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Green preparation of flaky silver powders with nano-thickness towards electrically conductive adhesives through nanofilm transition method

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Flaky silver powders were prepared through nanofilm transition method, in which nano-thickness silver films were deposited on water-soluble resin coated substrates and then smashed into flaky silver powders with very smooth and flat surface. The electrically conductive adhesives, filled with 25 wt% of flaky silver powders, showed low resistivity of 4.10×10^{-5} Ω·cm.

In the past decade electrically conductive adhesives (ECAs) has drawn considerable and increasing attention due to their widely application in electronics industry,[1] for instance integrated circuit, solar cells, radio frequency identification (RFID) tags, package of light emitting diodes (LCD) screen, sensors, organic thin film transistor (OTFT),and etc.[2-4] Because of bonding and conductive properties, ECAs has been used to connect conductive materials or devices after cured.[5,6] Usually it consists of conductive fillers, polymer adhesive and diluents. Furthermore, coupling agent, thickener and other additives should be added into.[7]

As a widespread used fillers of ECAs, silver powder has many advantages, such as: high electrical conductivity and thermal conductivity among all metals,[8,9] chemical stability and oxidation resistance, high reflectivity and high plasticity.[10-12] The deeper application of silver powder has been injected new vitality with the development of nanotechnology. A variety of shapes of nanoscale silver particles have been prepared, for example, nanocube,[13] nanowires,[8,9,14-17] nanorods,[18] nanotube,[19,20] nanoprism,[21] nanoflakes/nanoplates,[22-24] nanobelt,[25] nanosphere,[26] nanoribbon,[27] nanochain,[28] nanosheets.[29-31]

Because of face-to-face contact mode, rapid electrons transport among silver flakes could be happen, which means high electrical conductivity. Although there are many ways to fabricate silver flakes, such as mechanical ball milling,[32] polyol processes,[22] liquid phase reduction,[33,34] soft colloidal templates,[35,36] photo-induced method,[21,37] and electrochemical method,[38] only mechanical ball milling method is widely used in industrial manufacture. However, ball-milling technique would results in a series of problems, such as rough surface, nonuniform thickness and lubricant residues, which in turn cause the deteriorative conductivity.

To improve the electrical conductivity of ECAs, the silver flakes should be well controlled to ensure smooth and flat surface and uniform thickness, particularly nanoscale of thickness, so as to obtain ideal face-to-face contact model. Therefore, our research group put forward a nanofilm transition method to synthesize this kind of silver flakes,[23] in which silver mirror reaction was used to deposited silver films and then the silver films were smashed into fine flaky powders. Considering silver mirror reaction would produce great amount of waste water and consume numerous organic solvents and then led to environmental pollution, we illustrate a novel nanofilm transition method, with which waste water was no longer produced and only a small amount of organic solvents was needed.

The nanofilm transition method to fabricate silver flakes with smooth and flat surface and uniform nanoscale thickness, is shown in Fig.1. Firstly, water-soluble resin solution was coated on polyethylene terephthalate (PET) substrate with screen printing process. After heated at 120 ^{o}C for 30 minutes, a smooth resin layer would formed on PET substrate (shown as Fig.S1(a)).Then the substrate was placed on the turnplate in the vacuum evaporation coating machine. A quantitative of silver wire, which surface had been previously cleaned and polished, was put in the tungsten boat under the turnplate. When the vacuum of chamber was decreased to 3.0×10^{-3}Pa, the voltage was slowly adjusted to make the silver wire gasificated. Finally silver vapour would deposit on the water soluble resin layer and the thickness of silver film was controlled about 40-60 nm. Fig.S1 (b) shows that the as-prepared silver film has a smooth and flat surface with high reflectivity and silvery metallic lustre.

Then, the silver films deposited on the resin-coated PET substrates, were immersed into deionized water to strip the silver film. Because the hydrophilic group of the resin could combine with hydrone, resin layer would dissolve in deionized water. With the dissolve of water-soluble resin, silver films would fall off from the

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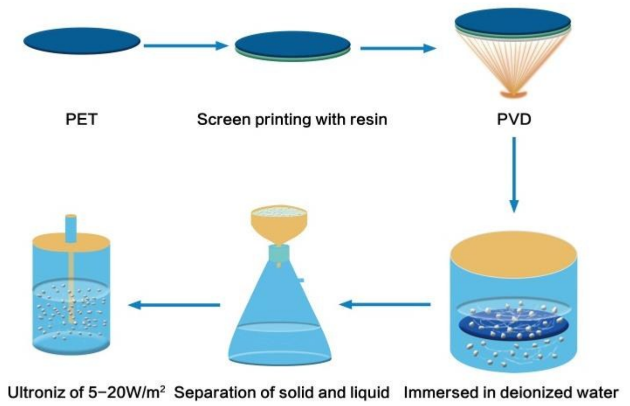

Fig.1 Fabrication of flaky silver powders through nanofilm transition method.

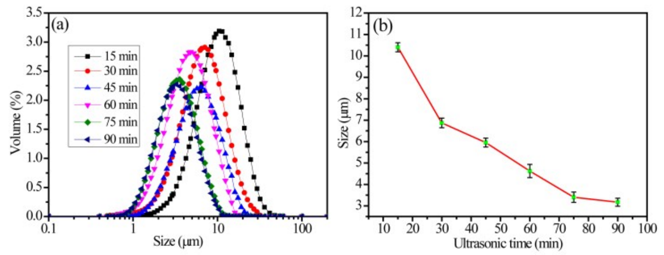

Fig.2 Particle size of the flaky silver powders (a) particle size distribution (b) mean particle sizes.

substrate as coarse silver flakes. After suction filtration and washing, the wet cake of coarse flakes was thrown into a high-energy ultrasonicator to smash into fine silver flakes. The filtrate which contained water-soluble resin could be reused for manufacturing resin solution by adding the corresponding quality of water-soluble resin.

The particle size of the flaky silver powders was analyzed with Mastersizer 2000. To investigate the effect of size of flaky silver powders on conductive properties, the ultrasonication time was varied from 15 minutes to 90 minutes and the result is shown in Fig.2. With the extension of ultrasonication time, the particle size is gradually decreased. Ultrasonic smashed for 60 minutes, the average particle size decreases to 4.6 μm, which is suitable for application in ECAs.

After ultrasonic grinding, the silver flakes were separated from

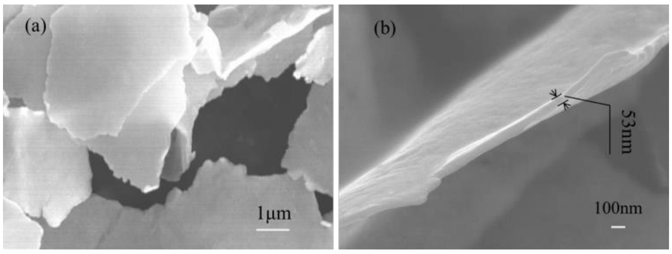

Fig.3 SEM images of silver flakes ultrasonically treated for 60min (a) surface topography; (b) cross-section.

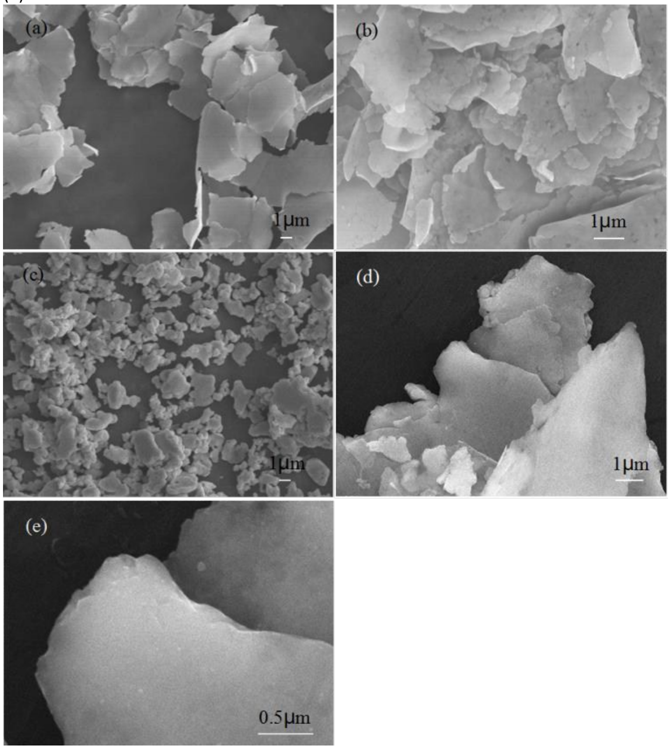

Fig.4 SEM images of silver powders (a) As-prepared (b) Xinshengfeng (c) FAgL 6501 (d) Acheson ED 427SS (e) sideward thickness of Acheson ED 427SS.

the slurry through suction filtration and vacuum drying. For flaky silver powders ultrasonic treated for 60 minutes, its SEM imagine is shown in Fig.3. The coarse flakes are fractured into fine flakes, which present extremely smooth and flat surface (shown in Fig.3(a)and Fig.4(a)) and highly uniform thickness about 53 nm (shown in Fig.3(b)). Compared with as-prepared flakes, Xinshengfeng silver flakes (produced by Xinshengfeng technology Co. Ltd) and FAgL 6501 silver particles (produced by Sino-Platinum Metals Co. Ltd) have porous and jagged edge(Fig.4(b),(c)), agglomerate particles (Fig.4(c)), which means poor face-to-face contact and then poor electrical conductivity. Although silver flakes in Acheson ED427SS conductive paste (purchased from Acheson Industries-USA) possess smooth and flat surface (Fig.4(d)), its thickness is micrometre-scale (Fig.4(e)).

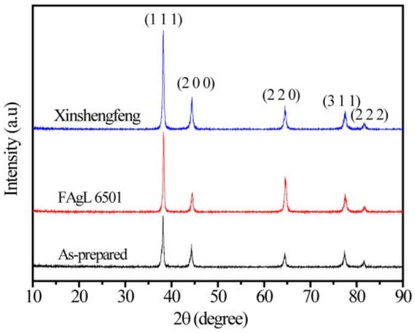

Fig.5 X-ray diffraction (XRD) patterns of flaky Ag powders.

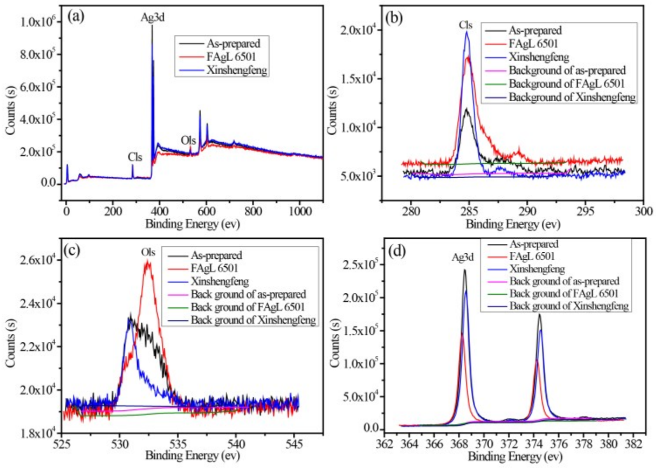

Fig.6 X-ray Photoelectron Spectroscopy of as-prepared, FAgL 6501 and Xinshengfeng silver flakes (a) survey graphs of them (b) auger electron spectrum of carbon (c) of oxygen (d) of Ag3d.

Fig. 5 illustrates the result of X-ray diffraction analysis of silver powders. All the major peaks occupy position of about 38.1°, 44.5°, 64.5°, 77.4° and 81.6° standing for the (111), (200), (220), (311) and (222) crystal indices of silver atoms with fcc structure, proving that the silver powders haven't been oxidized.

Then, X-ray Photoelectron Spectroscopy (XPS) was measured to determine the amount of organics residual (except hydrogen) on the particle surface and the survey of XPS is shown in Fig. 6(a). Fig.6(b),(c) shows respectively the auger electron spectroscopy of carbon and oxygen, which content on the flaky silver surface can be deduced from the area integral of surrounded auger electron spectrum and background line. Fig. 6(d) is the spectroscopy of silver, from which silver content in the samples can also be derived. Table 1 reveals the atomic weight of carbon, oxygen and silver, in which Start BE, Peak BE and End BE respectively represent for Start Binding Energy (eV), Peak Binding Energy (eV), End Binding Energy (eV), all of them could been inferred from Fig. 6. It is found that the mass fraction of Ag of as-prepared silver powders reaches to 90.5%, which obviously exceeds FAgL6501 silver flakes (76.1%) and Xinshengfeng silver flakes (82.1%). The high silver content on the surface of as-prepared silver flakes helps to improve the electrical conductivity of ECAs.

Table 1 X-ray Photoelectron Spectroscopy of as-prepared, Xinshenfeng and FAgL-6501 silver powders.(AP, FAgL, XSF and MCPS stand for As-prepared, FAgl 6501, Xinshengfeng and Mass content on particle surface respectively)

Sample	Name	Start BE (eV)	Peak BE (eV)	End BE (eV)	MCPS (%)
AP	Cls	293.70	284.19	280.10	5.54
	Ols	541.10	531.01	526.70	3.96
	Ag3d	378.65	368.47	365.00	90.5
FAgL	Cls	293.30	284.82	280.85	13.6
	Ols	540.15	532.38	526.20	10.3
	Ag3d	379.00	368.25	364.85	76.1
XSF	Cls	292.30	284.81	280.50	13.6
	Ols	539.43	530.87	526.85	4.30
	Ag3d	378.95	368.55	365.05	82.1

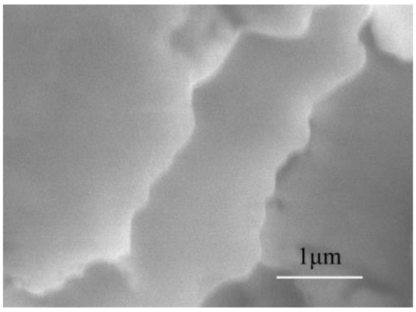

Fig.7 SEM image of ECAs patterns (filled with 25 wt% of as-prepared silver flakes) printed on PET substrate.

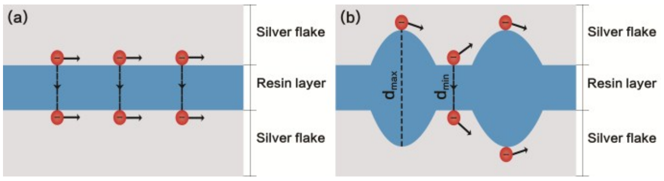

Fig.8 Conductive model of different flaky silver powders (a) as-prepared; (b) commercially available.

To estimate the volume resistivity of the as-prepared ECAs, we selected a conductive model of a size of long 50 mm (l) × width 10 mm (w) (see literature 20). The volume resistance (R) and the thickness (t) of the samples were tested by a Low DC Resistance Tester and a film thickness gauge (accuracy 1 μm). Then, the volume resistivity (ρ) was worked out through the following expressions. [6, 23, 39,40]

$$\rho = R\frac{A}{l} = R\frac{wt}{l}$$

Where A is the cross-sectional area of ECAs. The conductive sample filled with 25 wt% of as-prepared flaky silver powders showed a volume resistivity of 4.10×10^{-5} Ω·cm, which was much lower than that of FAgL 6501 silver flakes (60 wt% of silver powders content, 2.2×10^{-4} Ω·cm) and Xinshengfeng silver flakes (60 wt% of silver powders content, 2.8×10^{-4} Ω·cm) and was close to Acheson ED 427SS (66 wt% of silver powders content, 4.0×10^{-5} Ω·cm). The volume resistivity of ECAs made from as-prepared flaky silver powders was better than the industrial ECAs that filled with about 70 wt% of flaky silver powders.[41, 42]

It is found from Fig.7 that for ECAs made from as-prepared flaky silver powders, the silver flakes form face-to-face contact pattern. The excellent conductivity of our ECAs is mainly ascribed to the face-to-face contact pattern among the fine silver flakes with uniform nanoscale thickness and flat surface, that is benefit for further formation of decent conductive network. Moreover, the higher silver content on the surface of as-prepared powders virtually helps to improve the electronic transmission. For commercially available silver flakes, not only the surface is bumpy and defective, but also its thickness is nonuniform, which means the surfaces cannot well contact between each other and electrons will partly drop out from the hole (Fig.8(b)). Furthermore, compared with the commercial silver flakes, the as-prepared flakes have a larger specific surface area (Fig.S (2), S(Tab.1)), that means a higher contact area.

Conclusions

A novel type of nanofilm transition method is put forward, in which silver films with nanoscale thickness were deposited on water-soluble resin coated PET substrates through physical vapor deposition method (PVD) and then deionized water was used to dissolve the water-soluble resin so as to prepare coarse flaky silver powders with nanoscale thickness. For 53 nm thickness of coarse flaky silver powders, it could be smashed into fine powders through intensive energy ultrasonication method and its particle size could be adjusted by varying the ultrasonic time. Ultrasonic treated for 1 hour, the silver film with 53 nm of thickness could be smashed into fine flaky silver powders with 4.6 µm of average particle size. The as-prepared fine flaky silver powders possessed of a smooth and flat surface and uniform thickness, which prompt the formation of outstanding conductive network. Furthermore only 9.5 wt% of organic matter was found remained on the surface of the silver flakes, which helps to promote the electronic transmission. Lastly the as-prepared silver flakes possess of larger specific surface area comparing with commercial flaky silver powders. Once filling with 25 wt% of such flaky silver powders in ECAs, electrically conductivity could reach to 4.1×10^{-5} Ω·cm. Because of environment-friendly technique and high electrical conductivity, this type of flaky silver powders has great potential application in the microelectronic industry.

Acknowledgements

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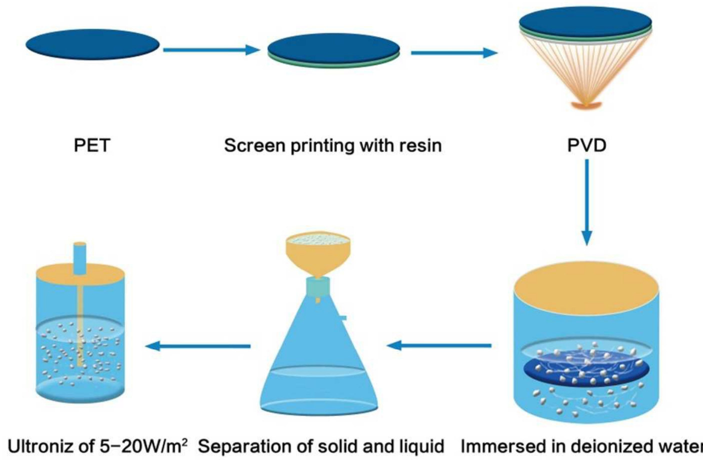
Graphical Abstract



Flaky silver powders with nano-thickness and smooth surface were prepared through nanofilm transition method which production process is environmental-friendly.