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# Synthesis and characterization of mesoporous silica core-shell particles

Milan Nikolić[1], Konstantinos P. Giannakopoulos[2], Vladimir V. Srdić[1]

[1]*Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Novi Sad, Serbia*
[2]*Institute of Materials Science, National Centre for Scientific Research "Demokritos", Athens, Greece*

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## Abstract

*Core-shell particles were formed by deposition of primary silica particles synthesized from sodium silicate solution on functionalized silica core particles (having size of ~0.5 μm) prepared by hydrolysis and condensation of tetraethylortosilicate. The obtained mesoporous shell has thickness of about 60 nm and consists of primary silica particles with average size of ~21 nm. Scanning electron microscopy and zeta potential measurements showed that continuous silica shell exists around functionalized core particles which was additionally proved by FTIR and TEM results*

***Keywords**: silica, core-shell particles, synthesis*

## I. Introduction

Mesoporous silica particles have found applications in a number of areas such as heterogeneous catalysis, adsorption, molecular separation and enzyme immobilization, as they are environmentally acceptable, structurally stable, chemically resistant to organic solvents and microbial attack and have high surface area and average pore size between 2–50 nm [1]. There are several reasons for using enzyme in an immobilized form [2–4]. Above all, the immobilizing methods make separation of the enzyme from reaction medium easy enabling its reuse and eliminating protein contamination of product. A further benefit is often enhanced stability, under both storage and operational conditions, e.g. towards denaturation by heat or organic solvent. These are the reasons for intensive studies of immobilization of various enzymes onto mesoporous silica materials as supports [5–9].

Recently, major challenges for the preparation of nanoparticle systems include development of new compositions and the fabrication of multifunctional systems with specific architectures. Thus, numerous particle systems have been developed and fabricated by assembling diverse nanoparticles on, encapsulated within, or integrated both inside and on the surface of silica nanoparticles using different synthesis methods. Properly coated or surface-modified nanoparticles can offer a high potential for numerous applications, due to change of their interfacial characteristic and electrical, magnetic or optical properties [10,11]. Thus, extensive research has been devoted to the synthesis of core/shell particles including copolymerization of hydrophobic monomer core-hydrophilic shells [10], template-directed self-assembly [12], template-directed living polymerization [13], intramicellar polymerization [14] and encapsulation of silica nanoparticles by in situ polymerization [15]. Very attractive method involves the heterocoagulation of oppositely charged core and shell particles, which was the basic idea in this work. It is known that silica particles synthesized by the Stöber method [16] are uniform spheres, but have very small pore size and total pore volume, which make them unfavourable for enzyme immobilization [17]. On the other side, silica particles synthesized from highly basic sodium silicate solutions have nonuniform size and shape, but have pore size and average total pore volume large enough for the enzyme immobilisation to take place inside pores of these particles [18]. In this paper, monodispersed silica spheres, synthesized by the Stöber method (i.e. by hydrolysis and condensation of tetraethilortosilicate), were used

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[*] Corresponding author: tel: tel: +381 21 485 3665,
fax: +381 21 450 413, e-mail: *milanik@uns.ac.rs*

as templates for assembly of silica nanoparticles synthesized from highly basic sodium silicate solutions, which resulted in the formation of core-shell particles. The obtained particles were characterised for their suitability for enzyme immobilization inside mesoporous shell.

## II. Experimental

### *2.1 Preparation of silica core particles*

Silica core particles (sample C) were synthesized by hydrolysis and condensation of tetraethylortosilicate, TEOS ($Si(OC_4H_9)_4$, Fluka). TEOS was dissolved in anhydrous ethanol and hydrolized with distilled water under basic condition (25% $NH_3$, Merck). The sample was synthesized using a molar ratio TEOS : $H_2O$ : $NH_4OH$ = 1 : 40 : 4 and TEOS concentration of 0.25 mol/l. After feeding, the product suspension was continuously stirred at room temperature for 1h. The white precipitated powder was centrifuged and washed with distilled water until the effluent was free of $NH_4^+$ groups, and finally dried at 120°C for 1 day.

### *2.2 Functionalization of silica particles*

In order to enable attractive electrostatic assembly of silica nanoparticles on silica core, the functionalization of core with 3-aminopropyltriethoxysilane was performed (sample $C_f$). The modified silica particles were prepared according to the following procedure: silica particles (1.2 g) were suspended in dry acetone (70 ml) under mechanical stirring followed by addition of 1 ml of aminopropyltriethoxysilane. The suspension was stirred for 24 hour. Modified particles were centrifuged and washed with anhydrous acetone. The excess of solvent was evaporated at 80°C.

### *2.3 Synthesis of silica shell on functionalized silica core particles*

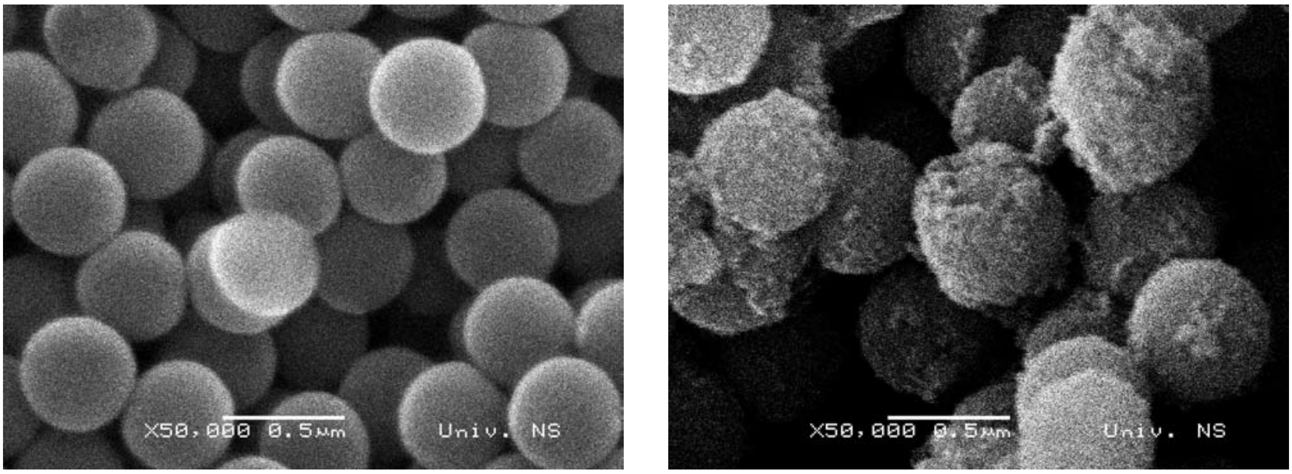
The as-synthesized $SiO_2$ core particles were used as templates for assembly of mesoporous silica layer on their surface. The $SiO_2$ core particles were dispersed in highly basic sodium silicate solution (Water glass, Alumina Factory-Birač, Zvornik) having $SiO_2$/$Na_2O$ molar ratio 3.5 mol/mol and concentration of $SiO_2$ 0.6 mol/l. The weight ratio between $SiO_2$ core particles and $SiO_2$ in sodium silicate solution was 1.5. To precipitate silica particles on a $SiO_2$ core particles, a sulfuric acid ($H_2SO_4$=2 mol/l) was slowly added into a well stirred sodium silicate solution at 85°C and after several minutes the silica particles were formed. The as-synthesized core-shell particles were washed with distilled water, separated from liquid phase by centrifugation and finally dried at 120°C for one day (sample $C_f$S-1.5).

### *2.4 Characterization of silica particles*

Particle size was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, Malvern, United Kingdom) and zeta potential of particles was determined by phase analysis light scattering and mixed mode measurement (Zetasizer Nano ZS with MPT-2 Autotitrator Malvern Instruments, Malvern, United Kingdom). Fourier-transform infrared (FTIR) spectra were collected in transmission by Nicolet-Nexus 670 FT-IR instrument from 650–4000 $cm^{-1}$ using KBr as reference. Size and morphology of particles were examined using a scanning electron microscope (SEM JEOL, 6460 LV, Tokyo, Japan) operating at 20 kV. Transmission electron microscopy (Philips M 20, Eindhoven, The Netherlands) was used to monitor the morphology and thickness of nanoparticle layers.

## III. Results and discussion

Silica nanoparticles were formed by polymerization of silicic acid which was induced by acidic neutralization of sodium silicate solution, and then precipitated on functionalized $SiO_2$ core particles to form



a) b)

**Figure 1. Morphology of $SiO_2$ particles. (a) SEM image of $SiO_2$ core particles, (b) SEM image of core-shell particles synthesized by precipitation of silica nanoparticles on functionalized $SiO_2$ core particles ($C_f$S-1.5)**

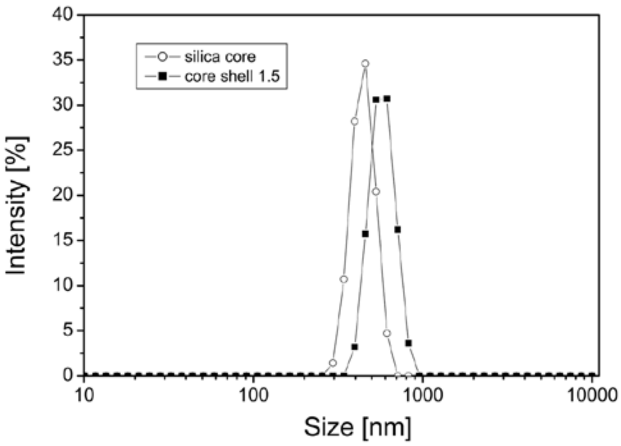


**Figure 2. Particle size distribution of silica cores (C) and core-shell particles ($C_f$S-1.5)**

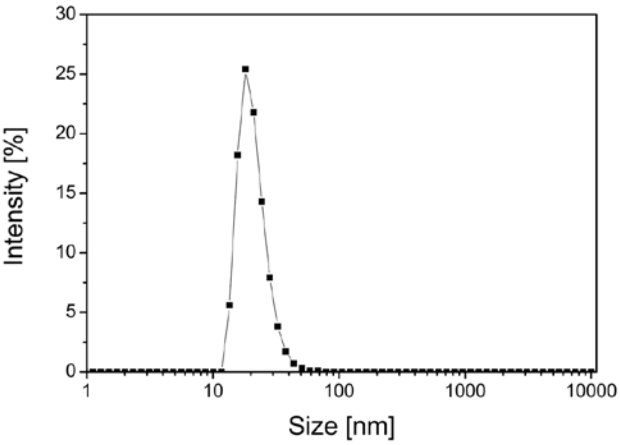


**Figure 3. Particle size distribution of primary particles before aggregation on silica core particles**

shell layer. The smooth surface of the $SiO_2$ core particles (Fig. 1a) was roughened due to deposition of the silica nanoparticles and shell was obtained around silica cores (Fig. 1b).

Number particle size distribution of the samples C and $C_f$S-1.5 is presented in Fig. 2. The average particle size of the samples C and $C_f$S-1.5 is 448 nm and 581 nm, respectively, and reveals the existence of silica shell on functionalized silica cores as it is also visible on SEM micrograph (Fig. 1b). Size distribution of silica nanoparticles attached on the surface of silica core was also determined. The measurement was done on the separately prepared sample at the moment of aggregation of small silica nanoparticles on the surface of core spheres. As it can be seen from Fig. 3 the average size of these primary particles is ~ 21 nm.

The zeta potential versus pH of the core-shell particles was measured to confirm shell continuity around functionalized silica core particles, as presented in Fig. 4. As it was shown, isoelectric point of functionalized silica particles (the sample $C_f$) was 8.2, while the isoelectric point of the core-shell particles (the sample $C_f$S-1.5) and non-functionalized silica core particles (the sample C) was 2.62 and 2.5, respectively. Thus, in the case of core-shell particles (the sample CS-1.5), behaviour of the surface charge according to the pH was very similar to that of non-functionalized silica particles, implying that functionalized silica core particles were mostly shelled with silica nanoparticles.

The difference in pore structure between core and core-shell particles was confirmed by FTIR measurement, as it was shown in Fig. 5. The peak at about 960 $cm^{-1}$ which corresponds to stretching vibration of Si-O-H bonds [19] is very pronounced in the sample $C_f$S1.5 and this could be explained by the existence of higher portion of surface O-(H...$H_2$O) groups bounded to Si. This is due to the higher specific surface area and finer pore structure [17], which originates from mesoporos shell around core particles. The shoulder at about 1200 $cm^{-1}$, which is due to three dimensional Si–O–Si work asymmetric stretching vibrations [20] is more pronounced which also indicates high specific area and finer pore structure as a consequence of mesoporous shell synthesized from highly basic sodi-

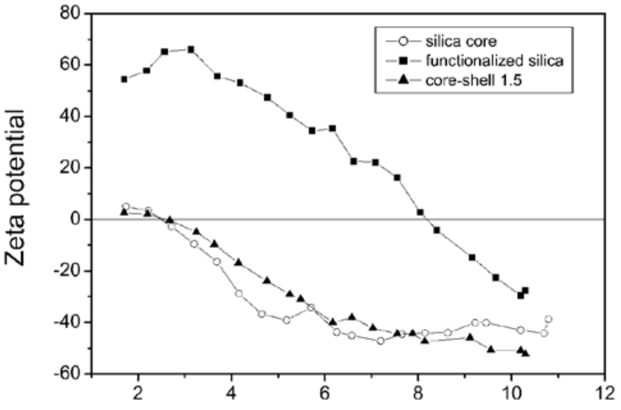


**Figure 4. Isoelectric titrations graphs of pure silica particles (C), amino-modified silica particles ($C_f$) and core-shell particles ($C_f$S-1.5)**

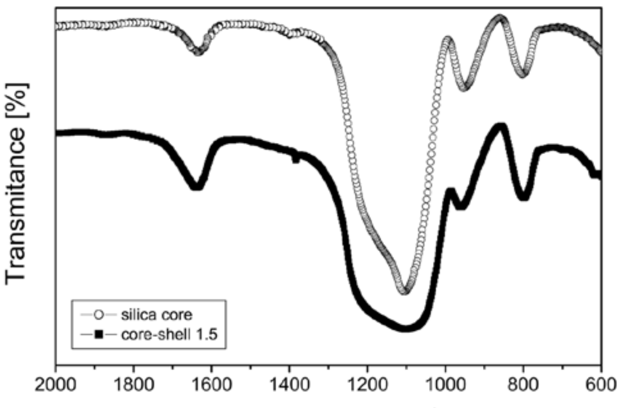


**Figure 5. FTIR spectra of core and core-shell silica particles**

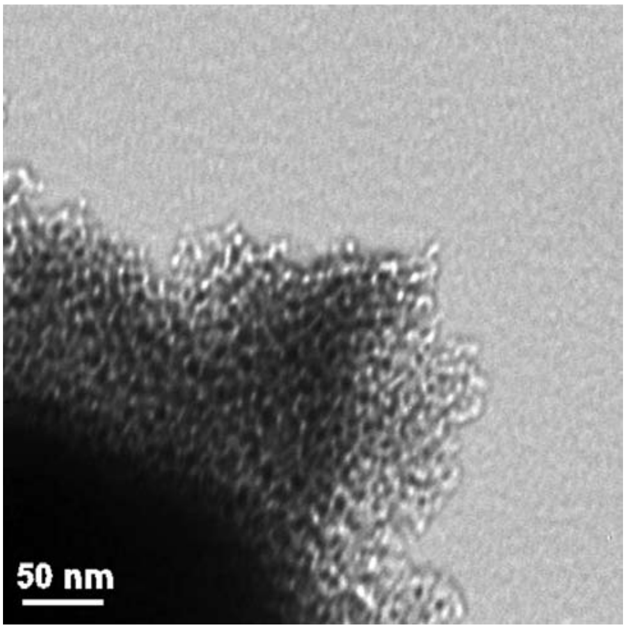


Figure 6. TEM micrograph of mesoporous silica shell

um silicate solution [17]. Mesoporous structure of silica shell was also confirmed by TEM micrograph as it was shown in Fig. 6.

## IV. Conclusions

Core-shell particles were formed by deposition of primary particles synthesized from sodium silicate solution on functionalized silica core particles prepared by hydrolysis and condensation of tetraethylortosilicate. Average shell thickness is about 60 nm that is consisted of primary silica particles with average size of ~21 nm. Zeta potential measurements and SEM analysis showed that continuous shell exists around core particles. FTIR measurements indicated on the complex structure of core-shell particles and mesoporous structure of shell was confirmed by TEM measurement.

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