



Methylviologen mediated electrochemical reduction of AgCl—A new route to produce a silica core/Ag shell nanocomposite material in solution



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ABSTRACT

Methylviologen mediated electrochemical reduction of AgCl precipitate to Ag⁰ in the presence of alkylamino-modified silica nanoparticles (SiO₂-NHR) in an aqueous medium was performed. The main products of reduction at potentials of the MV²⁺/MV^{•+} redox couple are spherical SiO₂-NHR/Ag core/shell nanoparticles (size range 120–160 nm) in solution.

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1. Introduction

In recent years, metal nanoparticles are one of the most widely studied nano-objects. The keen interest in these objects is due to the wide variety of their potential applications in catalytic, biomedical, optical, electronic and other fields [1–7]. The methods of preparation of metal nanoparticles are quite diverse. They can be tentatively divided into physical, chemical, biochemical and electrochemical methods. Currently, chemical reduction of metal ions (complexes) in solution using various reducing agents is the most successful method.

The electrochemical method is widely used to produce metal nanoparticles immobilized on a conducting support (electrode). Various implementations of this method are summarized in the fundamental review by O.A. Petrii [8]. However, electrochemical methods for the preparation of metal nanoparticles in other states (in solution, on non-conductive solid supports, in matrices, in nanocapsules, etc.) that are in greater demand have been developed much less thoroughly. Metal nanoparticles are prepared in solution using pulse sonoelectrochemistry [9–11], Reetz's method [12–16] and mediated electrosynthesis [17–20]. The latter method compares favorably with the previous two ones in that the reduction of metal ions is moved from the electrode surface into solution. This method gives a principally new possibility for production of metal nanoparticles in the case where direct reduction of metal ions at the electrode is difficult or impossible, for instance due to

insolubility or low solubility of their salts; when they are encapsulated in the micelles, polymer globules or other matrices; and when they are immobilized on a non-conductive solid support. This paper demonstrates this possibility for methylviologen mediated reduction of insoluble AgCl salt in the presence of alkylamino-modified silica nanoparticles

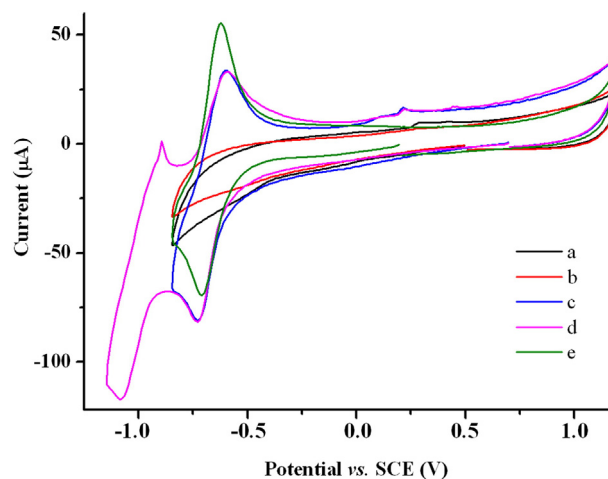
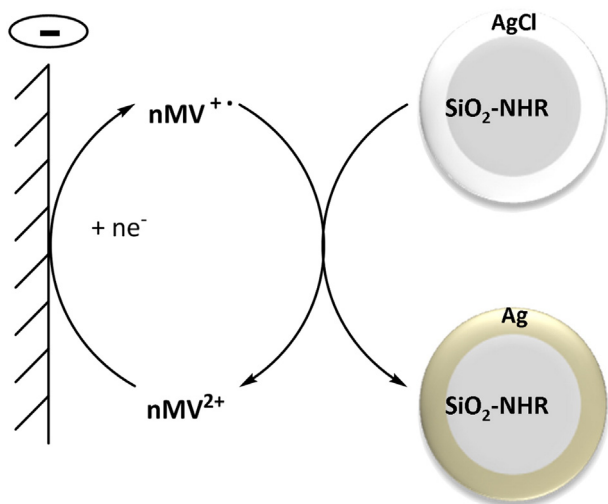


Fig. 1. CV curves for 0.2 g/L AgCl (a), 0.2 g/L AgCl + 1.0 g/L SiO₂-NHR (b), 0.2 g/L AgCl + 1.0 g/L SiO₂-NHR + 2 mM MV²⁺ (c, d) and 1.0 g/L SiO₂-NHR + 2 mM MV²⁺ (e). H₂O, 0.1 M NaBF₄, glass carbon electrode. $\nu = 00$ mV/s.

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Scheme 1. Mediated electrochemical reduction of AgCl.

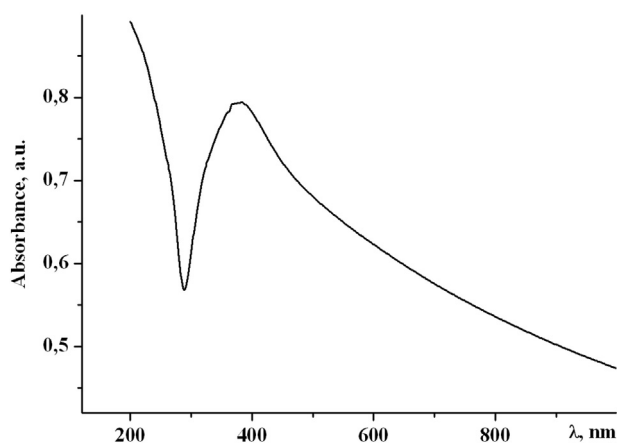


Fig. 2. UV-vis spectrum of the system 0.2 g/L AgCl + 1.0 g/L SiO₂-NHR + 2 mM MV²⁺ after reduction at -0.9 V ($Q = 125,450$ C/mol AgCl) in H₂O/0.1 M NaBF₄ media, followed by isolation of nanoparticles and dispersing in water.

(SiO₂-NHR) in water/0.1 M NaBF₄ as an example. These particles were added to bind and stabilize the metal nanoparticles in solution. This utilization of amino-modified silica nanoparticles is a well known approach that is popular in chemical syntheses of metal nanoparticles [21–23]. However, yet another goal of electrosynthesis of silica core/silver shell nanocomposite material was pursued. Particles of this type are of

interest in themselves, in particular due to their high specific catalytic activity [24].

2. Experimental section

CV curves were recorded with a P-30J potentiostat in argon atmosphere in H₂O/0.1 M NaBF₄. A glassy carbon disk electrode ($\varnothing = 3.4$ mm) pressed into Teflon was used as the working electrode. The electrode was cleaned by mechanical polishing before each measurement. Platinum wire was used as the counter electrode. The potentials were measured relative to an aqueous saturated calomel electrode (SCE), $E_0'(Fc/Fc^+) = +0.41$ V. The aqueous SCE was connected by a bridge filled with the supporting solution. The temperature was 295 K.

The microelectrolysis was carried out in a three-electrode cell separated with a porous glass diaphragm in potentiostatic mode (-0.9 V vs. SCE) in argon atmosphere at room temperature ($T = 295$ K) using a P-30J potentiostat. For electrolysis, the working solution (20 mL) was prepared in the following way: 20 mL of an aqueous solution containing 0.1 M NaBF₄ (220 mg), 1.5 mM AgNO₃ (5.1 mg) and 1.0 g/L of silica nanoparticles was magnetically stirred for 2.5 h. Then 12.6 mg of methylviologen MV²⁺ · 2Cl⁻ ($C = 2$ mM) was added and the solution was stirred for another 2.5 h. During the electrolysis, the solution was stirred with a magnetic stirrer. A glassy carbon plate was used as the working electrode ($S = 9$ cm²). SCE was used as the reference electrode and was connected by a bridge filled with the supporting solution. A Pt wire immersed in the supporting solution was used as the auxiliary electrode.

When the electrolysis was over, the solution was controlled by CV on the indicator glassy carbon disk electrode ($\varnothing = 3.4$ mm), and then the nanoparticles formed in the electrolysis were analyzed by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). To this end, the nanoparticles were separated by centrifugation (15,000 rpm) for 2 h. The precipitate was washed with water (3 times) and was dispersed in double-distilled water by sonification. For the SEM analysis, the resulting solution was applied to the surface of a titanium foil. Then the sample was exsiccated by low heating (not higher than 40 °C). The morphology of the SAMPLE surfaces was characterized in plan-view with SEM using a high-resolution Merlin microscope from Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for energy-dispersive X-ray spectroscopy (EDX) analysis with AZTEC X-MAX energy-dispersion spectrometer from Oxford Instruments. The analysis of nanoparticles was carried out using a MERLIN field-emission scanning electron microscope (STEM-mode). The suspension of nanoparticles was deposited on a formvar (tm) coated 3 mm copper grid, then dried and analyzed by the scanning electron microscope.

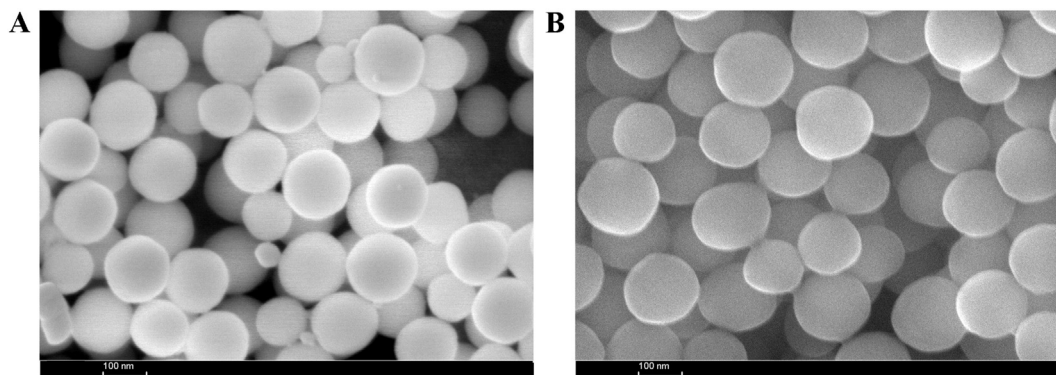


Fig. 3. SEM image of SiO₂-NHR/Ag nanoparticles (A) and SiO₂-NHR (B).

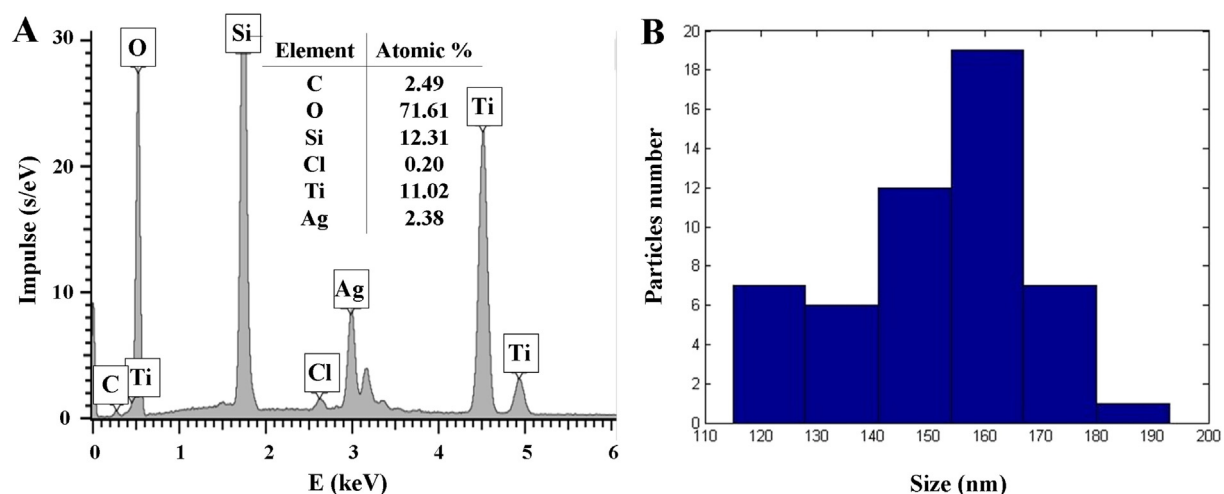


Fig. 4. Energy-dispersive spectrum of SiO₂-NHR/Ag nanoparticles (A) and their size distribution histogram (B).

Methylviologen dichloride MV²⁺·2Cl⁻, AgNO₃, the supporting NaBF₄ electrolyte (Aldrich), were used as purchased without additional purification. The alkylamino-modified silica nanoparticles (SiO₂-NHR) were synthesized through the well-known Stöber procedure with the use of 3-[2-(2-aminoethylamino)ethylamino]-propyltrimethoxysilane as previously described [25]. Twice distilled water was used in the experiments.

3. Results and discussions

Silver chloride is almost quantitatively precipitated at a concentration of 0.2 g/L in 0.1 M NaBF₄ aqueous solution and only poorly defined steps of its reduction and re-oxidation of generated Ag⁰ are recorded on a glassy carbon electrode on the CV curves (Fig. 1a). In the presence of SiO₂-NHR, AgCl is not directly reduced on the electrode (Fig. 1b).

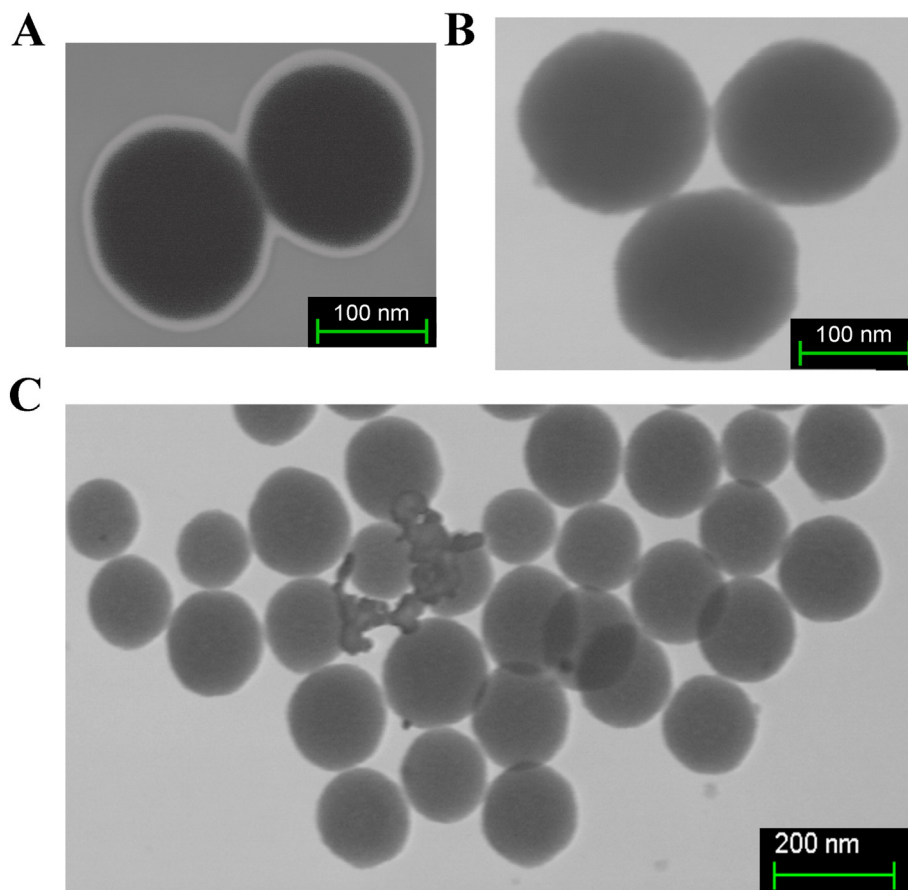


Fig. 5. STEM images of SiO₂-NHR (A) and SiO₂-NHR/Ag core/shell (B,C) nanoparticles.

Therefore, in a ternary mixture methylviologen (2 mM) – AgCl (0.2 g/L) – SiO₂-NHR (1.0 g/L), only two reversible peaks of stepwise reduction of methylviologen to a radical cation MV^{•+} and a neutral diamine MV⁰ are recorded on the CV curves (Fig. 1c,d). The first reduction peak is higher and the associated re-oxidation peak is lower than those in the methylviologen + SiO₂-NHR system (Fig. 1e). Furthermore, a small peak of Ag⁰ re-oxidation is observed on the reverse CV curve. These data indicate that methylviologen mediated reduction of AgCl to Ag⁰ occurs (Scheme 1).

Preparative reduction of this solution (20 mL) was carried out at the controlled potential of MV^{•+} generation (–0.9 V). The current decreases during the electrolysis (6.3 min) but remains rather high ($I \approx 12 \rightarrow 6$ mA), $Q = 125,450$ C/mol AgCl. The original slightly turbid colloidal white solution turns dark during the electrolysis and becomes dark brown by the end of the electrolysis. In the UV–vis spectrum a broad band is recorded at 383 nm (Fig. 2), which indicates that metallic silver nanoparticles are formed [26]. The mass of the cathode does not change, hence nothing is deposited on the electrode. The CV curves recorded after the electrolysis contain only peaks of methylviologen reduction and re-oxidation, the intensity of which matches the initial concentration of methylviologen alone. Apparently, methylviologen is not consumed in the reduction and performs only the mediator function in AgCl reduction (Scheme 1).

It follows from the SEM photomicrographs (Fig. 3A) that electrolysis mainly produces spherical nanoparticles with sizes in a narrow range, mostly 120–160 nm, which matches the size of SiO₂-NHR particles (Fig. 3B). According to elementary analysis, beside silica, a nanoparticle contains a noticeable amount of silver (Ag/Si $\sim 1/5$) (Fig. 4A). Differences between the nanoparticles obtained and the SiO₂-NHR nanoparticles are also evident from scanning transmission electron microscopy (STEM). SiO₂-NHR nanoparticles have a characteristic halo due to the modifying alkylamino layer (Fig. 5A). On the other hand, the nanocomposite material obtained by electrolysis is homogeneous (Fig. 5B), which indicates that SiO₂-NHR is completely coated with metallic silver and SiO₂-NHR/Ag core/shell nanoparticles are formed. The particle size distribution is shown in Fig. 4B.

The modifying surface layer of SiO₂-NHR nanoparticles contains amino groups capable of complexation with Ag⁺ ions, as well as hydrophobic alkyl moieties that are principally capable of binding hydrophobic AgCl. Apparently, this results in uniform binding of a certain limiting amount of AgCl in the modifying layer. Reduction of this precursor by electrochemically generated methylviologen radical cations occurs rather quickly, and it is apparently responsible for building the final nanocomposite material (Scheme 1). Some excess amount of AgCl exists in the solution, and its reduction results in the formation of some amount of nanoparticles in the solution bulk. These particles are not stabilized. They undergo aggregation and therefore have quite diverse and non-controllable shapes and sizes (Figs. 3A, 5C).

4. Conclusions

Thus, electrochemical reduction of AgCl precipitate to Ag⁰ was accomplished using methylviologen as a mediator at potentials of the MV²⁺/MV^{•+} redox couple in the presence of alkylamino-modified silica nanoparticles (SiO₂-NHR) in an aqueous medium. Apparently, the major fraction of AgCl is bound on the surface of silica nanoparticles at the SiO₂-NHR ratio used, and their reduction with electrochemically generated methylviologen radical cations leads to the formation of spherical SiO₂-NHR/Ag core/shell nanoparticles (Scheme 1) with size mostly in the range 120–160 nm in the solution. The other minor fraction of AgCl remains as a precipitate in the solution and is reduced to give silver nanoparticles with uncontrollable shapes and sizes.

Conflict of interest

The authors declare that there are no conflict of interest.

Acknowledgment

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