Synthesis and electrical properties of uniform silver nanoparticles for electronic applications

Dapeng Chen · Xueliang Qiao · Xiaolin Qiu · Jianguo Chen

Abstract Silver nanoparticles are considered to apply a silver paste for electrode because of their high conductivity. However, the dispersion of silver nanoparticles in electronically conductive adhesives (ECAs) restricts them used as conductive fillers. A simple method had enabled the synthesis of silver nanoparticles by reducing silver nitrate with ethanol in the presence of poly(N-vinylpyrrolidone) (PVP). Reaction conditions, such as silver nitrate concentration, PVP concentration, reaction time, and reaction temperature, had been studied. Fine dispersion and narrow size distribution of silver nanoparticles were obtained. They were added to ECAs by re-dispersing them in ethanol while it was used as the diluent to adjust the volatility of ECAs, preventing them from the aggregation and increasing the chance to fill the gaps between silver flakes. This proposed process offers the possibility to effectively use these synthesized silver nanoparticles for improving the conductivity of ECAs.

Introduction

Silver nanoparticles have attracted extensive research interest because of their unusual optical, electronic, and chemical properties which depend on their size, shape, composition, crystallinity, and structure [1, 2]. They have been widely exploited for use as microelectronic materials [3, 4], antibacterial materials [5, 6], catalytic materials [7], and sensor materials [8] due to these unique properties. For example, the melting point of silver nanoparticles can be drastically reduced because the surface energy of the nanoparticles tremendously increases on account of the extremely small size of the particles [9]. It is possible for them to fill the gaps between silver flakes during the preparation of ECAs and combine them to improve the conductivity when ECAs are cured at the low temperatures. In these regards, silver nanoparticles used as conductive fillers in electronically conductive adhesives (ECAs) are beneficial for electronic device application [10].

Therefore, it is very essential to develop a simple and effective preparation method of silver nanoparticles with controlled size and shape. In recent years, many methods for silver nanoparticles synthesis are used. These methods include chemical reduction [11, 12], template [13, 14], electrochemical methods [15, 16], photoinduced reduction [17, 18], microwave-assisted synthesis [19], and so forth. Silver nanoparticles used in electronic device application are generally prepared by chemical reduction methods. Using these methods, silver nanoparticles with spherical [20], cubic [21], wire [22], and triangular shapes [23] have been manufactured. However, the dispersion of silver nanoparticles has been a bottle neck for them to be used in ECAs due to their aggregation. It is impossible to effectively use silver nanoparticles for improving the conductivity of ECAs.

In this paper, we describe the synthesis of PVP-capped silver nanoparticles in ethanol. Also ethanol is used as the diluent in ECAs. It has been shown that fine dispersion and narrow size distribution of silver nanoparticles can be

D. Chen · X. Qiao (✉) · J. Chen
State Key Laboratory of Plastic Forming Simulation and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China
e-mail: dpchenhust@yahoo.com.cn

X. Qiu
Nanomaterials Research Center, Nanchang Institute of Technology, Nanchang, Jiangxi 330013, People's Republic of China

achieved by this method. UV–visible absorption spectrometer and transmission electron microscopy (TEM) are used to monitor the morphological evolution of silver nanoparticles. Effects of silver nitrate and PVP concentrations, reaction time, and reaction temperature on particle size are discussed. Silver nanoparticles are added to ECAs by re-dispersing them in ethanol while it is used as the diluent to adjust the volatility of ECAs, preventing the particles from the aggregation and effectively filling the gaps between silver flakes during the preparation of ECAs. It has been found that the improved conductivity of ECAs can be achieved.

Experimental section

Materials

Silver nitrate (Hubei Xinyin Noble Metal Co. Ltd., 99.9%) was the starting material for silver nanoparticles, and poly(N-vinylpyrrolidone) (PVP, molecule weight ≈ 40000, Sinopharm Chemical Reagent Co. Ltd, the concentration was calculated in terms of repeating unit.) was used as capping agent. The reducing agent and solvent used for silver nanoparticles synthesis was ethanol. Ethanol and acetone were purchased from Shanghai Zhenxing No. 1 Chemical Plant. All chemicals were of analytical grade and were used without further purification.

Methods

In a typical procedure, 20 mL of ethanol solution of silver nitrate was put into a 50 mL vial equipped with a magnetic stirring bar. Then this vial was put into a 30 °C water bath monitored by a thermometer, and 20 mL of ethanol solution of PVP was added at a rate of 0.667 mL/min. The reaction mixture was continued with heating at 30 °C for another 90 min. The typical synthesis went through a number of color changes before the color became stable. Silver nanoparticles were easily separated from ethanol by addition of a large amount of acetone, followed by sonication and centrifugation. Then they were re-dispersed in ethanol and precipitated again by acetone addition for purification.

Characterization of silver nanoparticles

The transmission electron microscopy (TEM) images were taken by FEI transmission electron microscopy (Tecnai G2 20) operated at 200 kV accelerating voltage. The samples for TEM studies were prepared by placing small drops of the solution copper grids covered with carbon films, and allowing the solvent to slowly evaporate under vacuum for 30 min at room temperature. A UV-2010 UV–Visible spectrophotometer was used to record the absorbance at room temperature with quartz cuvettes (1 cm optical path) as the containers. All samples were all obtained by diluting original solution with ethanol.

Measurement of bulk resistivity of ECAs

Resistivity of the ECAs was calculated from the bulk resistance of the specimen with a size about 76 mm (L) × 6 mm (W) × 0.5 mm (T). Uncured ECAs were spread within space between two strips of an adhesive tape applied on a pre-cleaned glass slide by means of a doctor blade, and then the tapes were removed. After curing at 150 °C for 2 h, the bulk resistance (R) of this ECAs strip was measured as well as the size of the specimen by the four point probe method. The bulk resistivity (ρ) was calculated using following equation: $\rho = R * T * W/L$.

Results and discussion

Roles of PVP and ethanol

In this method, PVP is used to protect the particles from the aggregation to form large particles. It exhibits favorable protecting properties due to its unique structure [24, 25]. It is a homopolymer whose polyvinyl skeleton contains polar groups. The N and O in these polar groups probably have a strong affinity for silver ions and silver nanoparticles. At the early stage, a complex compound containing silver ions and PVP is easily reduced, increasing the probability of nucleus formation. Moreover, due to the presence of PVP, the rate of spontaneous nucleation increases and a higher number of nuclei are formed, decreasing the mean size of the particles. Otherwise, PVP plays the main role of preventing silver nanoparticles from the aggregation by covering on their surface.

Ethanol is employed as reducing agent and solvent during silver nanoparticles synthesis, and as at that, it can be also used as the diluent to adjust the viscosity of ECAs without affecting the mechanical and conductive properties owing to its volatility. It is possible that silver nanoparticles are incorporated to ECAs by re-dispersing them in ethanol while it is used to adjust the viscosity of ECAs, which prevents the aggregation of the particles and makes them effective to fill the gaps between silver flakes.

Effects of the concentrations of PVP and silver nitrate on the synthesis of silver nanoparticles

Figure 1a shows the influences of the concentrations of PVP on the preparation of silver nanoparticles. There is an
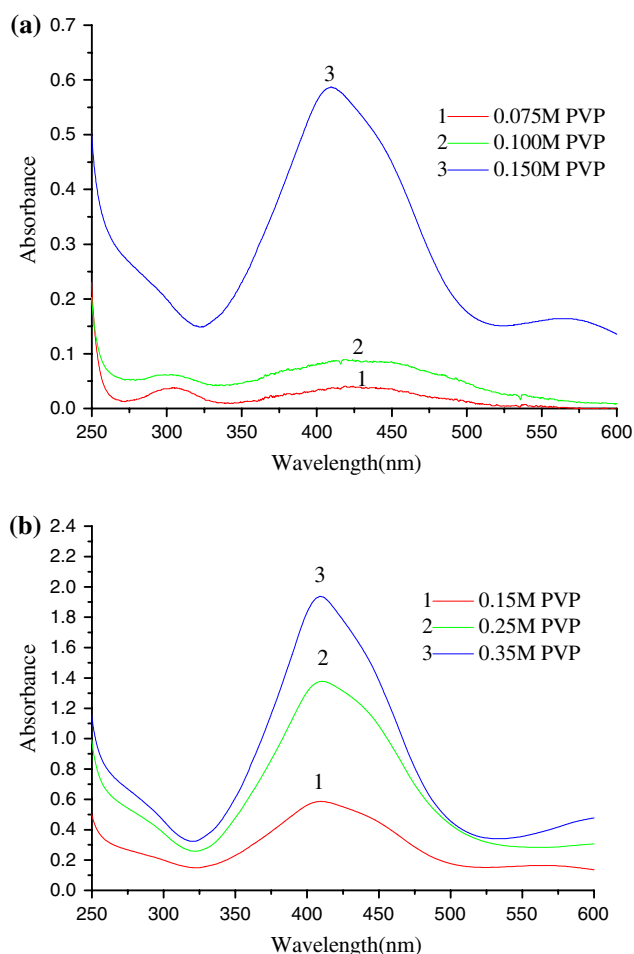
Fig. 1 The UV–visible of silver nanoparticles synthesis with different concentrations of PVP. The concentration of AgNO$_3$ is the same (0.05 M)

Fig. 2 The UV–visible of silver nanoparticles synthesis with different concentrations of AgNO$_3$. The concentration of PVP is the same (0.5 M)

Figure 2 shows the UV–visible spectra of silver nanoparticles prepared with different concentrations of silver nitrate. As can be found, the absorption peak at approximately 420 nm is consistent with that of silver nanoparticles [27]. With the increasing concentration of silver nitrate from 0.05 M to 0.15 M, the number of silver nanoparticles increases. This result is mainly attributed to the fact that the rate of spontaneous nucleation increases significantly more than the growth rate of silver nanocrystals. A larger number of nuclei are formed during the nucleation burst. However, the particle size does not become bigger owing to the presence of PVP. It is possible that a larger amount of silver nanoparticles with small particle size can be achieved.

Effects of reaction time and reaction temperature on the synthesis of silver nanoparticles

The reaction could be easily followed through its distinctive color changes. Within a few minutes of injection, the solution became light yellow in color, indicating the synthesis of silver nanoparticles. As the reaction proceeded, the yellow color changed to red color. The effect of reaction time on silver nanoparticles synthesis is summarized in Fig. 3. There is a red shift in the absorption peak of the spectrum by increasing reaction time. At the early stage of the reaction, the particle size becomes large rapidly due to the growth and aggregation of silver nanocrystals. With the increasing reaction time, the rate of the reaction becomes slow because of the protection of PVP, making the accretion of particles size inconspicuous.

absorption peak at approximately 310 nm when the concentration of PVP is lower. This result is because that the Ag$_2^+$ cluster and small clusters are produced [26]. With the increasing concentration of PVP, the 310 nm peak decreases to disappear and the 420 nm absorption band increases gradually. It is clear from this result that PVP accelerates the reaction between silver ions and ethanol. Also the particle size gets smaller in the presence of PVP. This macromolecule often adopts a pseudorandom coil conformation which may be in association with the metal atoms, increasing the probability of nucleus formation [24, 25]. However, as can be seen in Fig. 1b, the particle size does not continue to get smaller by changing the concentrations of PVP from 0.15 M to 0.35 M because PVP at the solid/liquid interface does not interfere with the silver diffusion-surface deposition process since the particles grow to a definite size. It is further confirmed by the TEM results (Fig. 5).
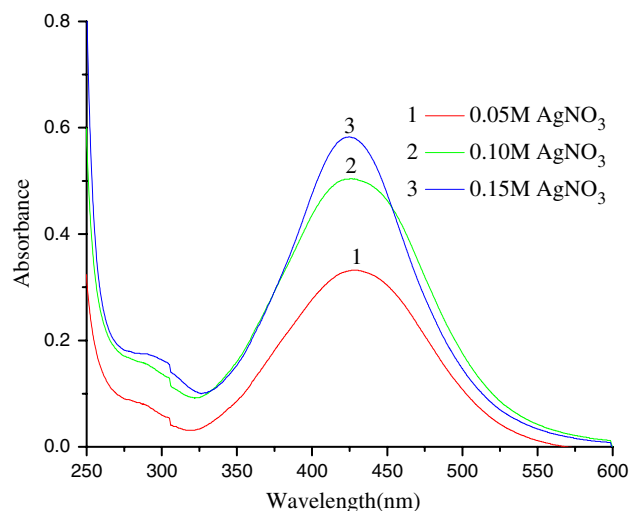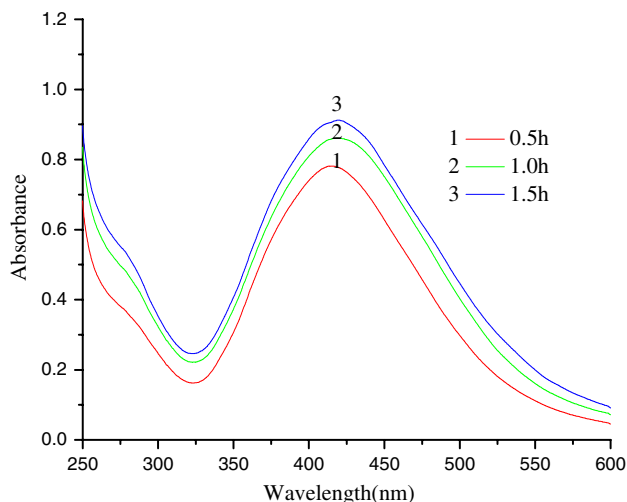
Fig. 3 The UV–visible of silver nanoparticles synthesis with different reaction times. The concentration of AgNO$_3$ and PVP are 0.20 M and 0.60 M, respectively
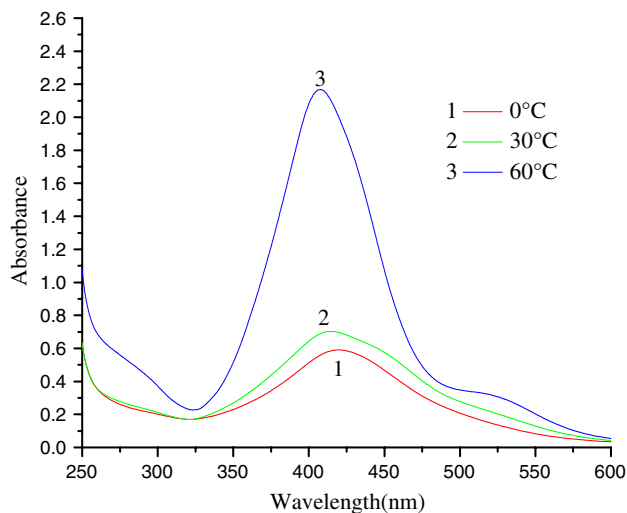

Fig. 4 The UV–visible of silver nanoparticles synthesis with different reaction temperature. The concentration of AgNO$_3$ (0.15) and PVP (0.50) are the same

As Fig. 4 shows, silver nanoparticles can be synthesized at a lower temperature, meaning that Ag$^+$ is still reduced by ethanol, but there is a slower reaction rate due to the low concentration of dissociative Ag$^+$. The influences of different reaction temperatures result in a blue shift of the absorption peak, indicating that the particle size of silver nanoparticles decreases with the reaction temperature changing from 0 °C to 60 °C when all the other reaction conditions are identical. Also there is much more amount of silver nanoparticles synthesized at the high reaction temperature (60 °C). It is suggested that small particle size and large quantity of particles are acquired by controlling reaction temperature.

The influences of PVP on dispersion and size distribution of silver nanoparticles

Figure 5 shows the influences of PVP on the dispersion and size distributions of silver nanoparticles. As Fig. 5a, c, e shows, fine dispersion of silver nanoparticles can be acquired because PVP plays important roles of the protection of silver nanoparticles to prevent them from the aggregation. Comparing Fig. 5b, d, and f, Fig. 5d and f shows narrower size distributions of silver nanoparticles while there is a wider size distribution in Fig. 5b on account of lower concentration of PVP. It is important to note that PVP as a protective agent plays a decisive part in controlling the size distribution of silver nanoparticles by reducing silver nitrate with ethanol. The particle size of all the samples is less than 10 nm, but there are not numbers of silver nanoparticles with smaller particle size synthesized when the concentration of PVP changes from 0.15 M to 0.35 M. This result is mainly because that the protection of PVP does not interfere with the process of silver nanoparticles synthesis until the particles grow to a definite size. This phenomenon can also be acquired by the analysis of UV–visible spectra.

The ways of adding silver nanoparticles to electronically conductive adhesives (ECAs)

Silver flakes are usually used as conductive fillers in electronically conductive adhesives [28]. However, there are gaps between silver flakes due to their different shapes, resulting in decrease in the conductivity of ECAs. Silver nanoparticles are incorporated for the purpose of the current density and contact resistance improvement of the ECAs [29]. There are two ways to add silver nanoparticles to ECAs. Usually they are added to ECAs directly during the preparation [29]. It is not effective for them to fill the gaps because of the aggregation of the particles. In this study, after the purification, silver nanoparticles are re-dispersed in ethanol which is used as the diluent in the preparation of ECAs. They are also added to ECAs when ethanol is used to adjust the viscosity of ECAs. It is possible for them to be well dispersed in ECAs, increasing the chance of filling the gaps between silver flakes. As Fig. 6 shows, the conductivity of ECAs is improved effectively while the amount of silver nanoparticles is no more than 1 part by weight per 100 parts by weight of silver flakes. The schematic diagram of an ECA interconnect junction containing silver nanoparticles is shown in Fig. 7. Due to fine dispersion of silver nanoparticles in ECAs, they can fill the gaps between silver flakes by two possible ways. On the one hand, there are wider conductive paths by filling the gaps between linked silver flakes. On the other hand, more conductive paths can form by filling the gaps between

Fig. 5 TEM images and size distributions of silver nanoparticles synthesis with different concentrations of PVP: **a**, **b** 0.15 M; **c**, **d** 0.25 M; **e**, **f** 0.35 M. The concentration of AgNO$_3$ is the same (0.05 M)
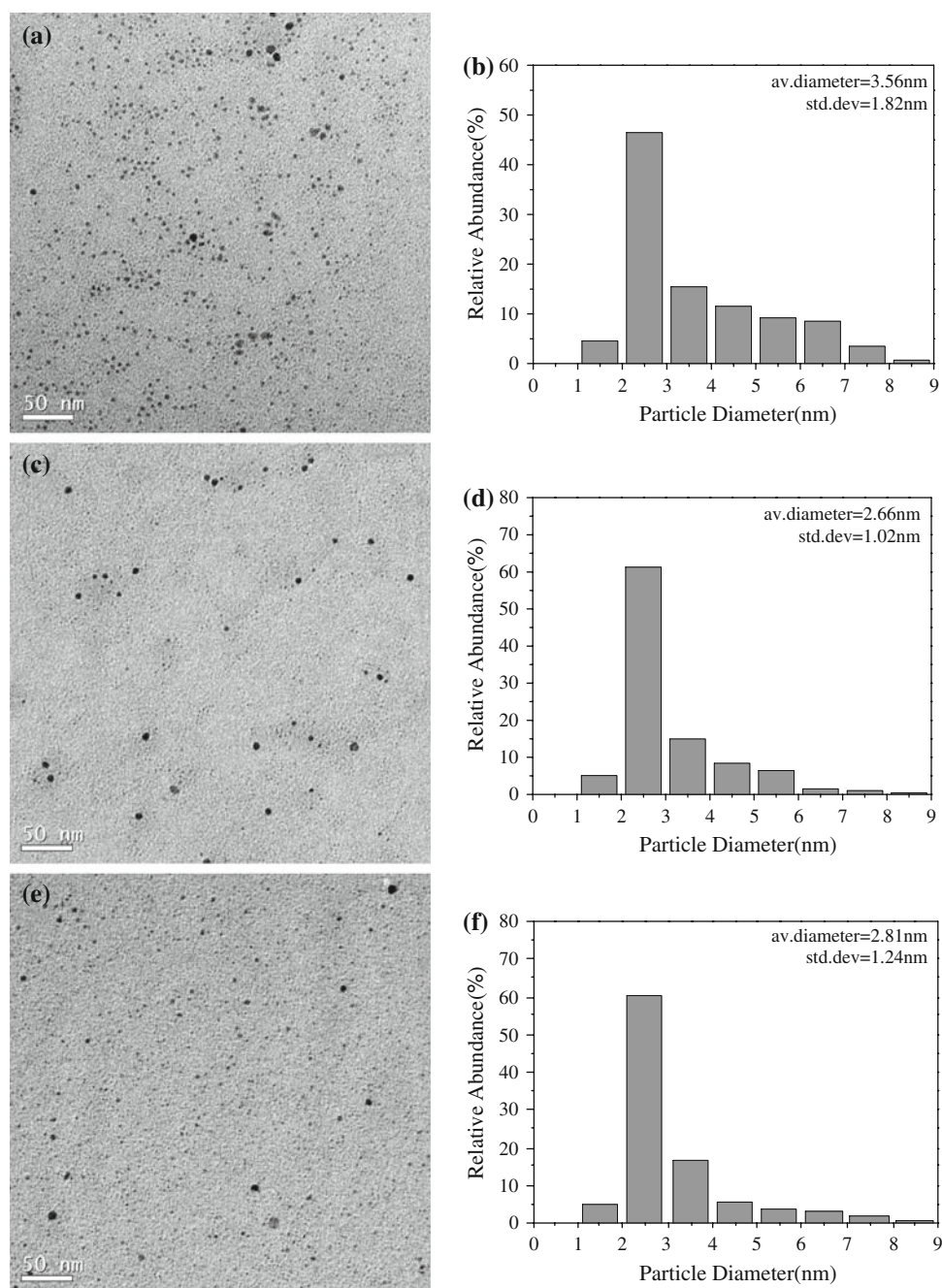
unattached silver flakes. It effectively uses silver nanoparticles to improve the conductivity of ECAs. Further study is needed to characterize the electrical property of ECAs systematically.

Conclusions

Silver nanoparticles are synthesized by a traditional chemical reduction method. The absorption peak at 410 nm

is a clear signature of the quantum size effect occurring in the absorption property of silver nanoparticles. Some reaction conditions, such as the concentration of silver nitrate and PVP, reaction temperature, and reaction time, play different roles on the size and distribution of silver nanoparticles. The particle size decreases with increasing the concentration of silver nitrate and with increasing reaction temperature. A long reaction time makes the particle size become large. Fine dispersion and narrow size distribution of silver nanoparticles can be acquired in the
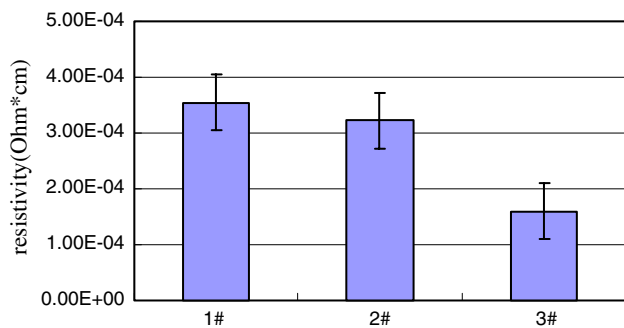
Fig. 6 Variance of resistivity of ECAs samples: 1# without diluents; 2# with diluents; 3# with diluents containing silver nanoparticles. The other components and curing process are the same
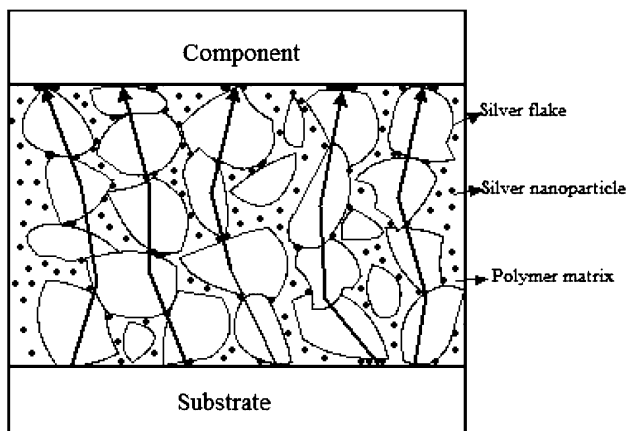

Fig. 7 A schematic diagram of an ECA interconnect junction containing silver nanoparticles

presence of PVP. They are incorporated to electronically conductive adhesives (ECAs) by re-dispersing them in ethanol which is used as the diluent in the preparation of ECAs. This proposed process offered the possibility to effectively use these synthesized silver nanoparticles for improving the conductivity of ECAs. Further study is under way to characterize the electrical property of electronically conductive adhesive.

References

1. Balan L, Malval JP, Schneider R, Burget D (2007) Mater Chem Phys 104:417
2. Jiang ZJ, Liu CY, Sun LW (2005) J Phys Chem B 109:1730
3. Hsu SLC, Wu RT (2007) Mater Lett 61:3719
4. Park S, Seo D, Lee J (2008) Colloids Surf A Physicochem Eng Asp 313–314:197
5. Morones JR, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramirez JT, Yacaman MJ (2005) Nanotechnology 16:2346
6. Martinez-Castanon GA, Nino-Martinez N, Martinez-Gutierrez F, Martinez-Mendoza JR, Ruiz F (2008) J Nanopart Res 10:1343
7. Shiraishi Y, Toshima N (1999) J Mol Catal A Chem 141:187
8. McFarland AD, VanDuyne RP (2003) Nano Lett 3:1057
9. Castro T, Reifenberger R, Choi E, Andres RP (1990) Phys Rev B 42:8548
10. Pothukuchi S, Li Y, Wong CP (2004) J Appl Polym Sci 93:1531
11. Slistan-Grijalva A, Herrera-Urbina R, Rivas-Silva JF, Avalos-Borja M, Castillon-Barraza FF, Posada-Amarillas A (2008) Mater Res Bull 43:90
12. Khanna PK, Kulkarni D, Beri RK (2008) J Nanopart Res 10:1059
13. Malandrino G, Finocchiaro ST, Fragala IL (2004) J Mater Chem 14:2726
14. Behrens S, Wu J, Habicht W, Unger E (2004) Chem Mater 16:3085
15. Yin BS, Ma HY, Wang SY, Chen SH (2003) J Phys Chem B 107:8898
16. Kim KD, Choi KY, Kim HT (2005) Scr Mater 53:571
17. Shchukin DG, Radtchenko IL, Sukhorukov GB (2003) Chemphyschem 4:1101
18. Jin RC, Cao YW, Mirkin CA (2001) Science 294:1901
19. Yamamoto T, Yin H, Wada YJ (2004) Bull Chem Soc Jpn 77:757
20. Oliveira MM, Zanchet D, Ugarte D, Zarbin AJG (2004) Prog Colloid Polym Sci 128:126
21. Sun YG, Xia YN (2002) Science 298:2176
22. Caswell KK, Bender CM, Murphy CJ (2003) Nano Lett 3:667
23. Jiang XC, Zeng QH, Yu AB (2007) Langmuir 23:2218
24. Carotenuto G, Pepe GP, Nicolais L (2000) Eur Phys J B 16:11
25. Zhang ZT, Zhao B, Hu LM (1996) J Solid State Chem 121:105
26. Linnert T, Mulvaney P, Henglein A, WeUer H (1990) J Am Chem Soc 112:4657
27. Joerger R, Klaus T, Granqvist CG (2000) Adv Mater 12:407
28. Lu DQ, Wong CP (2000) IEEE Trans Electron Packag Manuf 23:185
29. Lee HH, Chou KS, Shih ZW (2005) Int J Adhes Adhes 25:437