Supplementary Information

Facile synthesis of SnO₂ shell followed by microwave treatment for high environmental stability of Ag nanoparticles

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ABSTRACT

This study describes a new method of passivating Ag nanoparticles (AgNPs) with an SnO₂ layer and its further treatment by microwave irradiation. The one-step process of SnO₂ layer formation was carried out by adding sodium stannate to the boiling aqueous AgNPs solution and resulted in the formation of core@shell Ag@SnO₂ nanoparticles. The coating formation was a tunable process, making it possible to obtain an SnO₂ layer thickness from 2 to 13 nm. The morphology, size, zeta-potential, and optical properties of the Ag@SnO₂NPs were studied. The microwave irradiation significantly improved the environmental resistance of Ag@SnO₂NPs, which remained stable in different biological solutions such as NaCl at 150 mM and 0.1 M, Tris-buffered saline buffer at 0.1 M, and phosphate buffer at pH 5.6, 7.0, and 8.0. Ag@SnO₂NPs after microwave irradiation were also stable in out of biologically relevant values, both highly acidic (1.4) and alkaline (13.2). Moreover, AgNPs covered with a 13-nm-thick SnO₂ layer were resistant to cyanide up to 0.1 wt.% The microwave treated SnO₂ shell can facilitate the introduction of AgNPs in various solutions and extend their potential application in biological environments by protecting the metal nanostructures from dissolution and aggregation.

Na ₂ SnO ₃ ·3H ₂ O (0.25 %wt.) added to 40 ml AgNPs (25 ppm)	0.57 g	0.86 g	1.71 g	2.85 g	5.70 g
covering	partial	partial	full	full	full
shell thickness	2.0 nm	3.5 nm	6.5 nm	8.5 nm	13.0 nm
(% covering)	~30%	~50%	~100%	~130%	~200%
mean diameter of Ag@SnO ₂ NPs	17 nm	20 nm	26 nm	30 nm	39 nm
mean diameter of Ag@SnO ₂ NPs after irradiation	21 nm	22 nm	28 nm	31 nm	41 nm
increase of the diameter value after irradiation	4 nm	2 nm	2 nm	1 nm	2 nm

Table S1 STEM analysis of the morphology and shell thickness measurements of $Ag@SnO_2NPs$. The average diameter of AgNPs was estimated to be about 13 (± 1) nm.



Fig. S1 STEM image of core@shell Ag@SnO₂NP characterized by 13-nm-thick SnO₂ shell.

Calculation details of sodium stannate amount for the formation of the thickest shell of SnO₂

The AgNPs in our system have a mean diameter of about 13 nm.

40 g of AgNPs solution at a concentration of 25 ppm (C% = 0.0025% wt.) was taken for each shell synthesis process.

The assumption is that $Ag@SnO_2NP$ mean diameter is about 33 nm. It allows calculating the volume and final mass of each system component.

AgNPs mass and volume in 40 g of 0.0025%wt. colloid is 0.001g and $9.52 \cdot 10^{-5}$ cm⁻³, respectively (Ag density – 10.5 g/cm³).

The volume of single NP was calculated based on the assumption that it is a kind of sphere, which volume is defined by a formula of $V = 4/3\pi r^3$,

where r is a sphere radius (0.00000065 cm³ for AgNP and 0.00000165 cm³ for Ag@SnO₂NP). The volume of single NPs was calculated to be about $1.15 \cdot 10^{-18}$ cm³ and $1.88 \cdot 10^{-17}$ cm³ for AgNP and Ag@SnO₂NP, respectively. It means that shell volume on a single particle is about $1.766 \cdot 10^{-17}$ cm³.

The whole volume for SnO_2 in colloid $(1.46 \cdot 10^{-3} \text{ cm}^3)$ is defined by shell volume on a single particle and number of the particles in the colloid. The number of the particles in the colloid, it is a whole Ag volume in the solution divided by the volume of single AgNP and is about $8.28 \cdot 10^{-13}$.

The result of dividing the volume of SnO_2 in the solution (1.46·10⁻³ cm³) by the density of SnO_2 (6.99 g/cm³) determines its mass, which is about 0.01g. The molecular weight of SnO_2 is 150.71 g/mol, and for the previously calculated mass of 0.01g, there is 6.7 mol.

The multiplying 6.7 mol by the molecular weight of sodium stannate trihydrate $(Na_2SnO_3 \cdot 3H_2O - 212.69 \text{ g/mol})$ gives its final mass of 0.0142g. In fact that we introduce sodium stannate trihydrate as an aqueous solution at 0.25%wt. concentration, it means that the final amount of the added solution is **5.7** g.



Fig. S2 AgNPs covered with 0, 2, 3.5, 6.5, 8.5 and 13-nm-thick SnO₂ shell (from left to right), solutions at 25 ppm concentration of AgNPs.



Fig. S3 DLS size distribution by intensity and STEM image (inset) of unmodified AgNPs.



Fig. S4 EDS spectra of $Ag@SnO_2NPs$ covered with 13-thick-SnO₂ shell (a) before and (b) after microwave irradiation.



Fig. S5 (a-c) XPS survey spectra and (d-f) core level XPS (a) Ag 3d and (b, c) Sn 3d of (a, d) AgNPs, (b, e) Ag@SnO₂NPs and (c, f) Ag@SnO₂NPs after microwave treatment.



Fig. S6 AgNPs and Ag@SnO₂NPs samples after microwave treatment and four times rinsing in deionized water.



Fig. S7 UV/Vis diffuse reflectance spectra of (a) SnO₂NPs and (b) Ag@SnO₂NPs covered with 13–thick-SnO₂ shell, before and after microwave irradiation.



Fig. S8 Absorbance spectra of Ag@SnO₂NPs after microwave treatment and four times rinsing in deionized water.



Fig. S9 Absorbance spectra of AgNPs and $Ag@SnO_2NPs$ before (a) and after microwave treatment (b).



Fig. S10 Absorbance spectra of AgNPs and AgNPs covered with SnO_2 in 0.1M TBS before (a) and after microwave treatment (b).



Fig. S11 Absorbance spectra of AgNPs and AgNPs covered with SnO₂ in 150 mM NaCl (a) before and (b) after microwave treatment and images of the NPs treated with 150 mM NaCl (c) for 1h and (d) 72h.



Fig. S12 Absorbance spectra of AgNPs and AgNPs covered with SnO_2 in 150 mM NaCl before (a) and after microwave treatment (b).



Fig. S13 (a) Absorbance spectra of $Ag@SnO_2NPs$ (13-nm-thick SnO_2 shell) immersed in NaCl at concentration of 150 mM and 1.5 M and control samples: AgNPs and Ag@SnO_2NPs (13-nm-thick SnO_2 shell) immersed in water. (b) Image of AgNPs and Ag@SnO_2NPs (13-nm-thick SnO_2 shell) immersed in 1.5 M NaCl.



Fig. S14 Absorbance spectra of AgNPs covered with 3.5 and 13-nm-thick SnO_2 shell (a) non-treated and (b) treated with microwaves and further immersed in phosphate buffer at 0.1 M and pH of 5.6, 7.0 and 8.0.



Fig. S15 Images of AgNPs samples covered with 0, 2, 3.5, 6.5, 8.5, 13-nm-thick SnO_2 shell (a) before and (b) after microwave treatment, immersed in phosphate buffer at 0.1M and pH 5.6, 7.0 and 8.0.



Fig. S16 Absorbance spectra of aqueous solutions of (a) AgNPs and (b, c) Ag@SnO₂NPs covered with 3.5 and 13–thick-SnO₂ shell (a, b) non-treated and (c) treated with microwaves at pH 1.4 and 13.2.



Fig. S17 Absorbance spectra of AgNPs and AgNPs covered with SnO_2 in 0.005% wt. KCN after microwave treatment.



Fig. S18 Absorbance spectra of AgNPs and AgNPs covered with SnO_2 (13 nm) in different concentration of KCN (a) before and (b) after microwave treatment.