

Electrochemical Studies of Silver Nanoparticles Tethered on Silica Sphere

Zhong-jie Jiang, Chun-yan Liu,* and Yong-jun Li

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, P. R. China

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A good approach has been developed to study the electrochemical behavior of metal particles in sol. The technique to tether silver particles on silica sphere was established for the measurement of electrochemical behavior, which efficiently avoided the flocculation of colloidal metal particles in an electrolyte solution.

During the last decades, small metal particles have been extensively investigated in various fields of chemistry and physics.¹⁻³ It has been experimentally verified that the particles with diameters in the range of 1–100 nm exhibit unique properties different from their bulk counterparts.¹⁻⁵ The size effects have a profound influence on the chemical behavior of metal particles in a solution.^{6,7} Although Henglein et al.^{2,6} have demonstrated that the redox potential of silver nanoparticles closely depends on the size of particles, no previous work has been reported to directly measure the potential of colloidal silver nanoparticles. One problem associated with nanoparticles is that most of them will flocculate in the presence of electrolytes. Recently, a technique has been developed to tether silver particles on different substrates,⁸⁻¹⁵ which could effectively avoid flocculation of colloidal metal particles in the presence of electrolytes. In this work, we apply this technique to prepare SiO₂/Ag core-shell particles and directly study the electrochemical behavior of silver nanoparticles in a colloidal solution. The aim of this work is to develop a novel approach to directly study the electrochemical behavior of colloidal silver particles. It is expected that the relationship between the size of metal particles and redox potentials could be obtained through studying the electrochemical properties of metal particles tethered on substrates.

Silica substrates are prepared using the well-known Stöber-Fink-Bohn methods, which yields spherical silica particles with uniform size over a broad range.¹⁶ The silica particle surface was then functionalized with 3-aminopropyltrimethoxysilane (APTMS). This functionalized process provided an amine-moiety coating for the exterior of silica particles. Typically, 1 mL of 4×10^{-2} mol/L AgNO₃ aqueous solution was dropped into the mixture of silica (7.8×10^{13} silica nanoparticles/mL) and 9.1 mg excess sodium borohydride (NaBH₄) solid under vigorous stirring, which produced silica interspersed with well separated silver particles on the surface (Figure 1). Cyclic voltammetric measurements of silver particles tethered on the silica substrate were performed using a standard three-electrode system. A saturated calomel electrode (SCE) served as reference electrode and a platinum electrode was used as auxiliary electrode. The working electrode was a platinum sheet. 0.1 M KCl aqueous solution was used as electrolyte for the study of silver particles. All the above steps were done in ambient temperature. Solutions were purged with N₂ gas to remove all dissolved oxygen before the CVs and a weak stream of N₂ was maintained above the solution during the experiments.

Figure 1 showed the typical TEM micrograph of silver particles tethered on silica. Silver nanoparticles with a small size were tethered to the APTMS-functionalized silica surface by electrostatic effects and coordination between silver particles and amino group (–NH₂).^{8,13,17} Because of the electrostatic repulsive force among metal particles, the silver particles immobilized on the silica surface were well separated. The attachment was sufficiently strong so that the silver nanoparticles remain attached to silica spheres in an aqueous solution. It was found that KNO₃ as an electrolyte had no effects on the morphology and size of the supported silver particles with standing times (Figure 2a). However, when the KCl electrolyte solution was added into the composite colloid, the size of silver particles grew and the number of silver particles on each silica sphere distinctly decreased after standing for 30 min, but no dissociated silver particles were observed in the solution (Figure 2b), which indicated that the small nanoparticles of silver would spontaneously and slowly dissolved into the solution and recrystallized on the larger ones (Ostwald ripening) in the presence of the halide electrolyte. This experiment showed that the halide ions could promote the dissolution and recrystallization of silver particles in the electrolyte solution, owing to very strong interaction of silver particles with halide ions. In order to reduce the effects of halide ions, electrochemical experiments have been done immediately after the electrodes dipped into the electrolyte solution containing halides.

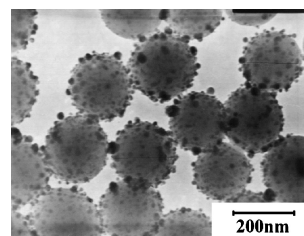


Figure 1. TEM micrograph of silver particles tethered on silica sphere.

Figure 3a showed the typical CVs of silver particles tethered on silica, which was completely different from the electrochemical behavior of solid silver electrode (Figure 3b). Two pairs of cathodic and anodic waves were observed in the voltammograms for the electrode with composite particles (Figure 3a). Evidently, silver particles with different sizes were expected to have different electrochemical potentials.^{2,6}

In general, silver particles attached to the surface of the working electrode were scarce, so that no distinct current peaks were observed when potassium nitrate (KNO₃) was used as an electrolyte, owing to difficulty in migrating silver particles and electron transfer to the surface of the work electrode, because the silver particles tethered on silica are well separated and aren't continuous (Figure 2). In the experiments, however, we

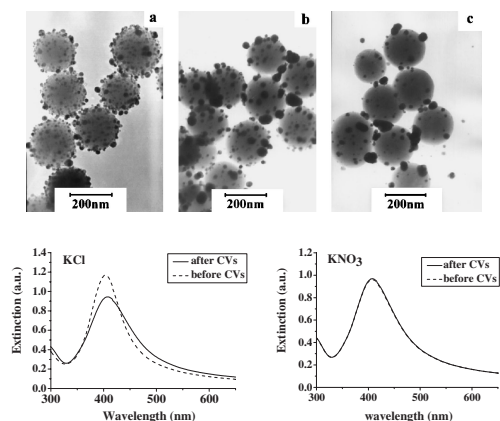


Figure 2. TEM micrograph and UV-vis spectra of silver particles tethered on silica in different electrolytes: (a) KNO_3 , (b) KCl before CVs, (c) KCl after CVs.

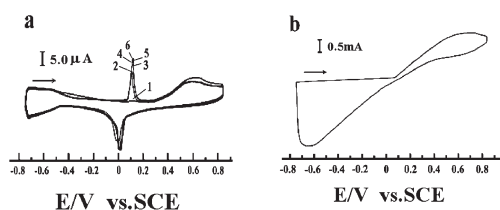


Figure 3. Cyclic voltammograms of silver particles tethered on silica. The solution is 1 mM Ag^0 + 0.1 M KCl. The scan rate is 100 mV/s. The number marks scanning times, and the arrow represents scanning orientation. a) silver particles on silica; b) solid silver electrode.

found that the electrolyte produced insoluble matter with silver ions, such as KCl, KBr, and KI, and contributed to reduction and oxidation of silver particles during the CVs, suggesting that halide ions might favor the migration of small silver particles to the surface of the electrode under an outer electric field. As a result, the size and concentration of silver particles closely near to the surface of the electrode increased with scanning times, and peak currents gradually increased (Figure 3a). Figure 2c showed the TEM micrograph of silver particles after CVs. Some dissociative silver particles were observed in Figure 2c, which suggested the transfer and congregation of silver particles on the surface of the electrode during the CVs. The UV-vis spectra (Figure 2) were well in agree with the TEM results, where the band at ≈ 401 nm developed after CVs, because of an increase in size and a decrease in number of silver particles when KCl was used as electrolyte. But no distinct change was observed in a KNO_3 solution. According to the result aforementioned, a feasible mechanism was proposed. Silver particles tethered on the silica sphere would migrate in the present of KCl electrolyte solution, which would shift to the surface of the working electrode and then be oxidized under an outer electric field. The Ostwald ripening promoted by halide ions might play an important role in the shift and the redox reaction of silver particles.

The change in redox potential of metal particles might partly arise from surface effects. Henglein et al.² had demonstrated that the adsorption of nucleophiles (e.g. PH_3 , I^- , $-\text{NH}_2$, S^{2-} , etc.) onto the surface of a metal nanoparticle will significantly increase its Fermi potential and thus lower its reduction potential. The

changes of the reduction potential have been rationalized in terms of transfer of electron density from nucleophiles to the metal particles.^{2,18} In contrast, a small positive shift of the reduction potential will be observed when electron donors depart from the surface of metal particles. In the present work, silver particles partly desquamated from $-\text{NH}_2$ on silica surface during the CVs, so that the electron density on the silver particles decreased, and thus a slight positive displacement of the potential took place. Also, the change in size of silver particles influenced the potential. As was shown in Figure 2c, the average size of silver particles increased after CVs, which also contributed to the positive shift of potential.

In summary, the electrochemical properties of silver particles tethered on silica sphere had been studied. The experiments showed that the nucleophiles and the size would influence the potentials of metal particles. The work described above is only an exploration, and further investigation is under the way to well understand the mechanism of electrochemistry.

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