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Oxidation stability of solid-phase $ZnS–Ag_2S$ heteronanostructures

Stanislav I. Sadovnikov and Aleksandr I. Gusev

1. Synthesis $(ZnS)(Ag_2S)_x$ heteronanostructures

Aqueous solutions of reagents for the synthesis of solid-phase heteronanostructures of zinc and silver sulfides were prepared using high-purity deionized water as a solvent.

Synthesis of solid-phase $(ZnS)(Ag_2S)_x$ heteronanostructures by hydrochemical two-stage co-deposition of ZnS and Ag_2S is described in detail earlier.[S1]

Aqueous solutions of reagents for synthesis of ZnS and Ag_2S sulfides and their heteronanostructures based on ZnS and Ag_2S sulfides were prepared with the use of high-purity deionized water as a solvent. Heteronanostructures $ZnS–Ag_2S$ have been synthesized in two stages. First, silver sulfide Ag_2S was synthesized by chemical deposition from aqueous solutions of silver nitrate $AgNO_3$ and sodium sulfide Na_2S in the presence of sodium citrate Na_3Cit. In aqueous solutions, sodium citrate can reduce Ag^+ ions to form silver metal nanoparticles and create a citrate shell on Ag_2S particles. The synthesis of a colloidal Ag_2S solution was carried out in the dark in a neutral medium at pH ~7 according to the following reaction scheme:

$$2AgNO_3 + Na_2S \xrightarrow{Na_3C_6H_5O_7} Ag_2S\downarrow + 2NaNO_3. \quad \text{(S1)}$$

For the synthesis of $(ZnS)(Ag_2S)_x$ heteronanostructures, solution of sodium sulfide Na_2S was added to an aqueous zinc nitrate or sulfate solutions under constant stirring and obtained ZnS solution was mixed with synthesized colloidal silver sulfide solution.

The deposition of zinc sulfide occurs by the following reaction scheme

$$Zn(NO_3)_2 + Na_2S \rightarrow ZnS\downarrow + 2NaNO_3. \quad \text{(S2)}$$

The $Zn(NO_3)_2$ and Na_2S concentration was 50 mmol dm^{-3} in all reaction mixtures. The synthesized solid-phase powders were washed by decantation and were dried by the sublimation method in an Alpha 1-2 LDplus freeze dryer (Martin Christ) at an ice condenser temperature of −55 °C.

1. Materials and methods

The deposited sulfide powders and the same powders after annealing were studied by X-ray diffraction (XRD) on a Shimadzu XRD-7000 diffractometer using Cu$K\alpha_{1,2}$ radiation at room temperature. XRD measurements were performed in the angle interval 2θ = 20-95° with a step $\Delta(2\theta)$ = 0.02° at a scanning time of 10 s per point. The determination of the crystal lattice parameters and the final refinement of the structure of the synthesized sulfide powders were carried out using the X'Pert Plus software package. The diffraction reflections of all synthesized nanopowders are significantly broadened due to the small a particle size. Nanoparticle size D of ZnS, Ag_2S, and ZnO was determined from the broadening of the diffraction reflections.

The microstructure of the synthesized $ZnS–Ag_2S$ heteronanostructures was studied using a ThemisZ transmission electron microscope (Thermo Fisher, USA) in direct image and in high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mode.

The oxidation of the synthesized heteronanostructures was studied on a Netzsch STA 449C Jupiter thermal analyzer coupled to a QMS 403C Aeolos quadrupole mass spectrometer. The measurements

were performed by combined thermogravimetry (TG) and differential scanning calorimetry (DSC) in lidless alundum crucibles under conditions of continuous heating of samples to 700 °C at a rate of 10 °C min^{-1} in a stream (30 cm^3 min^{-1}) of synthetic air (79% N_2 + 21% O_2). Analysis of gases formed during the heating of the samples was carried out taking into account the mass numbers 18, 44, 64 and 80 characteristic of water and CO_2, SO_2, and SO_3 oxides.

References

S1 S. I. Sadovnikov, A. V. Ishchenko and I. A. Weinstein, *J. Alloys Comp.*, 2020, **831**, 154846; https://doi.org/10.1016/j.jallcom.2020.154846.