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Formation of mesoporous silica coating on cores with different surface properties

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Abstract. An approach has been developed for the wet synthesis of mesoporous silica shell on the surface of various spherical composite particles with different zeta potential. It is demonstrated that the surface charge of the core particles influences the porous structure of the obtained shell. The proposed method allows obtaining a uniform layer of the same thickness on the surface of each core particle preventing their coalescence.

Keywords: spherical particles, core-shell nanostructures, silica, zeta potential, mesopores

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Формирование оболочки мезопористого кремнезема на частицах с разными свойствами поверхности

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Аннотация. Разработан подход к покрытию сферических композитных частиц с различным дзета-потенциалом, находящихся в жидкой среде, оболочкой мезопористого кремнезема. Показано, что заряд поверхности частиц, выступающих в качестве ядра, оказывает влияние на пористую структуру формируемой оболочки. Метод позволяет осуществлять равномерное покрытие каждой частицы оболочкой одинаковой толщины, не приводя к коагуляции исходных ядер.

Ключевые слова: сферические частицы, наноструктуры ядро-оболочка, кремнезем, электрокинетический потенциал, мезопоры

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Introduction

Nanotechnology has been a wide and growing field of research since the end of the last century. It deals with materials of various types at nanoscale level, where they demonstrate novel properties compared to their bulk counterparts. The synthesis, characterization, and applications of nanoparticles are among the most important sections of the wide range of nanotechnology areas [1]. To expand the functionality of this kind of materials researchers create not only single-composition nanoparticles, which are made from single substance, but also composite ones often possessing the so-called core-shell structure. The purpose of the coating can be varied, such as surface modification, increasing the functionality, stability, reduction in consumption of precious materials, and so on [1]. Core/shell nanoparticles are gradually attracting more and more attention, since they exhibit distinctive properties of the different materials applied together, which is especially important to meet the diverse application requirements. They are widely used in, for example, catalysis [2, 3], electronics [4, 5], biomedicine [6, 7]. For biomedical purposes silica shell is highly sought after, since silica is biocompatible (approved by FDA and EFSA), possess tunable surface functionalization, high adsorption capacity, and allows protecting healthy tissues from interaction with toxic drugs. Still the coating of various nanoparticle with silica shell may be challenging due to different surface properties especially zeta potential of the core particles, which is often not enough (in absolute value) to form stable suspension at neutral pH. As a result, the coagulation can occur hindering the formation of a uniform shell on the surface of each particle.

Materials and Methods

Materials. We used the following reagents: cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}N(CH_3)_3Br$), 99.99% (Acros Organics, Germany); aqueous ammonia (NH_3), 24 wt.%; ethanol (C_2H_5OH), 95.7 vol.%; deionized water (H_2O) with a resistance of 10 MΩ; tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$), 99.9% (Acros Organics, Germany); gadolinium oxide (Gd_2O_3), 99.99% (Sigma-Aldrich, Germany); Iron (III) nitrate crystal hydrate ($Fe(NO_3)_3{\cdot}9H_2O$) $\geq 98\%$ (Sigma-Aldrich, Germany); nitric acid (HNO_3), 70 wt.%; hydrochloric acid (HCl), 37 wt.%, ACS reagent grade; monosilane (SiH_4), electronic grade (Sigma-Aldrich, Germany). All the chemicals were of analytical purity grade commercially available. There was no need to additionally purify the reagents.

Methods. The core particles were obtained based on our previously developed methods for the synthesis of silica and various silica-based composite materials. In particular, the procedure for the synthesis of non-porous spherical silica particles ($nSiO_2$) was similar to that employed in [8, 9]. For the synthesis of spherical mesoporous silica ($mSiO_2$) particles filled with magnetite ($mSiO_2/Fe_3O_4$) we used the developed method for the filling of various silica matrices with iron oxides [10, 11]. Spherical mesoporous silica particles filled with gadolinium oxide ($mSiO_2/Gd_2O_3$) were synthesized based on the technique described in [12, 13]. For the synthesis of silicon within the pores of spherical mesoporous silica particles ($mSiO_2$/Si) we used the modified method of monosilane thermal decomposition [14, 15].

The synthesis of mesoporous silica shell was carried out via basic hydrolysis of TEOS in a water-ammonia-ethanol mixture containing organic pore-forming agent – CTAB. The molar ratio of the reagents TEOS:H_2O:NH_3:C_2H_5OH:CTAB was 1:370:10:230:0.2. The core particles added to the reaction mixture acted as nucleation centers. TEOS was added dropwise under stirring to the resulting solution. After 6 h of further stirring, the particles obtained were washed in an alcoholic solution (0.01 M) of HCl, centrifuged, dried in air at 80 °C for 24 h, and calcined at 250 °C for 5 h.

Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with Bruker XFlash 6T-30 energy dispersive X-ray (EDX) spectrometer. The nitrogen adsorption was performed using a Micromeritics 3FLEX at a temperature of 77 K. The specific surface area was calculated by the Brunauer – Emmett – Teller (BET) method, and the pore size distribution was found using the nonlocal density functional theory (NLDFT). The electrophoretic mobility of the particles was determined by the method of electrophoretic light scattering at a temperature of 25 °C with a Zetasizer Nano (Malvern, UK). The electrokinetic potential was calculated using the built-in software package of the analyzer.

Results and Discussion

We used various spherical particles, namely $nSiO_2$, $mSiO_2/Si$, $mSiO_2/Fe_3O_4$ and $mSiO_2/Gd_2O_3$ possessing different surface properties as the cores for the covering with mesoporous silica shell. The results of the zeta potential measurements show (Fig. 1, *a*) that all the particles possess different surface charge almost in the whole range of pH values under study.

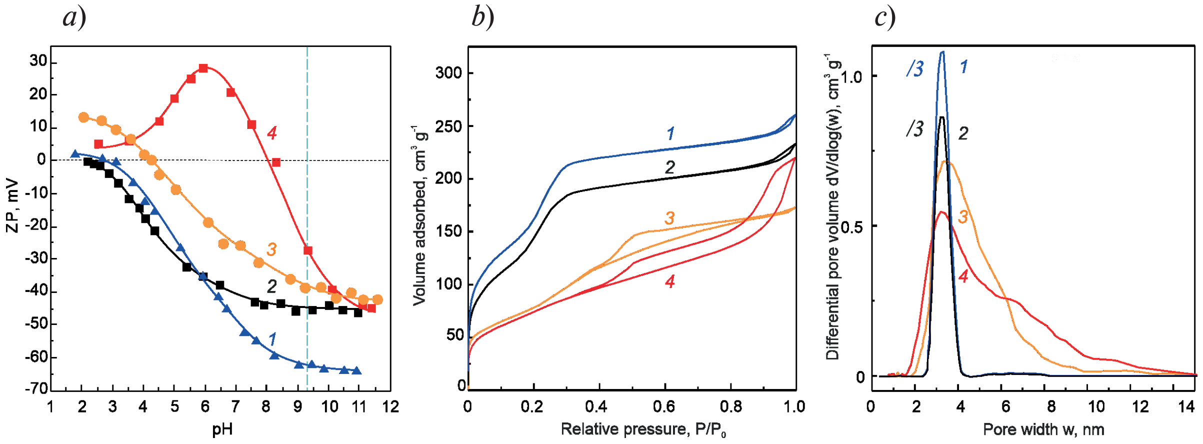

Fig. 1. Zeta potentials of $nSiO_2$ (*1*), $mSiO_2/Si$ (*2*), $mSiO_2/Fe_3O_4$ (*3*) and $mSiO_2/Gd_2O_3$ (*4*) particles at different pH (*a*); N_2 adsorption and desorption isotherms measured at 77 K (*b*) and NLDFT pore size distributions (*c*) for the same particles covered with a mesoporous silica shell. Blue vertical dashed line in panel (*a*) indicates pH of the reaction mixture used

As stated earlier the synthesis of mesoporous silica shell was carried out in the mixture of water, ammonia and ethanol containing core particles. After the addition of TEOS to the mixture the formation of mesoporous silica proceeds by an aggregative mechanism, when CTAB forms cylindrical micelles, which are covered, as a result of TEOS hydrolysis with a layer of amorphous SiO_2. Then, the 10-nm SiO_2/CTAB clusters coagulate with the formation of the shell on the surface of core particles [12]. Pores remain in place of CTAB after its removal by thermal annealing. The pH of the reaction mixture was adjusted to ~9.3 (marked by a blue dashed line in Fig. 1, *a*). At this value all the particles possess negative surface charge over −30 mV, which indicates their aggregative stability. This determines the fact that they do not coagulate and present in the solution as individual particles, which ensures the coating of each particle with a silica layer of the same thickness without their coalescence.

Fig. 1, *b* show the isotherms for the particles after coating with shell. It can be seen, that for the non-porous SiO_2 and $mSiO_2/Si$ particles possessing the highest in absolute value zeta potential the largest amount of the adsorbate is observed after the coating. The BET specific surface area (SSA) values calculated for these particles are 580 and 530 $m^2\,g^{-1}$ respectively. The corresponding pore volumes are 0.41 and 0.37 $cm^3\,g^{-1}$. The pore size distribution (Fig. 1, *c*) indicates the presence of one pronounced peak at 3.1 nm, which corresponds to the size of CTAB micelles. When the surface charge of core particles decreases in absolute value (in the case of $mSiO_2/Fe_3O_4$ and $mSiO_2/Gd_2O_3$ particles) isotherms of the particles after coating are lower indicating the lower BET SSA. Indeed, the corresponding values are 320 and 270 $m^2\,g^{-1}$. This may be due to that CTAB molecules in the vicinity of surface with lower charge form the so-called platelet micelles, rather than cylindrical produced in the case of $nSiO_2$ and $mSiO_2/Si$ particles possessing higher negative surface charge, which leads to the formation of larger pores with lower SSA. This is confirmed by the pore size distributions (Fig. 1, *c*), which is substantially wider in this case. Note, the pronounced peak at 3.1 nm remains. Probably, larger pores are formed closer to the cores in the place of platelet CTAB micelles. Then, after a certain thickness the subsequent growth of the shell continues via coagulation of SiO_2/CTAB clusters consisting of cylindrical CTAB micelles, which determines the formation of 3-nm pores. The obtained values of pore volume for $mSiO_2/Fe_3O_4$–shell and $mSiO_2/Gd_2O_3$–shell are 0.37 and 0.33 $cm^3\ g^{-1}$ respectively. The dependence of the zeta potential on pH for all the particles after coating is similar to that of $nSiO_2$ particles (Fig. 1, *a* curve *1*). Such values of the particles' surface charge ensure their aggregative stability at pH greater than 5, which is important from the practical point of view.

Fig. 2 shows TEM images of the obtained core-shell particles. The boundaries of the core and shell are clearly distinguishable. It can be seen that the covering of particles with mesoporous silica shell do not affect the morphology of the initial core particles, which remain spherical and do not coagulate. EDX elemental maps demonstrate that there is no redistribution of the core materials during silica shell synthesis. They are still homogeneously distributed within the cores of particles, and the shell in all the cases is fully composed of SiO_2. The TEM results are also confirmed the formation of a uniform mesoporous silica layer of the same thickness on the surface of cores. Note, the thickness of the shell can be controllably varied by the concentrations of reagents in the reaction mixture. The technique we developed allows obtaining shells with a thickness from tens of nanometers to several hundreds.

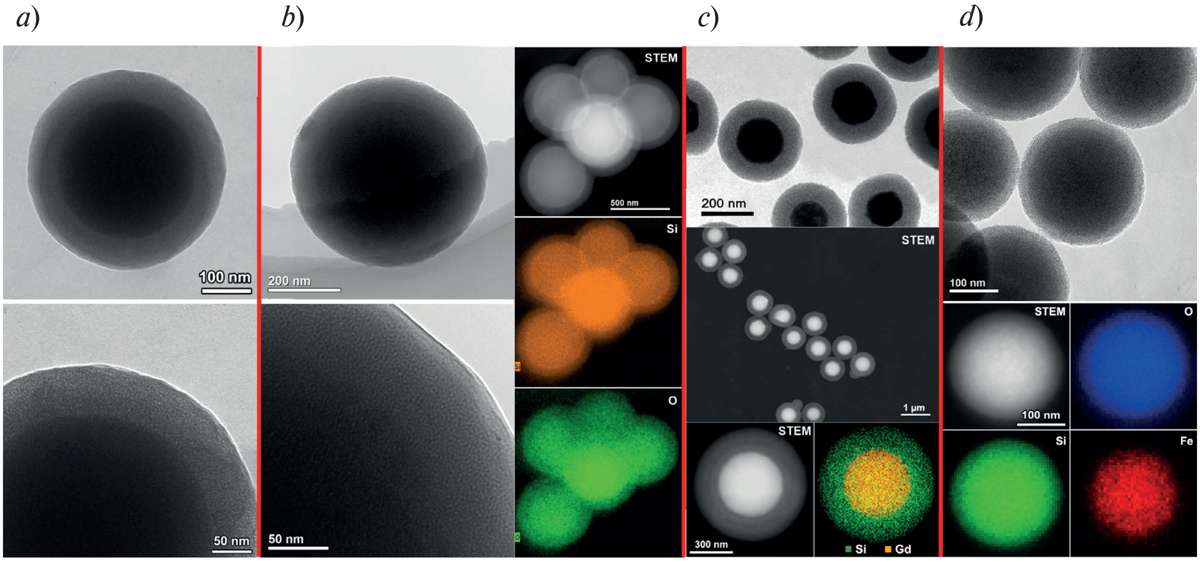

Fig. 2. TEM and STEM images and EDX elemental maps for the $nSiO_2$-shell (*a*), $mSiO_2$/Si-shell (*b*), $mSiO_2/Gd_2O_3$-shell (*c*) and $mSiO_2/Fe_3O_4$-shell (*d*) particles. There are no EDX maps for the $nSiO_2$-shell particles, since the core and the shell of the particles are made of the same material

Conclusion

An approach for the covering of various spherical particles having different surface charge with mesoporous silica shell possessing high SSA and pore volume is proposed. The synthesis of shell is carried out via basic hydrolysis of organosilane in a water-ammonia-ethanol mixture containing pore-forming agent. The synthetic conditions are selected in such a way that the cores are present in a form of aggregatively stable particles ensuring the formation of uniform layer of the same thickness on each particle. It is found that the lower the zeta potential of core is the wider the pore size distribution of the resulted shell is observed, however with the presence of a characteristic peak at 3.1 nm. The developed technique is a promising tool for the obtaining core-shell particles for biomedical applications that allows protecting the core and expanding the functionality of the particles.

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