

METHOD OF AEROSOL SYNTHESIS OF CORE-SHELL NANOPARTICLES AND REFINE CONDITIONS OF ITS APPLICABILITY

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Abstract

In this work we generalized and specified aerosol synthesis method of core-shell nanoparticles. This synthesis method was used with success in our previous publication about preparation of photocatalytic core-shell Si-ZnS nanoparticles. Reaction of two precursors takes place on the surface of carrier nanoparticles and leads to formation of photoactive shell. Likewise, in other microemulsion methods, desired thickness of shell is achieved by limiting the extent of reaction. Unlike to the conventional microemulsion methods, both precursors are dissolved in a same solvent. In our method of application aerosol synthesis, the carrier particles are dispersed in aqueous solution of the first precursor with a suitable concentration. This dispersion, which contains dispersed particles, is converted into a form of aerosol microdroplets in ultrasonic nebulizer. After that the aerosol is injected by air flow on the surface of a vigorously stirred solution containing the second precursor, which is in excess. The reaction near surface of carrier particles is largely heterogeneous and the shell growth is limited by an amount of the first precursor located in the aerosol droplet. Desired coating thickness is achieved by setting the initial parameters such as size and concentration of carrier nanoparticles and concentration of the first precursor. This work follows our previous publication, generalizes aerosol synthesis technology of core-shell nanostructures and discusses its prediction formulas accuracy.

Keywords: Core-shell, aerosol synthesis, nanoparticles, photocatalysis

1. INTRODUCTION

Nowadays photocatalytic materials are one of the promising possibilities of how to degrade harmful substances in the water (typically organic compounds) and in the atmosphere (CO, CO₂ or oxides of nitrogen NO_x and sulphur) [1, 2, 3]. It is essential to use cheap and effective production technology for practical application of prepared photocatalysts. There is also a requirement to maximize the efficiency of photocatalytic reaction. Therefore, nanoparticles and other nanostructured materials get a great attention mostly due to their high specific surface area. Bottom-up method of preparing nanoparticles is very common e.g. by precipitation reaction, but nanoparticles are produced in relatively small concentrations and handling of their dried form is very difficult. To solve these problems we can deposit them on carrier particles or on other nanostructured materials, which makes handling easier and functional material retains the most desired properties.

The photocatalyst may be deposited into the structure or on the substrate's surface [4, 5, 6]. In our laboratory, we are now focused mostly on preparing lamellar nanostructured photocatalytic composites [7, 8] and on the preparation of core-shell nanoparticles consisting of inner carrier particles and photocatalytically active shell [4, 9, 10]. The carrier particles are usually prepared by top-down method, which includes various types of milling e.g. using planetary or jet mills or even a new effective method of cavitation disintegration [11]. The shell is then formed on a substrate using a bottom-up method, a precipitation reaction in our case. The reaction takes place in microdroplets (microreactors) [9]. The shell thickness is dependent on the initial concentration

of the first precursor. This concentration significantly affects the final product and therefore should be determined as accurately as possible.

2. THEORY

2.1. Concept of core-shell nanoparticles preparation by aerosol method

When applying the aerosol method for preparation of core-shell photocatalytic nanoparticles, as described in [9], precipitation reaction (1) occurs in a limited space of an aerosol droplet. Droplets, containing carrier particles and the first reactant, are generated in the ultrasonic nebulizer and injected on the surface of a vigorously stirred solution of the second reactant (**Figure 1**). Precipitation reaction takes place only in a limited space which results in forming of a solid phase mostly on the surface of the nanoparticles and creates the desired core-shell structure. With a predominantly consistent droplet size, the reaction space can be considered stable and shells of similar thickness are forming on core particles. Thus, shell thickness is dependent on the concentration of the first reactant in the aerosol droplet.

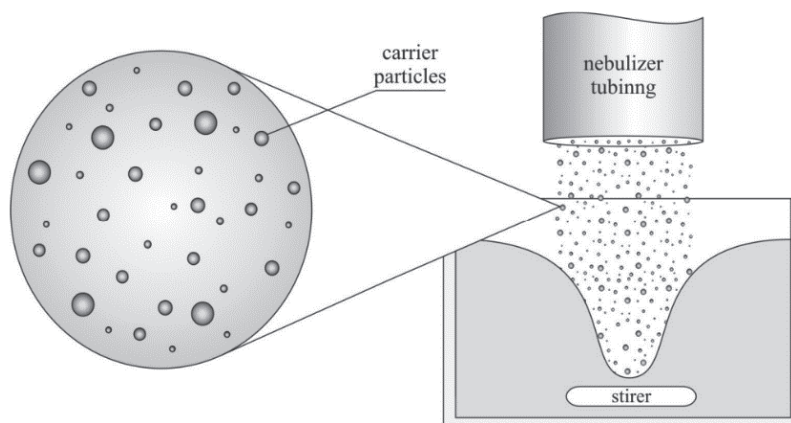


Figure 1 Scheme of a microdroplets injection into the vigorously stirred solution [9]

2.2. Theoretical calculation of the concentration of the first precursor for the preparation of the shell with specific thickness

To determine the needed amount of precursor for the formation of a required shell thickness we use the theoretical calculation of the shell volume. Shell grows as an additional layer on the carrier particle and increases the radius of the whole nanoparticle (**Figure 2**) [9].

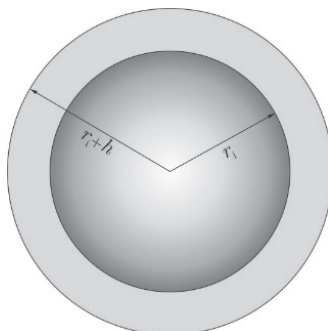


Figure 2 Carrier particle with radius r_i and shell thickness h

Thanks to the theoretically calculated volume of the shell for a specific thickness h , we can determine the amount of a precursor for synthesis of nanoparticles with shell thickness h . The equation (3) is based on the stoichiometry of reaction (1).

$$c_{Si} = \frac{m_{Si}}{V_{Si} + V_{shell-liquid}} = \rho_{Si} \frac{V_{Si}}{V_{Si} + V_{shell-liquid}} \rightarrow V_{shell-liquid} = \frac{V_{Si}(\rho_{Si} - c_{Si})}{c_{Si}} \quad (2)$$

$$V_{shell} \rho_{ZnS} = m_{ZnS} = \frac{M_{ZnS}}{M_{Zn(Ac)_2}} c_{Zn(Ac)_2} V_{shell-liquid} \rightarrow c_{Zn(Ac)_2} = \frac{M_{Zn(Ac)_2}}{M_{ZnS}} \frac{\rho_{ZnS} c_{Si}}{(\rho_{Si} - c_{Si})} \frac{V_{shell}}{V_{Si}} \quad (3)$$

The concentration of carrier particles in the dispersion c_{Si} with a first reactant $Zn(Ac)_2$ is equal to its weight m_{Si} divided by the total volume (sum of the volumes of carrier particles V_{Si} and the volume of liquid $V_{shell-liquid}$) (2). The desired concentration of the first precursor $c_{Zn(Ac)_2}$ depends on exact determination of the shell volume V_{shell} (3).

2.3. Theoretical calculation of the shell volume

Fraction $P_v(r_i)$, determined by dynamic light scattering method (DLS), is equivalent to volume portion v_i of particle with radius r_i divided by the total volume of all carrier particles V_{Si} . Particles are approximated by idealized sphere with radius r_i and n_i is their number (4).

$$P_v(r_i) = \frac{v_i}{V_{Si} = \sum_{i=1}^{\infty} v_i} = \frac{n_i \frac{4}{3} \pi r_i^3}{V_{Si} = \sum_{i=1}^{\infty} n_i \frac{4}{3} \pi r_i^3} \rightarrow n_i = \frac{P_v(r_i) V_{Si}}{\frac{4}{3} \pi r_i^3} \quad (4)$$

$$v_{ci} = n_i \frac{4}{3} \pi ((r_i + h)^3 - r_i^3) \quad (5)$$

Shell volume of one particle is a difference between core-shell particle volume and the volume of the core. The total volumetric increment of the shell of the fraction i (v_{ci}) is then the volume of the shell of one particle multiplied by their total number n_i (5).

2.4. Approximation of shell volume and its error

For very thin layers $h \ll r_i$, we can approximate (5) to the equation (6). The same treatment was used to calculate the shell volume and then the concentration of the precursor in [9].

$$v_{cia} = n_i 4\pi r_i^2 h \quad (6)$$

The size of the approximation error Δv_{ci} (7) is given by the difference between the total theoretical volume of the v_{ci} and the approximated volume v_{cia} .

$$\Delta v_{ci} = v_{ci} - v_{cia} = n_i \frac{4}{3} \pi (r_i h^2 + h^3) \quad (7)$$

We obtain relative error, that we make by approximation of the specific fraction i , by dividing residue of the approximation Δv_{ci} with total theoretical volume v_{ci} (8).

$$\delta_{vi} = \frac{\Delta v_{ci}}{v_{ci}} = 1 - \frac{3}{3 + 3\left(\frac{h}{r_i}\right) + \left(\frac{h}{r_i}\right)^2} \quad (8)$$

The chart in the **Figure 3** shows how this error grows with the h/r_i ratio. Enlarging the sphere by tenth gives the relative error of 10%. With a constant shell thickness h , the error is increasing with smaller radius r_i of the core of core-shell particle. However, to determine the effect of this error on the total volume of all particles we have to count with all particles in the sample.

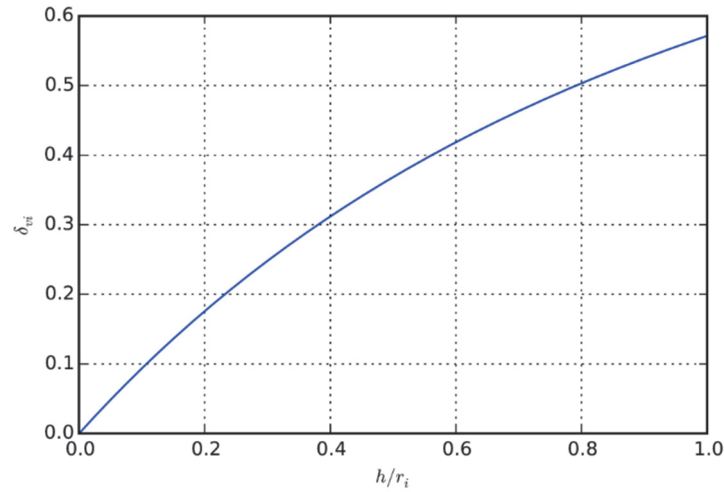


Figure 3 How the relative error changes with the h / r_i ratio

The complete relative error is then expressed by (9). This equation counts with all particles in the sample.

$$\delta_{cv} = \frac{\sum_{i=1}^{\infty} \Delta v_{ci}}{\sum_{i=1}^{\infty} v_{ci}} = \frac{\sum_{i=1}^{\infty} n_i \frac{4}{3} \pi (r_i h^2 + h^3)}{\sum_{i=1}^{\infty} n_i \frac{4}{3} \pi ((r_i + h)^3 - r_i^3)} \quad (9)$$

After substitution from equation (4), substituting $a_i = h / r_i$ and isomorphic transformation of distribution $P_v(r_i) \rightarrow P_v(a_i)$ the relative error δ_{cv} (9) value of approximation is expressed by formula (10).

$$\delta_{cv} = \left(1 + 3 \frac{\sum_{i=1}^{\infty} P_v(a_i) a_i}{\sum_{i=1}^{\infty} P_v(a_i) (3a_i^2 + a_i^3)} \right)^{-1} \quad (10)$$

The total error of approximation is then dependent on ratios $a_i = h / r_i$ of each fraction as well as to their distribution $P_v(a_i)$ in the sample.

If we want to calculate the needed concentration of the reactant $c_{Zn(Ac)_2}$, we substitute the total volume (11) into equation (3) to obtain the formula for calculating concentration of the first precursor (12).

$$V_{shell} = \sum_{i=1}^{\infty} v_{ci} = \sum_{i=1}^{\infty} n_i \frac{4}{3} \pi ((r_i + h)^3 - r_i^3) \quad (11)$$

$$c_{Zn(Ac)_2} = \frac{M_{Zn(Ac)_2}}{M_{ZnS}} \frac{\rho_{ZnS} c_{Si} h}{(\rho_{Si} - c_{Si})} \sum_{i=1}^{\infty} \frac{P_v(v_i)}{r_i} \left(3 + 3 \left(\frac{h}{r_i} \right) + \left(\frac{h}{r_i} \right)^2 \right) \quad (12)$$

The concentration of the first precursor depends on the molar weights $M_{Zn(Ac)_2}$ and M_{ZnS} ratio, densities of core and shell materials ρ_{Si} and ρ_{ZnS} , the concentration of core particles in the dispersion c_{Si} , shell thickness h and the relative distribution of the carrier particles in the dispersion.

3. EXPERIMENT

We have chosen silicon particles as a representative of the specific experimental data. The particles were prepared by cavitation disintegration in Water Jet Mill. From primary particles with an average size of 100 microns we prepared particles with a mean size of 116 nm. Their statistical distribution is shown in a chart (**Figure 4**). Using the approximation calculations (6) and the statistical distribution of primary Si particles (dashed chart in **Figure 4**), the required concentration of zinc acetate for the growth of a layer of thickness $h = 20$ nm was set at 5 g / l [9]. After a reaction, the resulting dispersion of core-shell nanoparticles

(Figure 4 right), was quickly frozen and subjected to vacuum sublimation at -18 °C. With this method, the chaotic distribution of particles is preserved, so they do not agglomerate [7,8,9]. For Si-ZnS core-shell nanoparticles we have achieved a specific surface area of 270 m² / g, which significantly contributes to the efficiency of photocatalytic reaction.

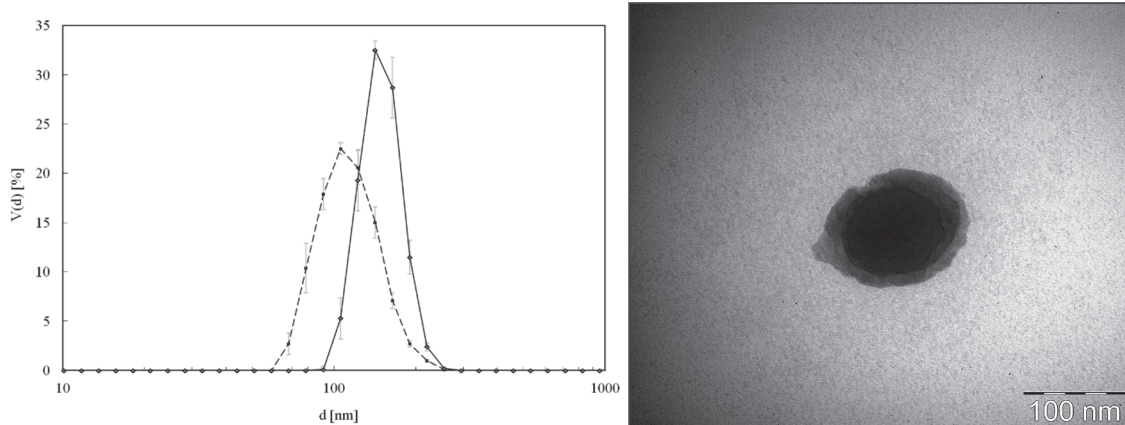


Figure 4 On the left, there are statistical volume sizes distributions of primary Si core particles with a mean diameter 116 nm (dashed line) and Si-ZnS core-shell particles with a mean diameter 150 nm (solid line). The measurement was done by DLS Malvern Zetasizer 360 ZEN Nano ZS analyzer [9]. TEM micrograph of core-shell particle Si-ZnS with mean thickness value of 18 nm (TEM Jeol JEM 1230, 80 kV) is on the right side [9]

4. CONCLUSION

The exact model, discussed in this paper, is a generalization and refining of reactants amount calculation that is needed for core-shell particles synthesis using aerosol droplets. We can synthesize photocatalytic nanoparticles with a narrow size distribution with this method. Moreover, we can adjust their size by changing input parameters. The results show, that in our case, it is reasonable to calculate the theoretical volume of the shell without any approximation. But we also should take into account that we use only a simple geometry, which counts with smooth surface of the core particles and uniform shell thickness. Shell growth is also affected by the reaction kinetics, which slow down with decreasing amount of reactants. As a consequence, not all of the Zn(Ac)₂ transforms to ZnS. Another source of errors, especially for wider size distributions, is also the dependence of the saturation level of the reaction product concentration on the surface curvature of carrier nanoparticles. This is also cause of Ostwald ripening. It can be stated that the discussing of approximation is particularly suitable for narrow size distributions of the core particles and a thin outer shell of the reaction product.

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