Suspensive Electrode Formation in Pulsed Sonoelectrochemical Synthesis of Silver Nanoparticles

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We report here a new understanding of the mechanisms involved in the sonoelectrochemical synthesis of nanoparticles. Our results indicate that, in addition to the deposition-break processes, a suspended electrode that is formed by the ultrasonic wave has a major effect on the particles' properties. This new understanding of the sonoelectrochemical mechanisms clarifies some unsolved issues and allows for better design of sonoelectrochemical synthesis. However, we believe that the major significance of this new insight is the opening up of new possibilities for sonoelectrochemical synthesis of composite and core-shell materials.

Introduction

The synthesis of nanosized particles is a growing research field in chemical science, in accordance with the extensive development of nanotechnology.[1−3] The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics, and energy conversion and storage.[4−7] Several synthetic methods are commonly used for the preparation of nanosized materials, of which sonoelectrochemistry is among the least popular, despite its being one of the most flexible techniques with respect to its ability to control particle parameters.

Sonoelectrochemistry is conceptually different from sonochemistry. Sonochemistry is a very useful method that has been known since the 1930s[8] and has increased in popularity over the past decade. It is based on processes that occur during the collapse of gas bubbles that are condensed by ultrasonic waves, generating a localized ultrahot spot.[9] On the other hand, the relatively new approach of sonoelectrochemistry utilizes the ultrasonic power primarily to manipulate the material mechanically.[10] Pulsed sonoelectrochemical synthesis, first introduced by Reisse et al.,[11] involves alternating sonic and electric pulses. The present understanding of the sonoelectrochemical mechanism describes an electrochemical deposition of a thin layer on the sonoelectrode during the electric pulse. The thin layer is then destroyed by the coming sonic pulse, to form jet-suspended nanoparticles in the solution.[11,12] Thus, the electrochemical and sonic parameters, including the pulse duration, can be used to control the particles' parameters. For example, Gedanken et al.[12] have reported the use of pulse sonoelectrochemistry for the preparation of silver nanoparticles with different shapes, including spherical, rodlike, and dendritic, and uncovered the crucial role of electrolyte composition in the shape formation. According to their explanation, during the reaction, the particles are not completely detached from the sonoelectrode by the ultrasonic oscillations, so that the particles formed in the next pulse can further grow on seeds that are left on the sonoelectrode.

Experimental Section

The experimental setup employed in this study (Figure 1) was similar to those of Reisse et al.[11] and Gedanken et al.[13] It contained an electrochemical cell (cathode, anode, electrolyte), an ultrasonic pulse generator (sonicator), a direct-current power source, and a synchronizer. The synchronizer was used to drive both the ultrasonic generator and the power source in a predefined subsequence, enabling a variation of relative delay and durations of ultrasonic and electric pulses. Each sonoelectrochemical cycle lasted 1.2 s, consisting of a 600 ms electric current pulse of 100 mA, a 300 ms sonic pulse immediately following the electric pulse, and a 300 ms rest (see Figure 1).

The cathodic deposition of the silver was done directly on the titanium horn of the sonicator. A platinum foil served as the anode. A Vibracell 750W was used as the sonicator. The power source (Regulated Power Supply from Extech Instruments) was limited to 30 V. The synchronizer (based on M-90 from Unitronics) provided delays and durations, with an accuracy of 10 ms. Voltage and current pulses were monitored with a Digital Palm Scope 320c oscilloscope.

The electrolyte used in this study was 0.6 g/L $AgNO_3$ in water. Oxygen was removed from the water by nitrogen bubbling, and the electrolyte was mixed under a nitrogen atmosphere. A complexing agent, nitrilotriacetate (NTA), was added at the 1 g/L level to avoid aggregation[12] (without NTA, the particle size reaches 2 μm after 0.5 h, and this process is of little interest in the context of nanochemistry). The starting pH of the electrolyte solution was 4.4.

The experimental cell had dimensions as follows. The horn diameter was 12.5 mm; the horn's side was isolated by a Teflon cylinder, leaving 2 mm of free surface and making the effective

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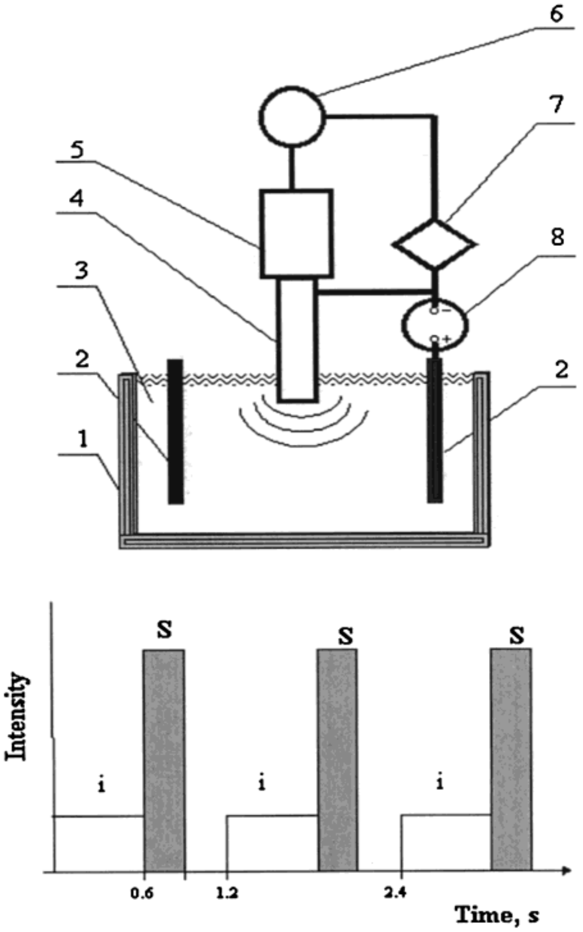

Figure 1. Experimental setup and sonoelectric cycle. Top: 1, vessel; 2, anode; 3, electrolyte; 4, sonic horn/cathode; 5, sonic driver; 6, sonicator's controller; 7, synchronizer; 8, dc power source. Bottom: i, electric current pulse of 0.6 s duration; s, sonic pulse of 0.3 s duration; the total cycle is 1.2 s long. The usual value of electric current density was 50 mA/cm^2.

surface area 2 cm^2. The anode diameter was 50 mm, 32 mm deep in the solution (the effective surface area was 50 cm^2). In all of the experiments, the amount of electrolyte was 100 cm^3. The temperature was stabilized by a water bath and kept in the temperature range 25−27 °C, controlled by a mercury thermometer.

The standard operation parameters followed previous reports. The cathodic current density (at the ultrasonic horn) was 50 mA/cm^2. The sonicator pulse amplitude was set to 12 μm, and the appropriate ultrasonic power was about 5 W.

The silver particles were characterized by transmission electron microscopy (TEM) and by photon correlation spectroscopy (PCS) (often referred to as dynamic light scattering[14,15]). The TEM studies were performed with a JEOL, JEM-1200EX microscope. The PCS measurements were performed with a N4 Plus submicron particle sizer, manufactured by Coulter Corp.

The TEM provides both qualitative (visual) and quantitative (particle size distribution) information. Two hundred particles were counted for each size distribution calculation using the Scion Image software. In the case of the PCS studies, no visual information is available and the resulting information is a probability distribution function of particle size. It should be stressed here that PCS is unable to differentiate between large single particles and agglomerates of many single particles; thus, it is unable to yield any information about the single particles forming the agglomerate. Using nanosized TiO$_2$, a correlation between the TEM and the PCS was studied. The difference between the mean particle sizes measured by the two methods was about 10%.

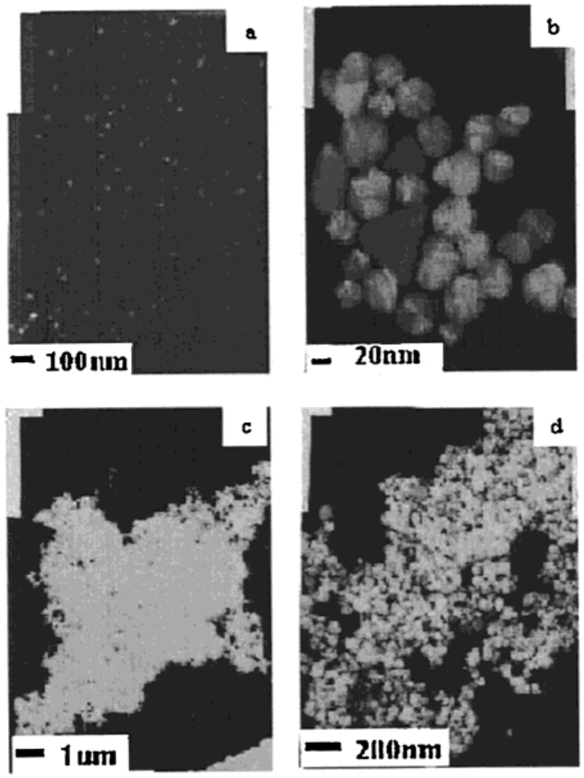

Figure 2. TEM pictures of silver particles obtained by pulsed sonoelectrochemical treatment of different durations: (a) 5 min; (b) 1 h; (c and d) 30 h.

The concentration of the Ag$^+$ ions in the electrolyte was measured by atomic absorption (Perkin-Elmer 2380). The electrolyte was centrifuged before the measurements were taken, to extract particles from the solution. The centrifugation was performed at about 1800*g*. The accuracy of the measurement was checked with etalone solutions and found to be better than 0.1%.

Results and Discussion

The TEM pictures of the produced silver nanoparticles are shown in Figure 2. One can readily see that, at the initial time interval, up to about 1 h, single crystallites grow. The mean size of the crystallites increases from 5 ± 2 nm after 5 min of sonoelectrochemical processing to 60 ± 30 nm after 60 min. At later stages, a growth of agglomerates takes place. One such agglomerate is shown in Figure 2c and d. One can see that it consists of single crystallites, each having a size of 75 ± 25 nm.

Numerical data of the particle size distribution obtained by PCS confirm the behavior described above (Figure 3). For up to 1 h of sonoelectrochemical processing, relatively small particles grow. After 1 h, we see both the 20 nm sized particles and larger ones of about 100 nm. After 56 h of processing, the single crystallites are nearly gone, and the agglomerates grow to micron sizes.

Figure 4 shows the silver ion concentration and the electrochemical cell resistance as a function of processing time. The cell resistance was calculated from the change in the applied voltage, which was needed to maintain a constant current, that is, Ohm's law. In the absence of a supporting electrolyte, one would expect that the resistance would increase with silver ion depletion. However, as shown in Figure 4, the trend is opposite, as the cell resistance falls with ion depletion, reaching a minimum after about 4 h of processing when the solution is fully

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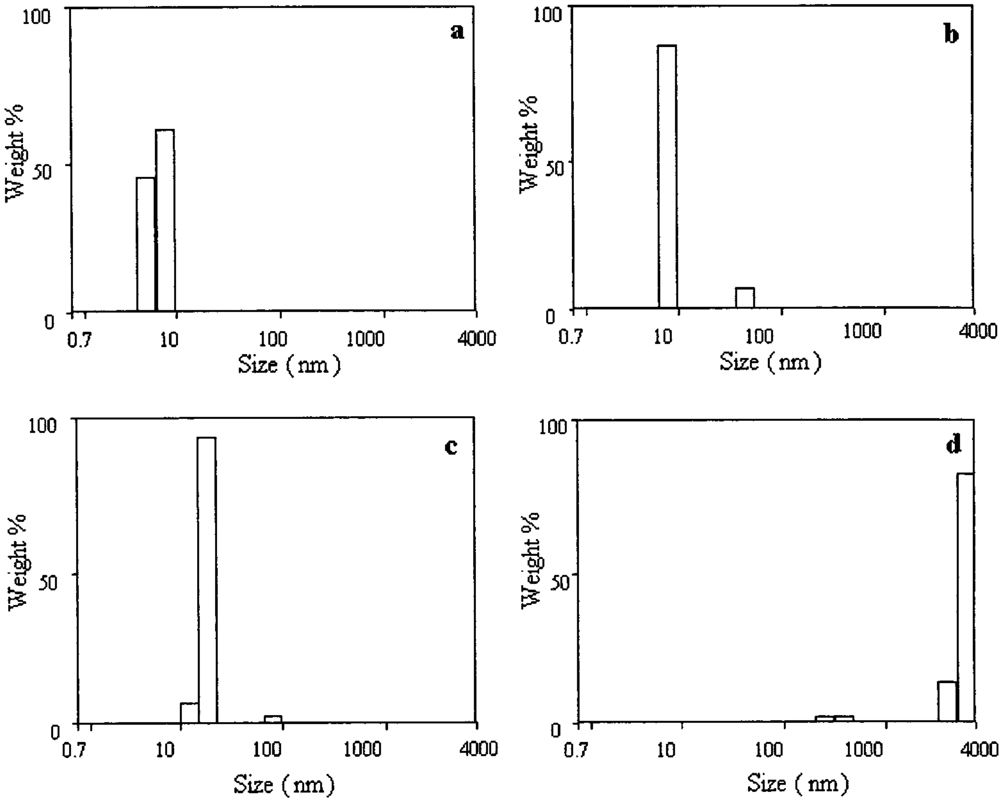

Figure 3. Particle size distributions as measured by the method of photon correlation spectroscopy: (a) 5 min, mean size 7.9 nm; (b) 25 min, mean size 11.4 nm; (c) 1 h, mean size 22.3 nm; (d) 56 h, mean size 2.67 × 10^3 nm.

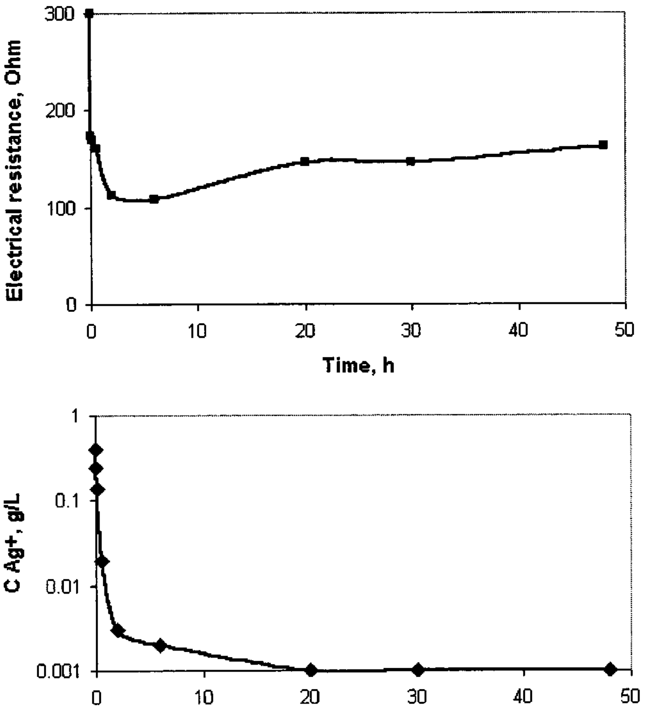

Figure 4. Electrical resistance and residual concentration of silver ions in the course of the sonoelectrochemical treatment. One can readily see that the system has reasonable conductivity while even completely depleted of silver ions.

depleted of the initial charge carriers. Only after 4 h of processing does the cell resistance gradually increase.

It should also be noted that as the solution becomes depleted of ions, the conductivity must fall, unless other charge carriers enter the game. Under our operating conditions, the total silver-depletion time is calculated to be 22.7 min according to Faraday's law, if the electrical current is purely ionic. This estimation is in fair comparison with the experiment (95% depletion after 1 h). However, such depletion should also cause about a 95% decrease of conductivity. And experimentally we see that the cell conductivity even increases, persisting for at least 50 h.

We should also mention that when we switch off the ultrasound in the course of the experiment, it usually takes about five sonoelectric cycles (6 s) for the conductivity to stabilize on a lower value. This new "sonic-less" conductivity is about 70−80% of the value before ultrasound was switched off. At this moment we do not have an explanation for the above phenomenon, but it proves that some ultrasound-initiated processes take place long after the ultrasound is switched off.

To exclude possible artifacts and to be sure that the observed time evolution is unique to the sonoelectrochemical processing, we performed the following experiment. After 1 h of pulsed sonoelectrochemical treatment, the solution was divided into two equal parts. One should note that at this stage the solution is already nearly depleted of silver ions; their concentration, as seen in Figure 4, drops from 400 to 20 mg/L. One part was subjected to the same sonoelectrochemical treatment, and the second part was subjected to purely sonic processing (of a similar pulse cycle, without switching the voltage on). The results of the PCS study of particle size distribution are shown in Figure 5. One can clearly see that sonic processing without electric current leads only to a decrease of particle size, by a factor of approximately 2 after 48 h, whereas, in the portion that was subjected to the sonoelectrochemical treatment, the particles grow by an order of magnitude.

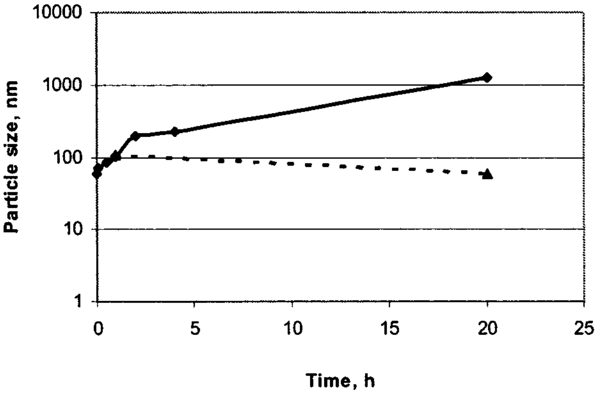

Figure 5. Particle growth during sonotreatment with (solid line) and without (dashed line) electric pulses (i.e. pure sonochemical treatment). The latter leads only to a decrease of particle size.

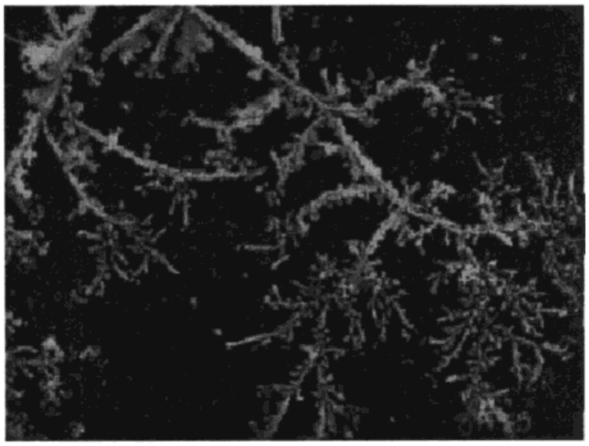

Figure 6. TEM picture of fractal-like agglomerate. Such shapes were obtained at low values (15 mA/cm^2) of electric current.

When the current density was lowered by a factor of 3 down to 33 mA/cm^2, the shape of the resulting particles was significantly different from that obtained under standard conditions. Figure 6 presents the TEM pictures of the obtained particles, showing a dendrite (or fractal-like) structure very similar to those obtained by Gedanken et al.[12] under quite different conditions.

The common model of the sonoelectrochemical synthesis involves two successive processes: the silver deposition on the cathode during the electric pulse which is followed by the breaking up of the thin layer into nanoparticles and their dispersion in solution during the sonic pulse. We can point to two groups of facts that cannot be explained by this simple model. First, the particle enlargement is characterized by two stages: growth and agglomeration. The agglomeration occurs when the solution is already depleted from silver ions and only in the presence of the electrical power. The second group of facts involves the abnormal dependence of the solution resistance on the Ag$^+$ concentration in the solution. Thus, a more comprehensive model is suggested.

The new model is based on the suspensive electrode concept; that is, the particles suspended in solution obtain the electrode potential, thus acting as part of the electrode. The sonoelectrochemical system may be described as follows. Initially, when the solution contains only Ag$^+$, the original model holds. A thin silver layer is deposited on the cathode by the electric pulse. The following sonic pulse leads to the destruction of this layer, and a suspension of nanosized silver particles is formed. At this point, when the solution contains some suspended silver particles, the suspensive electrode is formed. From that point on, two simultaneous processes occur. First, the sonoelectrode continues in the electrodeposition and break down of the original model. And second, the suspended particles are moved in the solution by the sonic wave, hit the sonoelectrode, accept its potential, and travel back to the solution. These charged silver particles acting as part of the cathode can cause electrodeposition of silver ions and therefore grow.

The particle growth stops after all the dissolved silver ions are depleted. At this time, the second stage of particle agglomeration begins. Since the agglomeration occurs only in the presence of the electric pulse, we relate the agglomeration mechanism to the charging of the suspended silver particles by the electrodes. That is, the agglomeration allows for stabilization of the small particles carrying the excess charge. Furthermore, it is possible that the agglomeration also involves a reaction between counter-charged particles. Strictly speaking, agglomeration may take place from the very beginning, but its rate is much lower than the rate of electrodeposition on the suspended particles when there is enough dissolved silver. While the electrolyte becomes depleted of Ag$^+$, the negatively charged silver particles move to longer and longer distances before they are neutralized. At this point, they can reach the anode region when still charged, thus increasing the possibility of joining other particles that have hit the anode and become positively charged. This process can occur only close to the anode, since the positively charged particles have a very short lifetime. The suspensive electrode model also explains at least qualitatively the abnormal dependence of the solution resistance on the Ag$^+$ concentration in the solution. The system resistance falls at the beginning of the sonoelectrochemical operation, since the silver particles formed increase the effective cathode surface area. In addition, the original charge carriers, the silver cations, are replaced by the charged nanoparticles that travel to long distances, thus decreasing the distance between the sonocathode and the anode. After the solution is fully depleted of the silver ions, the nanoparticles become the sole kind of charge carriers. Thus, after hours of operation, the resistance increases because of agglomeration of the particles that makes this charge transport shuttle less effective.

The proposed model seems to be the only one that explains qualitatively all the observed phenomena. There are two major facts to be mentioned. First, the current persists well after the solution is depleted of the silver ions, which leads to the conclusion that the electric current is carried by the nanoparticles. Second, particle growth in the depleted solution occurs only in the presence of electric current. Conductivity persistence itself could have other explanations; one can suppose that the nanoparticles become electrically charged because of electrocolloidal effects at creation and not because they come in touch with electrodes. However, in this case all the nanoparticles would be similarly charged, and therefore we should expect no difference in behavior induced by the electric current. Similarly, any model describing particle size and shape dynamics in terms of dissolution-and-growth by the influence of an ultrasonic field can explain neither why this process does not take place in the absence of electric current nor why the electric current persists at all.

An understanding of the underlying mechanisms may lead to wide opportunities in regulating particle size by varying different parameters of the sonoelectrochemical sequence, such as electric and sonic pulse height and duration, their respective synchronization, forced convection, and so forth. However, it seems that the ability to employ this method for the synthesis of composite and core−shell nanosize materials is even more important. Several possible schemes can be pointed to. One is based on the electrodeposition of dissolved ions on suspended “matrix” nanoparticles. Another approach may involve a mixture of several ions having different electrochemical potentials, which can be deposited on top of each other sequentially as the applied voltage increases, resulting in multishell nanoparticles. These methods should lead to efficient production of very special layered nanostructures and are currently being studied.

Conclusions

In summary, sonoelectrochemical synthesis of silver nanoparticles was used as a model case to study the processes involved in this synthetic approach. The results show that the synthesis is highly affected by the formation of a suspensive electrode in the system, consisting of the sonoelectrode and the nanoparticles, which are initially formed by an electrochemical deposition of a thin layer on the sonoelectrode and a sonic dispersion of the layer. On the basis of the suspensive electrode concept, a new model that describes the sonoelectrochemical mechanism has been proposed. By identifying the factors that affect the sonoelectrochemical synthesis, we suggest unique possibilities for employing the suspension electrode scheme for the synthesis of complex nanostructured materials by pulsed sonoelectrochemistry.

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