Preparation of Photocatalytic Silicon Core-shell Nanoparticles Covered by ZnS Shell in Solid-Gas Reaction

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ABSTRACT

The method of effective creation of ZnS thin layer on the carrier silicon nanoparticles surface via the reactive synthesis on the interface of solid-gas reactants was presented. The crucial step, which led to significant enlargement of the reaction interface on the surface of carrier nanoparticles, was the vacuum sublimation, controlled so that the sublimate formed into simple lamellae where the free reaction surface was least impaired by the mutual shielding of the particles. The final material is, thanks to its relatively high specific surface area of 154,3 m^2g^{-1} usefull for photocatalytic applications, especially in a dry environment.

Keywords: nanoparticle, silicon, ZnS, core-shell, photocatalytic, vacuum freeze-drying

1 INTRODUCTION

For easy handling in some practical processes, active nanoparticles are usually deposited on surfaces of larger carrier particles [1-2]. In our previous work [3-6], the particles of montmorillonite with a mean size of 300 nm served as carriers for individual photocatalytic ZnS nanoparticles, prepared by precipitation in the presence of CTAB surfactant, limiting their size to less than 4 nm. In this subsequent work, we present the first results of an alternative method of creating a thin ZnS shell on silicon nanoparticles via the reactive synthesis on the interface of solid $Zn(OAc)_2$ shell and gaseous H_2S.

2 METHOD OF Si NANOPARTICLES COVERAGE BY ZnS SHELL IN SOLID-GAS REACTION

The carrier Si nanoparticles in an aqueous dispersion had the maximum size fraction at 56,6 nm, as found by the integration of 100 DLS (dynamic light scattering) measurements and checked by the TEM image analysis. Then, the appropriate amount of $Zn(OAc)_2$ reactant was added to dissolve in the dispersion which, for the given total area of Si–H_2O interface, produces the desired thickness of the future ZnS shell. After intense sonication and rapid freezing, the dispersion solution was desiccated by controlled vacuum freeze-drying [7-9]. The surface temperature during the sublimation was adjusted to -23 ˚C to enable self-organization of the sublimate into mostly single-layer lamellar agglomerates of Si nanoparticles with a thin $Zn(OAc)_2$ reactant coating, see Figure 1.

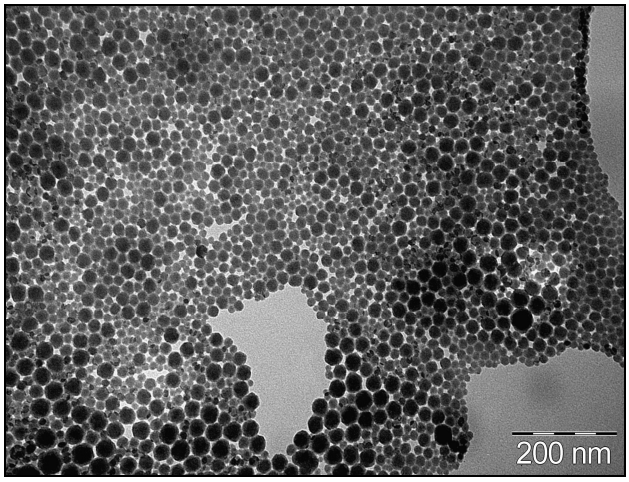

Figure 1: TEM micrograph of lamellar agglomerates of Si nanoparticles with a thin coating of $Zn(OAc)_2$ reactant after vacuum-freeze drying at -23 ˚C (TEM Jeol JEM 1230, 80 kV).

This intermediate lamellar product was exposed to gaseous hydrogen sulphide in a flow mode for 48 hours, so that the whole $Zn(OAc)_2$ layer reactively converted to the ZnS coating of silicon carrier particles. Figure 2 shows the external structure of lamellar agglomerates of core-shell nanoparticles Si(ZnS) depicted by a scanning electron microscope (SEM).

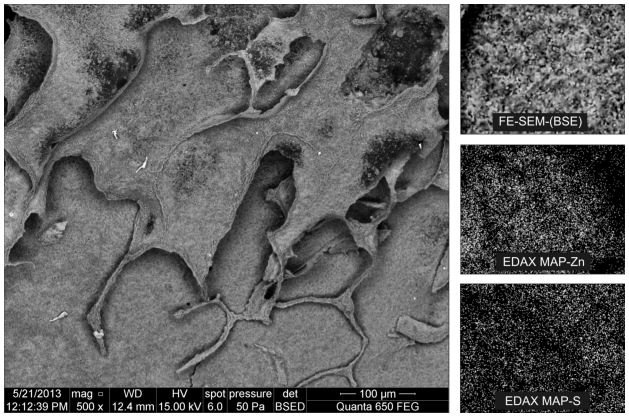

Figure 2: SEM micrograph of lamellar aggregates of core-shell Si(ZnS) nanoparticles and their EDAX (energy dispersive spectroscopy microanalysis mapping) confirming the presence of the two elements of Zn and S in the ratio and with the distribution corresponding to ZnS.

On the right side of Figure 2, there is the result of the energy dispersive microanalysis mapping, detecting the two elements of Zn and S in the ratio and with the distribution indicating the dominant presence of ZnS. Thus produced lamellar nanostructures were further deagglomerated via strong sonication in demineralized water. The obtained nanodispersion was then, like the original dispersion of the pure silicon, analyzed by DLS. The comparison of the two particle size distributions, shown in Figure 3, enables to determine the shell thickness through the extent and the character of the change between them [10].

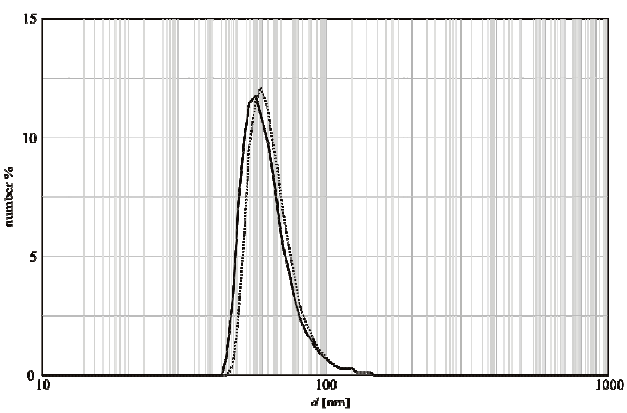

Figure 3: Comparison of particle size distributions according to the diameter d, measured by DLS (dynamic light scattering). The solid line corresponds to the original distribution of pure silicon carrier particles with the maximum at d = 56 nm, the dashed line represents the distribution of compound core-shell Si(ZnS) particles with the maximum at d = 59 nm.

The analysis of the size distributions based on the method introduced in [11] leads to the thickness of the ZnS shell on the Si core particles between 2 and 3 nm. In addition, transmission electron microscopy (TEM) image was also taken, see Figure 4.

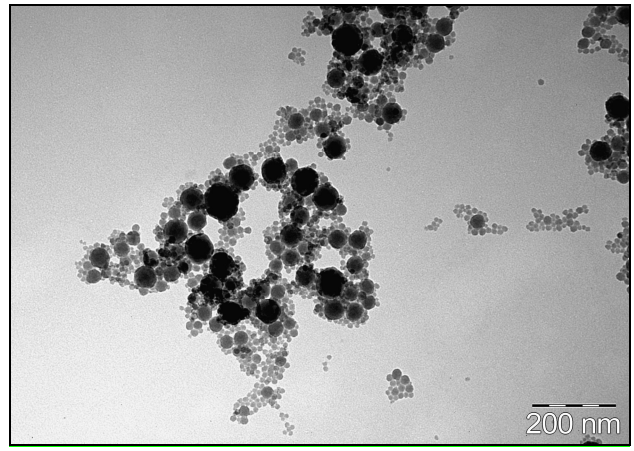

Figure 4: TEM micrograph of core-shell Si(ZnS) nanoparticles after ultrasonic dispersion in demineralised water, application to a carbon-coated microscope grid and drying. (TEM Jeol JEM 1230, 80 kV)

Similarly to the $Zn(OAc)_2$ coating in the first picture in Figure 1, the TEM image of the ZnS shell in Figure 4 is also rather indistinct. However, after performing the image analysis of the larger particles in Figure 4 and further pictures, the shell thickness was estimated about 4 nm. This significantly exceeds the values derived by the analysis of the change in the size distribution obtained by DLS. The disparity is partly due to inaccuracies in the estimates based on TEM image analysis, but the dominant part of the deviation is most likely caused by the natural presence of SiO_2 surface nano-layer on the original Si particles in an aqueous environment, which is indiscernible from the added ZnS shell in TEM. Therefore, to determine the real thickness of the ZnS shell, we rather rely on the results obtained by the analysis of the size distribution transformation due to the Si → Si(ZnS) process.

3 CONCLUSIONS AND FUTURE DIRECTIONS

The presented results confirmed that the above described method is effective to create a ZnS thin layer on the surface of carrier silicon nanoparticles via the reactive synthesis on the interface of solid and gaseous reactants. The crucial step, which led to significant enlargement of the reaction interface on the surface of carrier nanoparticles, was the vacuum sublimation, controlled so that the sublimate formed into simple lamellae where the free reaction surface was least impaired by the mutual shielding of the particles. The final material is, thanks to its relatively high specific surface area of 154,3 m^2g^{-1}, advantageously

applicable to photocatalysis, especially in a dry environment.

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