) and Cu^{2+} (c) on their concentration in the reacting mixture.

On the other hand, results of quantitative analysis of the surface contents of silver and copper ions provided the data required for evaluation of the surface occupational ratios for each substitute ion throughout a series of the CdS samples [13]. A dependence of the surface occupational ratio on concentration of the substitute ions in the reaction mixture is shown in Fig. 1 (rest of the synthesis conditions was kept constant).

At the initial stages of embedding of the substitute ions into the surface layer of CdS, only few separated defects could appear. Due to the chemical bonds formed between the defects and the substrate lattice, they can be considered either as molecular ions AgS^-, CuS^- or as molecules Ag_2S, Cu_2S and CuS. The number of the defects is rising in course of the substrate processing, and interaction between them appears and grows resulting formation of the nanosized semiconducting islands of the substitutes on the surface of CdS. Thus, two separate groups can be identified among the substituted CdS materials. The low concentrated substitute products fall into the first group. As the substitute components concentrations are low, they can be considered as two-component systems: molecule (or molecular ion)/semiconductor. The second group includes the highly concentrated substituted products. As content of silver and copper sulfides are high in the products, they exhibit no molecular properties and play role of classic semiconductors only. According to [11, 12], the latter materials are nanostructured semiconducting composites containing a mixture of nanoparticles of CdS and the other sulfides.

Investigation of photocatalytic activity of the above mentioned materials was carried out using the model reaction of oxidation of iodides. It proved that the activity depends on the nature and concentration of the substitute ions in the material (see Fig. 1).

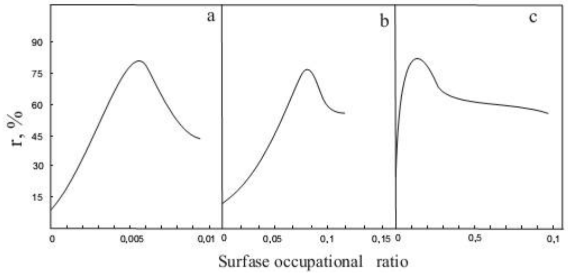

Fig. 2. Efficiency of the free iodine formation by the implanted CdS products with ions of Ag^+ (a), Cu^+ (b), Cu^{2+} (c) as a function on the surface monolayer occupational ratio.

As seen from Fig. 2, the rise in the free iodine production is registered even for the slightly substituted examples. It can hardly be expected that any semiconducting islands of AgS or CuS can be formed on such low-substituted material. Therefore, the first class of substituted materials appears to have some advanced photoactivity similarly to the two-semiconductor nanocomposite materials as it was described for the process of the molecular hydrogen production [12] or reduction of methylene blue on Bi_2S_3/CdS [13].

The process of phototransformation involving the second class material will run similarly to that for the first class. The only difference in the process scheme is related to the charge separation stage involving transfer of the charges between the likely charged areas. As seen from the energy transformation diagram analysis [10], the conductivity band of the nanosized Ag_2S is located above the conductivity band of CdS while the gap between the valence bands of these components is 0.4-0.6 eV wide. That is why the electron transfer processes are thermodynamically hindered while the hole transferring is not. The latter process will result in separation of the photogenerated charges. As a result, the electron-holes recombination will be inhibited in such a particle meaning that its redox activity will rise.

Analysis of the energy transformations during light absorption by the synthesized sulfides shows that two different mechanisms of photocatalysis can actually take place. The first mechanism is exhibited by the materials with low content of Ag^+, Cu^+ and Cu^{2+} ions sitting in the lattice and bonded chemically with sulfur. This mechanism implies transfer of the photogenerated electrons from the conductivity band to the above mentioned ions and formation of highly reactive atoms of silver and copper. The second mechanism is more intrinsic for the copper and silver-enriched materials. In involves separation of the photogenerated charges by their transfer between the likely charged areas of cadmium sulfide and nanoparticles Ag_2S, Cu_2S, CuS resulting in oppressed charges recombination.

4. Conclusion

New CdS-based catalysts were developed on the basis of the low-doped or composite nanostructured sulfides containing nanoparticles of Ag_2S, Cu_2S, CuS. An extremal pattern has been found for the dependencies of the materials photoactivity on their composition and synthesis conditions.

The first class of photocatalytic materials includes the polycrystalline CdS-based products with Ag^+, Cu^+ and Cu^{2+} surface implants similar to those applied to technologies of molecular hydrogen production by photodecomposition of water or photoreduction of methylene blue. Our results prove that potential applicability of such photoactive materials can also be widened to some other processes. Besides, new reliable methods of synthesis of various implanted CdS-based materials with preplanned photocatalytic activity have been developed and tested.

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