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RESEARCH PAPER

# Electrochemical method for the synthesis of silver nanoparticles

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**Abstract** The article deals with a novel electrochemical method of preparing long-lived silver nanoparticles suspended in aqueous solution as well as silver powders. The method does not involve the use of any chemical stabilising agents. The morphology of the silver nanoparticles obtained was studied using transmission electron microscopy, scanning electron microscopy, atomic force microscopy and dynamic light scattering measurements. Silver nanoparticles suspended in water solution that were produced by the present technique are nearly spherical and their size distribution lies in the range of 2 to 20 nm, the average size being about 7 nm. Silver nanoparticles synthesised by the proposed method were sufficiently stable for more than 7 years even under ambient conditions. Silver crystal growth on the surface of the cathode in the electrochemical process used was shown to result in micron-sized structures consisting of agglomerated silver nanoparticles with the sizes below 40 nm.

**Keywords** Silver · Nanoparticle · PVP · Electrochemical synthesis · Colloids

## Introduction

The last decade has seen the development of a hoist of different methods for the synthesis and characterization of metal nanoparticles and powders thereof (Feldheim and Foss 2002). Owing to their properties being distinctly different from those of the bulk metal, nanoparticles are finding their way into various areas of science and technology (Mazzola 2003; Anselmann 2001; Bönnemann and Richards 2001; Biswas and Wu 2005). In particular, nanoparticles of silver have attracted much attention because of a broad range of their possible applications including medicine (Salata 2004), catalysis (Lewis 1993), textile engineering (Lee and Jeong 2005), biotechnology and bioengineering (Niemeyer 2001), water treatment (Solov'ev et al. 2007), electronics (Li et al. 2005) and optics (Murphy et al. 2005). Many approaches were developed to obtain silver nanoparticles of various shapes and sizes,

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including laser ablation (Lee et al. 2001), gamma irradiation (Long et al. 2007), electron irradiation (Bogle et al. 2006), chemical reduction by inorganic and organic reducing agents (Bönnemann and Richards 2001), photochemical method (Mallick et al. 2004), microwave processing (Yin et al. 2004), and thermal decomposition of silver oxalate in water and in ethylene glycol (Navaladian et al. 2007). Reetz and Helbig (1994) were the first to describe in detail an electrochemical technique for the synthesis of nanoparticles, in which a metal sheet was anodically dissolved and the intermediate metal salt formed was reduced at the cathode, giving rise to metallic particles stabilised by tetraalkylammonium salts. This work was successfully adopted for the electrochemical synthesis of the silver nanoparticles in acetonitrile containing tetrabutylammonium salts by Rodríguez-Sánchez et al. (2000). Using a similar approach, silver nanoparticles were obtained by potentiostatic or galvanostatic polarisation of silver in ethanol solution by Starowicz et al. 2006). In the work of Yin et al. (2003), Poly(*N*-vinyl-2-pyrrolidone) (PVP) was essential in the process of electrochemical synthesis of silver particles. The main advantages of the electrochemical methods lie in the high purity of particles and the possibility of the nanoparticle size control by adjusting the current density without a need for expensive equipment or vacuum. The key to the success of electrochemical methods is the right choice of the chemical agents and the process conditions. However, as pointed out earlier (Rodríguez-Sánchez et al. 2000), the method has its limitations, as the deposition of silver on the cathode during the electrochemical process diminishes the effective surface available for particle production. As the entire cathode surface gets covered with the silver electrodeposits, the particle production comes to a halt altogether.

An important issue in the current search for simpler and cost-effective methods for the synthesis of nanoparticles is finding ways to avoid the use of stabilising agents in the electrochemical processes involved. In this article, we present a novel electrochemical method for preparing long-lived silver nanoparticles suspended in aqueous solutions as well as silver powders deposited on the electrodes, which does not involve any chemical stabilising agents.

## Materials and methods

The proposed process for obtaining silver nanoparticles is based on the use of an inexpensive two-electrode setup in which the anode and the cathode are made from the bulk Ag metal to be transformed into Ag colloidal particles. We employed two polished silver plates (85 mm × 20 mm × 4 mm) as the anode and the cathode, being vertically placed face-to-face 10 mm apart. The electrodes were immersed in an electrochemical cell filled with 500 mL of distilled water obtained from an ordinary commercially available water distiller (DE-25, Russia). Electrolysis was performed in the temperature range 20–95 °C at a constant voltage of 20 V. Additional technological keys to the electrochemical synthesis of silver nanoparticles lie in changing the polarity of the direct current between the electrodes every 30–300 s, and intensive stirring during the process of electrolysis to inhibit the formation of precipitates. The silver nanoparticle solutions produced in this way were stored under ambient conditions in glass containers.

The concentration of the silver nanoparticles in solutions was determined by neutron activation analysis (Soete et al. 1972). The samples were irradiated in the nuclear reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). The product of the nuclear reaction $^{109}\mathrm{Ag}(\mathrm{n},\gamma)^{110\mathrm{m}}\mathrm{Ag}$ has the half-life $T_{1/2} = 253$ days. The silver concentration was determined from the measurements of the intensity of gamma radiation with the energy of 0.657 MeV and 0.884 MeV emitted by $^{110\mathrm{m}}\mathrm{Ag}$. A Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and a 6144-channel analyser were used for recording gamma-ray quanta.

Dynamic light scattering (DLS) measurements were carried out at 25 °C using a Zetasizer (ZEN3600, Malvern Instruments, UK) to estimate the size distribution of silver nanoparticles in solutions. The morphology of silver powder deposited on the surface of the cathode during the electrochemical process was observed by field emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL, Japan). The size and shape of the nanoparticles in solution were determined by transmission electron microscopy (TEM) (LEO-912-OMEGA, Carl Zeiss, Germany). Energy dispersive X-ray spectrometer (EDS) attached to the TEM was used to determine the chemical composition of the samples. The size values were averaged over more than 150 nanoparticles from different TEM micrographs of the same sample.

The silver nanoparticles suspended in aqueous solutions were also imaged by atomic force microscopy (AFM) (Solver P47Bio, NT-MDT Co., Russia) in contact mode using freshly cleaved mica surfaces as substrates.

## Results and discussion

As distinct from most non-electrochemical methods (Lee et al. 2001; Long et al. 2007; Bogle et al. 2006; Mallick et al. 2004; Yin et al. 2004; Navaladian et al. 2007), the proposed approach of electrochemical synthesis does not require the use of vacuum chambers, sophisticated preparation or expensive equipment. The process of synthesis proposed here involves three major stages, which are described below.

### Stage I: formation of a colloidal solution of silver nanoparticles

This stage comprises the following steps (Fig. 1):

1. Oxidative dissolution of the sacrificial Ag anode:

$$Ag^0 - e^- \rightarrow Ag^{+1}$$

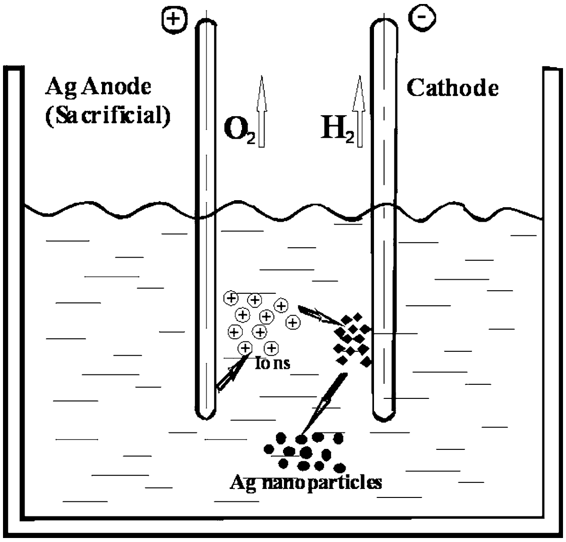


**Fig. 1** Electrochemical formation of silver nanoparticles in distilled water

2. Release of the oxygen gas:

$$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+$$

due to the electrolysis of water, with simultaneous $Ag_2O$ film deposition on the surface of the anode;

3. $Ag^+$ ions migration to the cathode;
4. Reductive formation of zero-valent Ag atoms on the cathode:

$$Ag^{+1} + e^- \rightarrow Ag^0$$

and release of the hydrogen gas:

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH$$

5. Formation of silver nanoparticles via nucleation and growth due to attractive van der Waals forces between Ag atoms;
6. Separation of synthesised silver nanoparticles from the cathode and their further migration caused by vigorous stirring of the solution.

Upon application of a voltage, the reactions described above set in and the electrical current continuously increased until it reached a saturation level. The warmer was the water, the faster was the reaction and the higher was the value of the saturation current (cf Fig. 2).

In the described first stage of the electrochemical synthesis, the polarity of the direct current between the electrodes was periodically changed, which significantly reduced the electrodeposition of silver on the cathode. As soon as the polarity changes, $Ag_2O$ on the surface of the former cathode starts reducing in a reaction with hydrogen

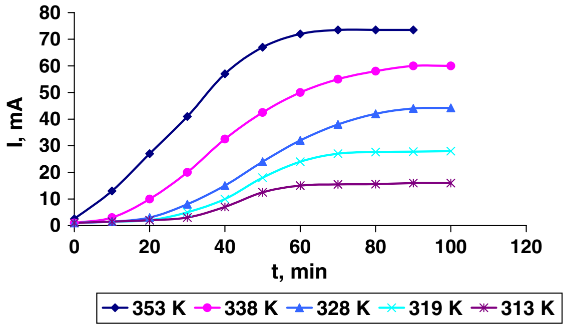


**Fig. 2** Current versus process time for different temperatures

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

at temperatures above 50 °C. We varied the period of the polarity changes in the range of 30 to 300 s. It was found empirically that 4 min was an optimum period. At smaller values, agglomeration of particles in the solution was enhanced at the cost of silver film deposition at the cathode. For values of the period exceeding 4 min, a gradual decrease of the effective surface for the particle production occurred, owing to a significant growth of silver electrodeposition on the cathode. By periodically changing the polarity every 4 min, the film deposition at the electrodes was reduced as compared to known electrochemical methods (Reetz and Helbig 1994; Rodríguez-Sánchez et al. 2000; Starowicz et al. 2006), and the production of nanoparticles was enhanced resulting in larger concentrations of silver colloids.

The solutions were tested for sizes of suspended silver nanoparticles as soon as current saturation was reached. TEM and DLS studies demonstrated that the average size of silver nanoparticles in the colloidal solution decreases with increase in the current density, as was shown in (Reetz and Helbig 1994) theoretically. The rate of the reaction was shown to increase with decrease in the distance between the electrodes and increase in the voltage. A longer reaction time for each individual trial resulted in a larger average size and a higher concentration of silver nanoparticles. In order to obtain stable silver nanoparticles with a concentration in the range of 20 to 40 mg/L, it was necessary to ensure a reaction time of 50–70 min in the temperature range of 50 to 80 °C.

## Stage II: filtration

As was shown by DLS and TEM measurements, a typical sample of silver nanoparticles solution contains a small amount of large Ag colloids after the first stage as well (see Fig. 3). In order to remove these larger colloids and to provide reduction of the silver ions present in the solution, we propose to implement a filtration stage. Passing the colloidal solution through a paper filter, narrows the range of size distributions of the synthesised silver nanoparticles (see Fig. 4) and also provides additional reduction of Ag ions:

$$Ag^{+1} + e^{-} \rightarrow Ag^{0}$$

As a result, the ratio $c(Ag^{+})/c(Ag)$ decreases, where $c(Ag^{+})$ is the concentration of silver ions and $c(Ag)$ is the concentration of silver nanoparticles suspended in the solution, respectively.

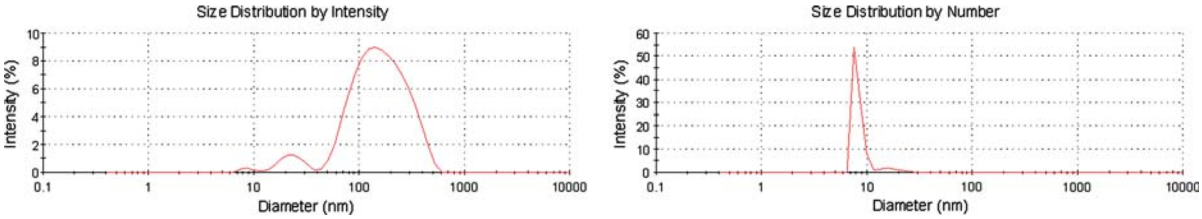
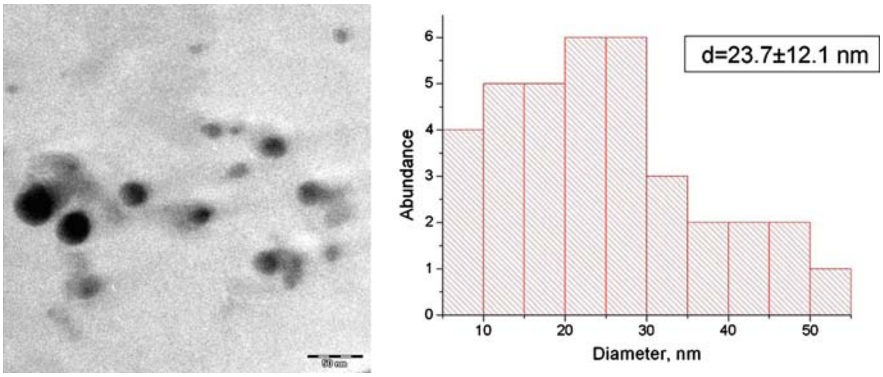


**Fig. 3** Typical DLS-images of size distribution by intensity (left) and number (right) of silver nanoparticles obtained after Stage I

**Fig. 4** Typical TEM image and size distribution of silver nanoparticles obtained after Stage II



### Stage III: additional treatment

A third stage of Ag nanoparticle synthesis involves the additional treatment of the smallest-size fraction of silver nanoparticles remaining in solution after the filtering stage. It consists in adding hydrogen peroxide to a level of up to 0.005% concentration of $H_2O_2$ to the solution. Due to the reaction

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2,$$

silver oxide is reduced to Ag which is released in the solution. Due to this process, the size of the silver nanoparticles is reduced while new Ag nanoparticles may be forming as well. The details of this process, whose outcome consists in a significant refinement of the nanoparticle size, are not fully understood as yet. Examination of TEM images taken 2 weeks after the addition of $H_2O_2$ revealed that silver nanoparticles suspended in water solution were nearly spherical and that their size distribution fell in the range of 2 to 20 nm, the average size being about 7 nm (cf. Fig. 5).

EDS analysis of silver nanoparticles (cf. Fig. 6) has shown a presence of $Ag_2O$ in the solution after Stage II and an efficiency of reduction of silver oxides in the solution during Stage III.

In our studies, as a variant of the processing, PVP was also used as a protective medium for the silver colloids. PVP is known to affect the molecular motion of reduced silver, inhibiting the aggregation of nanoparticles (Yin et al. 2004). Sustainability of the solution of nanoparticles after Stage II (‘Sample A’) and Stage III (‘Sample B’) of the proposed synthesis was monitored over 300 days and compared with that of the samples containing PVP (‘Sample A + PVP’ and ‘Sample B + PVP’). PVP was added to the samples in such a way as to produce a mass relation of Ag colloids and PVP of 1:20. As one can see from Table 1, the nanoparticles prepared can be stored for months under ambient conditions with only little coarsening; small additions of PVP to electrochemically synthesised silver nanoparticle solutions act to enhance their stability.

DLS and TEM measurements showed that an increase in the PVP concentration enhances the stability of colloids. On the other hand, it leads to more viscous colloidal solution potentially complicating the process of impregnating different materials with silver nanoparticles. This effect may be relevant for paints modified with silver nanoparticles, textile fabrics (Jeong et al. 2005; Lee and Jeong 2004) etc.,

**Fig. 5** Typical TEM image and size distribution of silver nanoparticles obtained after Stage III

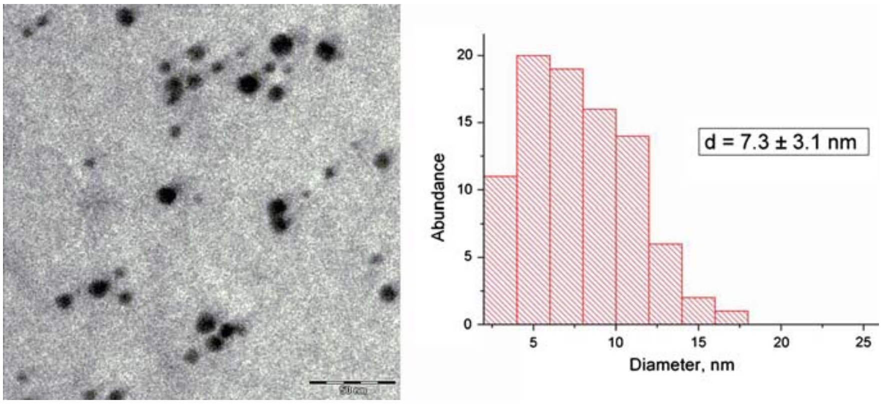


**Fig. 6** EDS analysis after stages II (left) and III (right). Carbon and copper peaks are from the carbon-coated copper sample grid

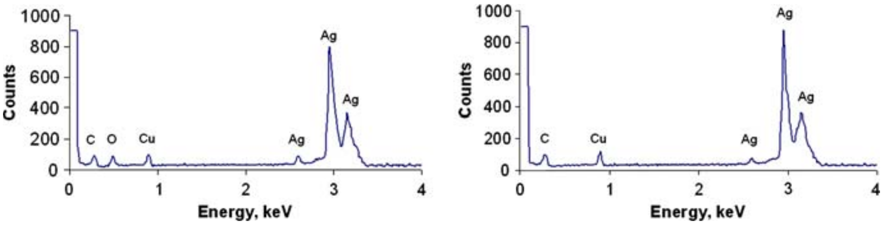


**Table 1** Mean size of silver nanoparticles from different colloidal solution samples

| Days | Mean diameter (nm) | | | |
|---|---|---|---|---|
| | Sample A | Sample A + PVP | Sample B | Sample B + PVP |
| 1 | 24 ± 12 | 24 ± 12 | 7 ± 3 | 7 ± 3 |
| 10 | 26 ± 12 | 24 ± 12 | 9 ± 4 | 8 ± 4 |
| 20 | 31 ± 15 | 26 ± 12 | 10 ± 4 | 9 ± 4 |
| 100 | 40 ± 17 | 28 ± 13 | 13 ± 5 | 11 ± 4 |
| 300 | 47 ± 20 | 31 ± 14 | 19 ± 7 | 13 ± 5 |

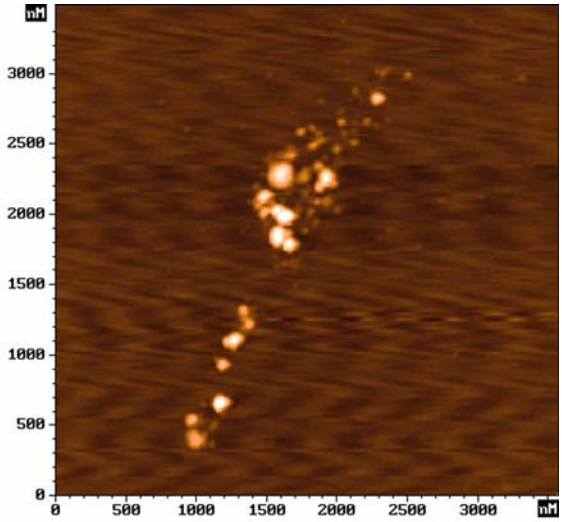


**Fig. 7** AFM image of silver nanoparticles obtained by the electrochemical method and stored for 7 years. (Substrate: freshly cleaved mica.)

and it needs to be considered in the light of potential industrial applications of the synthesised silver nanoparticles.

One of the main advantages of the proposed electrochemical method is a high degree of stability of the synthesised silver nanoparticles. As demonstrated by AFM measurements (see Fig. 7), a sample solution of silver nanoparticles obtained by the proposed method in a process involving stages I and II remained stable over 7 years of storage under ambient conditions. On average, only moderate growth of the particles was found, although coarse particles with the diameter of up to 100–150 nm occurred occasionally (cf. Fig. 7). Moreover X-Ray spectrum of the sample obtained by EDS is analogous to that shown in Fig. 6 (right), proving the purity of silver nanoparticles.

A ‘by-product’ of the silver nanoparticle production by electrolysis is the re-deposition of silver on the cathode. The morphology of the deposit was also studied in this work. Due to its weak adhesion to the substrate, it could be easily removed mechanically in the form of grey coloured powder consisting of rather large (~1 μm) polyhedron-shaped particles and micron-sized platelets (Fig. 8). These consisted of agglomerated silver nanoparticles with sizes up to 40 nm, cf. Fig. 9.

## Conclusions

Silver nanoparticles obtained in a three-stage process based on the electroreduction of anodically solved silver ions in water have been studied. Various technological keys to improve the output by varying the process conditions have been considered. The morphology of the colloidal silver nanoparticles and the powders deposited on the electrodes was studied using DLS, TEM and SEM measurements. These studies have shown that silver nanoparticles

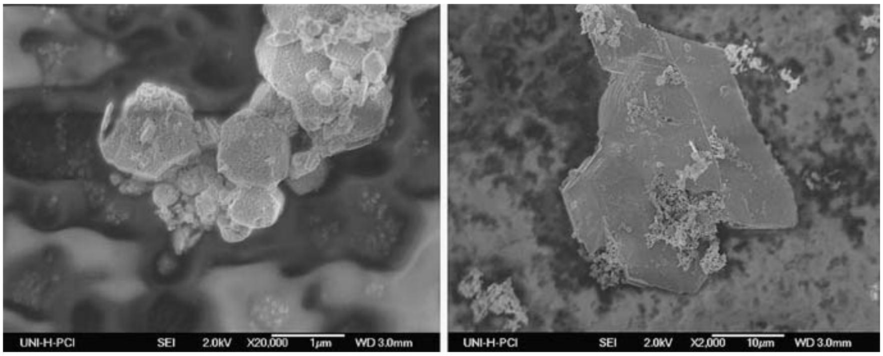


**Fig. 8** Typical SEM-images of polyhedron-shaped silver powders (left) and platelets (right). Note the scale bars of 1 and 10 μm, respectively

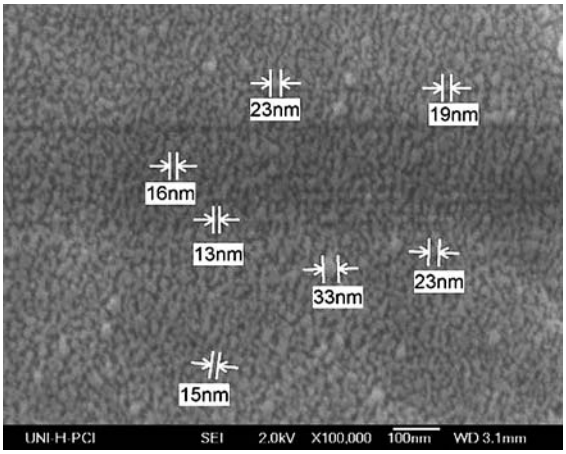


**Fig. 9** Typical structure of silver powders deposited on the cathode (FEG-SEM image). Some of the individual nanoparticles are indicated

suspended in water solution, which were produced by the present three-stage technique, were nearly spherical, their average size being 7.3 ± 3.1 nm. It was demonstrated by AFM measurements that silver nanoparticles synthesised by the proposed method were sufficiently stable for at least 7 years even under ambient conditions. Furthermore, it was shown that small additions of PVP to silver nanoparticle solutions act to enhance their stability. However, the effect is not very pronounced, and this step does not seem to be critical. The investigation of silver particles grown on the surface of the cathode during the electrochemical process showed that silver powders obtained were 'bi-modal': large micron-sized polyhedron-shaped particles and micron-sized silver plates consisting of agglomerated silver nanoparticles with the sizes up to 40 nm. This 'by-product' of electrolysis may also be of some use in applications requiring silver powders with a large surface area.

The simplicity of this synthesis route allows low-cost fabrication of large amounts of long-lived silver nanoparticles. No chemical stabilising agents are generally required, which extends the technological viability of the process and industrial applications of the method. We believe that the electrochemical method for the synthesis of silver nanoparticles presented provides an efficient processing route for the fabrication of colloidal solutions of silver nanoparticles in the concentration range of 20 to 40 mg/L or silver nanoparticulates. Depending on whether the process is terminated after Stage II or is continued to include Stage III, the average nanoparticle size of about 20 nm or 7 nm, respectively, can be achieved.

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