RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Fabrication of micron-SiO_2@nano-Ag based conductive line patterns through silk-screen printing

Man Wang,[a] Xuefeng Xu,[a] Bing Ma,[a] Yanyan Pei,[a] Changchun Ai*[b] and Liangjie Yuan*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Abstract

Here we present a cheap alternative for the fabrication of conductive line patterns printed on flexible PI substrate at intermediate temperature. In order to achieve this purpose, a low-cost and water-soluble screen printing conductive paste was prepared, with micron-SiO_2@nano-Ag particles as the conductive filler. Variations in the filling content of micron-SiO_2@nano-Ag, the addition of the coupling agent, curing temperature and time can remarkably affect the electrical and mechanical performance of the conductive paste. The optimal sheet resistance (at 62mΩ/□) and mechanical performance of the paste were achieved under the curing condition of 140 °C for 30 min, with the filling content of 53.6 wt% of micron-SiO_2@nano-Ag (32.4 wt% of Ag) and 1.0 wt% of the coupling agent APTES. The conductive mechanism of the paste was discussed according to the "percolation theory". The conductive line patterns fabricated through silk-screen printing were applied to be linked with a LED into a circuit, suggesting that the paste would have a potential application in electronic devices.

Key words: micron-SiO_2@nano-Ag composite; conductive paste; silk-screen printing; conductive line patterns

1. Introduction

In recent years, many efforts have been devoted to the development of convenient and low-cost processing techniques to fabricate conductive patterns for use in various electronic applications,[1] including flexible display, solar cell arrays, and radio-frequency identification (RFID).[2] Traditionally, the circuits of PCBs have been manufactured through electroplating and etching processes accompanied by lithography, which is time consuming and very complicated due to many steps.[3] Hence, the complementary printing techniques such as nanoimprinting, screen printing and inkjet imprinting have emerged as attractive direct patterning techniques and promoted a big development in flexible electronics fabrication fields.[4] Among them, silk-screen printing is the most promising route to fabricate conductive tracks on different kinds of substrate materials in one step, for its significant advantages in flexibility, high reproducibility and high-throughput mass production.[5]

Another critical issue that needs to be noticed when applying printed electronics to these applications is the development of conductive pastes,[6] which are composed of conductive particles, polymer binders, and dispersing solvents. In terms of the conductive particles, silver is one of the materials with the lowest electrical resistivity (1.59 μΩ·cm), and silver nanoparticles (NPs) based conductive pastes have been developed because of their unique electrical and mechanical properties.[7] Whereas, the agglomeration of Ag NPs occurs due to attractive interaction between NPs and worsens the physical properties of materials such as electrical conductivity, which is a long-lasting issue of interest both in industry and academics.[8] Besides, the high cost of silver NPs as noble metal material has hindered the use of them. Therefore, many researchers are seeking ways to find cheaper conductive fillers with higher reliability instead of Ag NPs. It is reported that copper is a promising alternative material, yet the formation of a surface oxide layer on Cu is inevitable in an ambient atmosphere.[9] Wei Wu et al. presented a facile approach to synthesize a cheaper conductive filler by coating Ag NPs on the surface of carbon, which was dispersed in epoxy resin and organic solvent to prepare a conductive paste.[10] However, the C@Ag particle suffered from low mobility and unavoidable aggregation in polymer matrix because of its submicron particle size. As an alternative of submicron-sized carbon particles, micron-silica spheres are a good candidate as the support material for Ag NPs, due to their non-toxicity to the environment, thermal stability, desirable mechanical strength and facile transportation ability. Typically, the synthesis of SiO_2@Ag was largely studied in the fields of catalysis,[11] anti-bacterial properties,[12] and surface-enhanced Raman scattering[13] etc.. But its application as a conductive filler in the conductive paste is seldom reported.

In the present work, Ag NPs were deposited on silica microspheres to prepare cheap conductive particles with electrical property. The size distribution of the utilized SiO_2 spheres is in the range of several micrometers to improve the packing density.[14] Various analysis techniques were adopted to confirm the composition and structure of the composite, including X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), scanning electron microscope (SEM) and transmission electron microscope (TEM). The as-synthesized micron-SiO_2@nano-Ag particles were mixed with aqueous polyurethane (PU) emulsion and some other additives to prepare a conductive paste, which could be silk-screen printed on the plastic substrate, namely polyimide (PI) substrate to form conductive line patterns. The conductive mechanism of the paste was discussed according to the “percolation theory”.

2. Experimental

2.1 Materials

The silica microspheres were obtained from Wuhan Shuaier Photo Electronic Materials Corporation, Ltd., which were synthesized according to Ai's method.[15] $SnCl_2 \cdot 2H_2O$, silver nitrate ($AgNO_3$), triethanolamine (TEOA), anhydrous ethanol were purchased from Sinopharm Chemical Reagent Corporation, Ltd.. Trifluoroacetic acid (TFA) was bought from Shanghai Lingfeng Chemical Reagent Corporation Ltd.. (3-Aminopropyl)triethoxysilane (APTES) was supplied by Aladdin Chemistry Corporation, Ltd.. 2-Hydroxyethyl acrylate (HEA) was purchased from Energy Chemical. The stable aqueous polyurethane (PU) emulsion was supplied by Wanhua Chemical Group Corporation, Ltd.. The polyimide (PI) substrate was received from Wuhan Huashuo technology Corporation, Ltd.. The polyethylene terephthalate (PET) was obtained from Wuhan ink market. All the reagents were AR (analytical reagent) grade in purity and employed without purification. In all the processes, deionized water was used.

2.2 Synthesis of micron-SiO_2@nano-Ag composite

The micron-SiO_2@nano-Ag composite was synthesized by the Sn^{2+} sensitization and “seed-mediated growth technique”. More specifically, 0.50 g of $SnCl_2 \cdot 2H_2O$ and 1 ml of CF_3COOH (the dispersant of Sn^{2+} ions) were dissolved in 50 ml of deionized water with the aid of ultrasound. Then 1.00 g of SiO_2 microspheres was soaked in the above mixture for 4 hours at 30 °C. The SiO_2 microspheres treated by Sn^{2+} were collected by filtration and dispersed in 100 ml of anhydrous ethanol. Subsequently, 50 ml of an aqueous solution of $AgNO_3$ (0.1176 M, 0.1764 M and 0.2353 M, respectively) was prepared, and TEOA was added until the solution turned from turbid to transparent for complexation of Ag^+ ions. The SiO_2@Sn^{2+}/ethanol dispersion was poured into the above freshly prepared $Ag(TEOA)_2^+$ solution immediately. After 4 hours of stirring at room temperature, 20 ml of HCHO (2 wt%) was added for complete reduction. The particles were collected and dried in a vacuum oven at 50 °C.

2.3 Preparation of the conductive paste

Firstly, the conductive particles were well dispersed in PU emulsion and the active solvent HEA in different mass ratios to explore the optimal filling content of micron-SiO_2@nano-Ag. Secondly, in order to keep balance between the electrical and mechanical performance of the paste, 53.6 wt% of micron-SiO_2@nano-Ag was chosen as the proper composition of the paste to study the influence of adding the coupling agent. Namely, 0.5 wt%, 1.0 wt% and 1.5 wt% of APTES were added into the above mixture, and the pastes were cured at 140 °C for 10 min, 30 min, 120 min, respectively. The formulated pastes were intensively mixed (10 min, 1800r/min) and degassed (2 min, 2000r/min) in a planetary motion mixer (Thinky Mixer ARE-310), and then painted into several films (0.10 mm of thickness) on PET substrates by an AFA-III Automatic thick film coater. The changes of the sheet resistance of the films with the amount of micron-SiO_2@nano-Ag, the addition of APTES, curing time and curing temperature were recorded using a RTS-9 four-point probe tester.

2.4 Silk-screen printing

Conductive line patterns were silk-screen printed on PI substrate through a silk-screen printing plate (200 mesh, polyester), and then placed in a temperature-controlled oven. A range of different temperatures and curing times were used to study the electrical and mechanical performance (adhesion and flexibility) of the paste, which are of great importance in the practical application of the conductive paste.

2.5 Characterization

The particle size distribution data of SiO_2 microspheres was measured using a Malvern Mastersizer 2000. The powder X-ray diffraction patterns of micron-SiO_2@nano-Ag particles were obtained by Bruker D8 advanced powder X-ray diffractometer with Cu Kα1 radiation (λ=1.54060 Å) at the scanning speed of 6° min^{-1} (2θ). The composition of micron-SiO_2@nano-Ag particles with different contents of Ag were confirmed by X-Ray fluorescence analysis (XRF, S4 PIONEER). The morphologies of silica microspheres and micron-SiO_2@nano-Ag particles were observed by scanning electron microscopy (Zeiss Sigma FEI SEM). A transmission electron microscope (TEM, JEOL JEM-100CX□) was employed to further characterize the morphology of micron-SiO_2@nano-Ag particles. Before examination, micron-SiO_2@nano-Ag particles were diluted with ethanol, and then dried onto carbon-coated copper grids. The synthesized micron-SiO_2@nano-Ag particles were made into tablets under the pressure of 10 MPa by an infrared tablet press, and the sheet resistance of them was examined using a RTS-9 four-point probe tester. The adhesion test was carried out by applying the Scotch 3 M $600^{\#}$ transparent tape to the surface of the cured line patterns in Figure 1 (a). The tape was pressed down to get rid of air bubbles, and then peeled off. The determination of adhesion is classified into “Zero”, “Poor”, “Fair”, “Good” and “Excellent”.[16] Flexibility test was experimented to the line patterns in Figure 1 (b). The PI substrate was bent 180 degree outward, 180 degree inward and then put flat in sequence. For each step, 2 kg of balancing weight was placed in the midline for 1 min. The resistance changes of the line patterns were examined by a digital multi-meter (Endura E9242). In accordance with the above procedures, the bending test was conducted for 3 times. The cross section area of the cured conductive line patterns was observed by FEI QUANTA 200 SEM. And the thickness of the patterns was examined by form talysruf profiler.

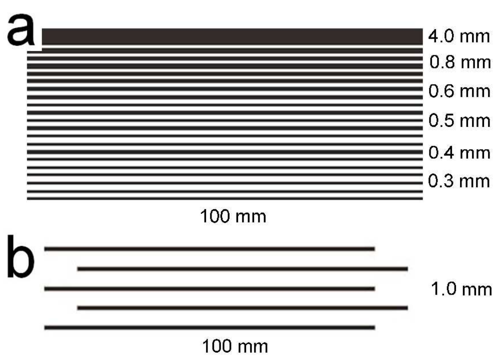

Figure 1 Conductive line patterns on PI substrate for (a) adhesion and (b) flexibility test

3. Results and discussion

3.1 Synthetic mechanism of micron-SiO_2@nano-Ag

For a typical silver mirror reaction, ammonia silver complexes are reduced by aldehyde compounds, and metallic silver is attached on the inner wall of the container. However, in the synthesis of micron-SiO_2@nano-Ag, silver should be deposited on the surface of silica microspheres, rather than on the wall of the round bottom flask. Consequently, SiO_2 microspheres are pretreated by the "sensitizer" (Sn^{2+}),[17] which is adsorbed onto the surface of silica microspheres through electrostatic attraction.[18] Then $Ag(TEOA)_2^+$ ions are reduced by Sn^{2+} to generate Ag seeds, which are served as nucleation sites for the growth of a silver nanoshell on the basis of "seed-mediated growth technique".[19] At the same time, the Sn^{2+} ions are oxidized to Sn^{4+} ions. When HCHO is added, $Ag(TEOA)_2^+$ ions are completely reduced and a silver nanolayer on the surface of micron-SiO_2 is formed, seen in Figure 2.

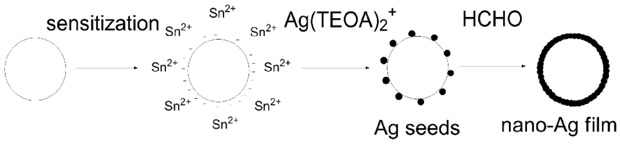

Figure 2 Synthetic mechanism of micron-SiO_2@nano-Ag

Significant advantages of selecting SiO_2 microspheres as the support material of silver NPs are supported by the following viewpoints. (1) Most importantly, to achieve the same electrical performance, the usage of the noble metal material Ag is remarkably reduced and the agglomeration of Ag NPs can be avoided; (2) SiO_2 microspheres are normally distributed, on this occasion, small spherical particles can fill into the gaps of large spherical particles to provide close contacts; (3) the density of SiO_2 microspheres is relatively lower than silver, so that the conductive particles will not be easily precipitated in PU emulsion; (4) the volume fraction of silver NPs is expanded in the conductive paste, and the "percolation threshold" can be achieved under low filling content of micron-SiO_2@nano-Ag, which is clearly explained in section 3.3.

3.2 Characterization of SiO_2 and micron-SiO_2@nano-Ag

The real size distribution of SiO_2 microspheres is shown in Figure 3, which indicates that SiO_2 microspheres are in the range of several micrometers and normally distributed with D_{50} at 4.714 μm. The particle size of SiO_2 microspheres larger than 20 μm does not meet the requirements of microfabrication. Meanwhile, smaller particle size leads to larger specific surface area of the SiO_2 microspheres, thus the amount of $AgNO_3$ will be increased to fully cover the surface of SiO_2. Figure 4 depicts the XRD patterns of the micron-SiO_2@nano-Ag composites synthesized by different $AgNO_3$ concentration. For each composite, there exists a broad peak of amorphous silica at 2θ angles of around 23°. The other peaks at 2θ angles of 37.9°, 44.1°, 64.3°, 77.2° and 81.4° correspond to the reflections of (111), (200), (220), (311) and (222) crystalline planes of Ag NPs (JCPDS No.04-0783), respectively. The SEM images of bare SiO_2 microspheres and micron-SiO_2@nano-Ag particles are shown in Figure 5 (a), (b), (c) and (d), respectively. As displayed in Figure 5 (a), silica microspheres are spherical with smooth edges and bare surface. In contrast, in Figure 5 (b), (c) and (d), the surface of SiO_2 microspheres is rough, and the thickness of the Ag films increases along with the increase of $AgNO_3$ concentration. It can be speculated that the as-prepared micron-SiO_2@nano-Ag particles are electrically conductive, since silica microspheres are almost wrapped in the silver film. The TEM images of micron-SiO_2@nano-Ag particles (prepared by 0.1764 M of $AgNO_3$) are displayed in Figure 6 (a) and (b). It shows the rough surface of SiO_2 microspheres, which further demonstrates that Ag NPs are deposited on the surface of micron-SiO_2 spheres.

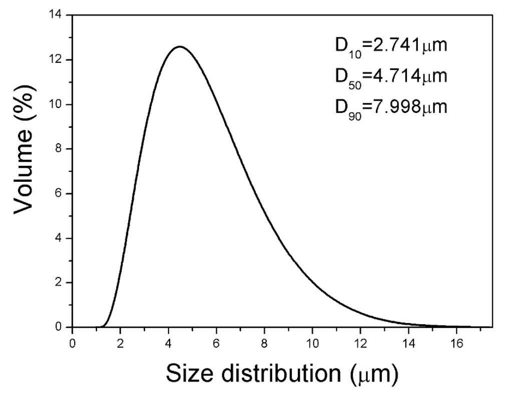

Figure 3 Real size distribution of SiO_2 microspheres

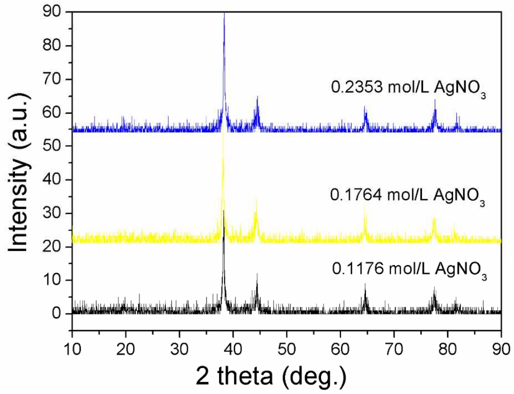

Figure 4 X-ray diffraction patterns of micron-SiO_2@nano-Ag synthesized from 0.1176 M, 0.1764 M and 0.2353 M of $AgNO_3$, respectively

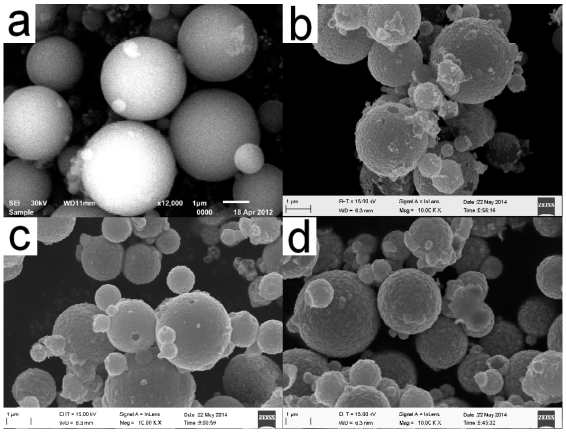

Figure 5 SEM images of (a) bare SiO_2 microspheres, (b) micron-SiO_2@nano-Ag particles synthesized from 0.1176 M of $AgNO_3$, (c) 0.1764 M of $AgNO_3$ and (d) 0.2353 M of $AgNO_3$

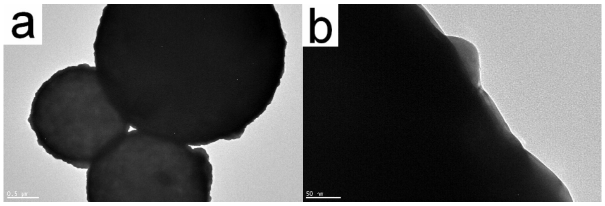

Figure 6 TEM images of (a) micron-SiO_2@nano-Ag particles (synthesized from 0.1764 M of $AgNO_3$) and (b) the edge of micron-SiO_2@nano-Ag particles (synthesized from 0.1764 M of $AgNO_3$)

The mass ratios of silver NPs deposited on SiO_2 microspheres according to XRF analysis and the sheet resistance of the composites are shown in Table 1. It demonstrates that with the increase of $AgNO_3$ concentration, the mass ratio of Ag in the composites has an increase, while the sheet resistance of the composites has a decrease. The decrease of the sheet resistance suggests that higher Ag NPs loading (thicker Ag layer) leads to better conductivity of the particles, which is consistent with the results of SEM observation. However, when 0.2353 M of $AgNO_3$ was utilized, a certain amount of silver was deposited on the wall of the flask, rather than on the surface of SiO_2 microspheres. And the particle size of silver plated on the flask was too large for silk-screen printing. As a result, 0.1764 M of $AgNO_3$ is chosen as the optimal concentration for preparing the composite.

Table 1 Influence of $AgNO_3$ concentration on Ag content and sheet resistance of micro-SiO_2@nano-Ag tablets

Concentration of $AgNO_3$ (mol/L)	Ag content (wt%)	Sheet resistance of the tablets (mohm/square)	Relative deviation (%)
0.1176	39.38	8.4	2.32
0.1764	60.43	2.5	3.75
0.2353	68.26	2.0	2.56

3.3 Conductive mechanism and percolation dynamics

The conductive mechanism of the paste can be explained by "percolation theory", which says that the conductive path can be formed under the circumstance that there exist a lot of conductive contacts or gaps (less than 1 nm) among the conductive fillers in the polymer matrix. It is worth noting that close contacts of the conductive fillers are influenced by two factors, namely the volume or mass fraction of conductive fillers and the curing process.

With the increase of the volume fraction of conductive fillers, the electrical performance of the paste has an improvement. And when the volume fraction of conductive particles reaches a critical amount, the sheet resistance of the conductive paste has a sudden decrease, called the "percolation threshold". When exceeding that level, a negligible decrease of the sheet resistance occurs. In the present work, the volume fraction of Ag NPs is expanded by loading them on SiO_2 microspheres. With the same mass fraction of micron-SiO_2@nano-Ag and Ag NPs, the former has much larger volume fraction in the polymer matrix than the latter. Thus the conductive network can be formed under lower filling content of micron-SiO_2@nano-Ag particles than that of Ag NPs. The percolation dynamics of micron-SiO_2@nano-Ag filled conductive paste under the curing condition of 140 °C for 10 min is shown in Figure 7. It is obvious that the filling mechanism of the paste follows the "percolation theory", and the percolation threshold is obtained at the filling content of about 53.6 wt% of micron-SiO_2@nano-Ag (32.4 wt% of Ag). However, with 32.4 wt% of Ag NPs filling in the same polymer matrix, the electrical performance of the paste was poor and not suitable for silk-screen printing due to low viscosity.

The curing process of the paste can be explained by Figure 8, provided that sufficient amount of conductive particles are well dispersed in the PU emulsion and some additives. Before curing, there exist few contacts among the particles. While after the heating curing process, the paste has a volume shrinkage, which leads to close connection between the conductive particles. The paste transforms from an insulator to a conductor, as the result of continuous linkages of filler particles. Based on the above discussion, it can be concluded that the curing condition plays an important role in the electrical conductive performance of the paste.

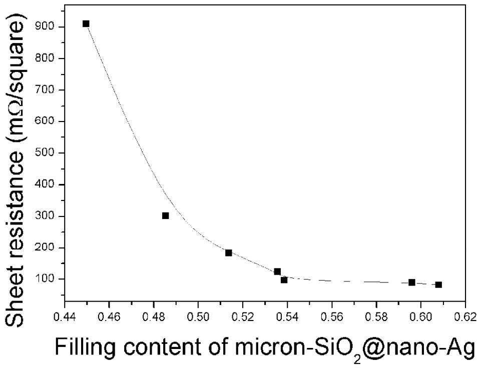

Figure 7 Relationship between sheet resistance and the filling content of micron-SiO_2@nano-Ag (synthesized from 0.1764 M of $AgNO_3$) under the cure condition of 140 °C for 10 min

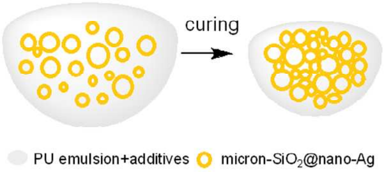

Figure 8 Curing process of micron-SiO_2@nano-Ag based conductive paste

3.4 Influence of coupling agent and curing condition on sheet resistance

The addition of coupling agent can greatly improve the compatibility of the conductive filler with the PU emulsion, which results in better conductivity of the paste, seen in Figure 9. The sheet resistance of the paste decreases dramatically when the addition of APTES changes from 0.5 wt% to 1.0 wt%. And when the paste was cured at 140 °C for 120 min with 1.0 wt% of APTES added, the sheet resistance is the lowest at 57mΩ/□. While, the sheet resistance of the paste has an increase with 1.5 wt% of APTES added. Conclusions can be drawn that 1.0 wt% of the coupling agent APTES is the optimum fill ratio and with the increase of curing time, there will be a decrease of the sheet resistance. The influence of curing temperature on sheet resistance was also discussed in Figure 10. It demonstrates that with the increase of curing temperature at the same curing time of 30 min, the sheet resistance of the paste has a decrease from 90mΩ/□ to 51mΩ/□.

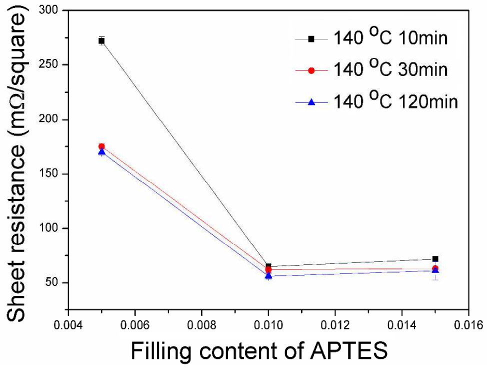

Figure 9 Relationship between sheet resistance and filling content of APTES under the curing condition of 140 °C for 10, 30 and 120 min, respectively

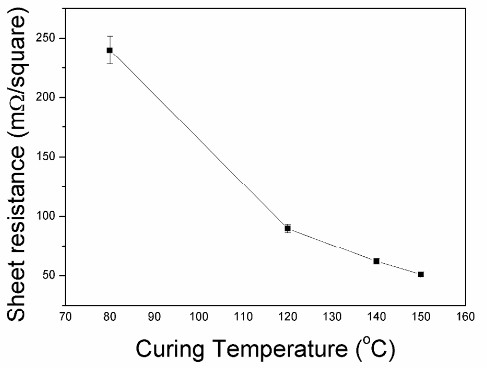

Figure 10 Relationship between sheet resistance and curing temperature at the curing time of 30 min

3.5 Mechanical performance tests

The adhesion test results are displayed in Figure 11 (a), (b), (c), (d), (e) and (f), respectively. Under the curing condition of 80 °C for 30 min and 140 °C for 10 min, the cured patterns were largely taken off by the 3M 600# tape, which suggests that their adhesion on PI substrate are poor; while, under the curing condition of 120 °C for 30 min, the adhesion of the ink have an improvement; and when the curing condition was 140 °C for 30 min, the paste barely came off with the tape and the paste surface was not noticeably disturbed, due to complete curing of the PU emulsion; however, the adhesion of the patterns cured at 140°C for 120 min and 150 °C for 30 min were not good because of the reduced strength of PU emulsion. Since the best adhesion was achieved at 140 °C for 30 min, the flexibility test of the paste was simply carried out at the same condition, as shown in Figure 12. When the conductive lines on the PI substrate were bent outward and inward for 3 times, there exist 144.9% change of the resistance. The results suggest that the best mechanical performance of the printed patterns on PI substrate can be achieved under the curing condition of 140 °C for 30 min and the sheet resistance of the paste is 62mΩ/□.

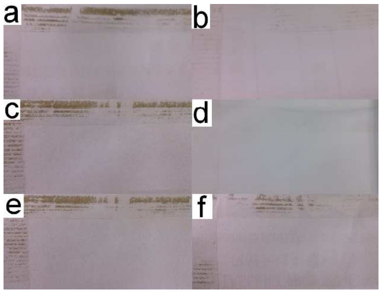

Figure 11 Conductive paste pulled off by 3M 600# tape under the curing condition of (a) 80 °C for 30 min, (b) 120 °C for 30 min, (c) 140 °C for 10 min, (d) 140 °C for 30 min, (e) 140 °C for 120 min and (f) 150 °C for 30 min, respectively

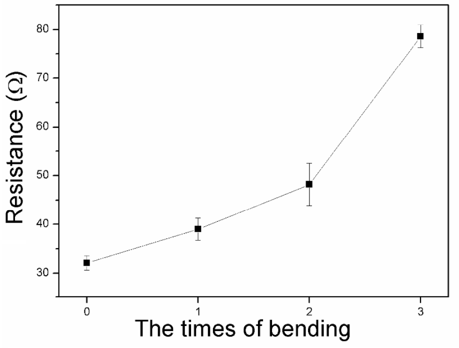

Figure 12 Relationship between resistance of the cured lines (1mm of width and 100 mm of length) and times of bending (180° outward, inward and lay flat with 2 kg of balancing weight on the midline)

3.6 SEM images of the cured ink on PI substrate

SEM images were taken to present the cross section of the conductive paste cured at 140 °C for 30 min on PI substrate. It could be seen that the micron-SiO_2@nano-Ag particles were compactly piled on the surface of the PI substrate (Figure 13), indicating the formation of conductive networks. And the thickness of the cured line patterns was uneven at about 25~30 µm examined by form talysruf profiler.

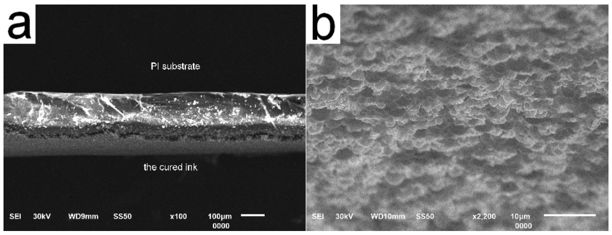

Figure 13 SEM images of (a) the cross section of cured paste on PI substrate and (b) the cross section of cured paste under 2, 200 times magnification

3.7 Application

To further illustrate the applicability of the micron-SiO_2@nano-Ag filled conductive paste, a conductive line pattern with 1 mm of width and 100 mm of length (Figure 14 (a)) was silk-screen printed on PI substrate, and cured at 140 °C for 30 min. Then, the conductive pattern, a light emitting diode (LED), a powder switch and a battery of 3V were connected into a circuit. When the power switch was on, the LED flashed with red colour, seen in Figure 14 (b). It is proved that the fabrication of micron-SiO_2@nano-Ag conductive line patterns will have a potential application in electronic devices.

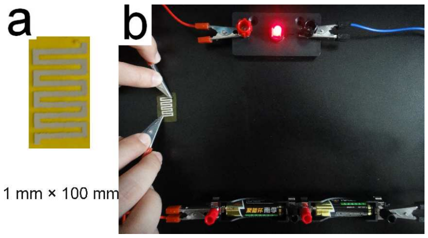

Figure 14 (a) the fabrication of conductive line pattern with 1mm of width and 100 mm of length through silk-screen printing; (b) the conductive line pattern connected with a LED into a circuit

4. Conclusions

Micron-SiO_2@nano-Ag composite was successfully synthesized by Sn^{2+} sensitization and seed-mediated growth technique. The composition and structure of the composite were characterized by various analysis methods. By coating Ag NPs on the SiO_2 microspheres, the composite as a low-cost conductive filler was not easy to agglomerate and had high dispersion in the polymer matrix. A conductive paste was obtained by mixing the composite particles with an aqueous PU emulsion, the coupling agent APTES, the active solvent HEA, and it could be silk-screen printed on flexible PI substrate. The printed conductive line patterns achieved good electrical (sheet resistance at 62mΩ/□) and mechanical performance under the curing condition of 140 °C for 30 min, with the filling content of 53.6 wt% of micron-SiO_2@nano-Ag, corresponding to 32.4 wt% of Ag. And it was linked with a LED into a circuit, which suggests that the paste will have a potential application for the fabrication of conductive lines in electronic devices.

Acknowledgements

This work was supported by grants of the National Nature Science Foundation of China (No. 21071112), and large-scale Instrument and Equipment Sharing Foundation of Wuhan University (No. LF20110063).

Notes and references

[a*] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China. Fax: +86-27-68752800; Tel: +86-27-68752800; E-mail: ljyuan@whu.edu.cn*

[b*] *School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan, China. Fax: +86-27-68752800; Tel: +86-27-68752800; E-mail: aicchun@whu.edu.cn*

1 S. Jeong, K. Woo, D. Kim, J.S. Kim, H. Shin, Y. Xia and J. Moon, *Adv. Funct. Mater.*, 2008, **18**, 679.

2 S. Chen, Z. Kao, J. Lin and Y. Liao, *Appl. Mater. Interfaces*, 2012, **4**, 7064.

3 K.J. Lee, B.H. Jun, T.H. Kim and J. Joung, *Nanotechnology*, 2006, **17**, 2424.

4 Y.X. Gao, H.Y. Li and J. Liu, *Plos One*, 2012, **7**, e45485.

5 J. Zhang, Z.B. Liang, T. Hreid, W. Guo and Z.B. Yuan, *RSC Advances*, 2012, **2**, 4787.

6 Y. Chang, D.Y. Wang, Y. L. Tai and Z.G. Yang, *J. Mater. Chem.*, 2012, **22**, 25296.

7 C. Kim, M. Nogi, K. Suganuma and Y. Yamato, *Appl. Mater. Interfaces*, 2012, **4**, 2168.

8 H.W. Cho, S. Nam, S. Lim, D. Kim, H. Kim and B.J. Sung, *J. Appl. Phys.*, 2014, **115**, 154307.

9 I. Kim, Y. Kim, K. Woo, E.H. Ryu, K.Y. Yon, G.Z. Cao and J. Moon, *RSC advances*, 2013, **3**, 15169.

10 W. Wu, S.L. Yang, S.F. Zhang, H.B. Zhang and C.Z. Jiang, *J. Colloid Interface Sci.*, 2014, **427**, 15.

11 Z.X. Wang, X.B. Chen, M. Chen and L.M. Wu, *Langmuir*, 2009, **25**, 7646.

12 G.X. Gu, J.X. Xu, Y.F. Wu, M. Chen and L.M. Wu, *J. Colloid Interf. Sci.*, 2011, **359**, 327.

13 Z.W. Deng, M. Chen and L.M. Wu, *J. Phys. Chem. C*, 2007, **111**, 11692.

14 H.S. Lim, S.N. Kim, J.A. Lim and S.D. Park, *J. Mater. Chem.*, 2012, **22**, 20529.

15 C.C. Ai, Y. Xiao, W. Wen and L.J. Yuan, *Powder Technol.*, 2011, **210**, 323.

16 L.M. Davis, D.W. Thompson, *Chem. Mater.*, 2007, **19**, 2299.

17 Y. Kobayashi, V. Salgueirino-Maceira, L.M. Liz-Marzan, Chem. Mater., 2001, **13**, 1630.

18 D. Chen, H.Y. Liu, J.S. Liu, X.L. Ren, X.W. Meng, W. Wu and F.Q. Tang, *Thin Solid Films*, 2008, **516**, 6371.

19 Z.J. Jiang, C.Y. Liu. *J. Phys. Chem. B*, 2003, **107**, 12411.