Electroless plating route to the synthesis of glass microspheres/copper composites with excellent conductivity

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A versatile electroless copper plating method for the fabrication of Cu-coated glass microspheres was successfully developed using hydrazine hydrate as the reducing reagent. To obtain the best morphology and electrical conductivity of Cu-coated glass microspheres, some main synthetic factors including the concentration of copper salt, volume of aqueous ammonia and bath temperature were investigated in detail. The crystal structure and shape of the copper layer were characterised by X-ray diffraction and scanning electron microscope techniques. The result showed that the glass microspheres with a uniform copper coating exhibited a face-centred cubic crystal structure and an excellent volume resistivity (ρ_v) of 4.28×10^{-4} $\Omega \cdot$cm. This method could also be extended for the fabrication of Ag- and Co-coated glass microspheres with superior conductivity.

1. Introduction: Electroless plating is a novel type of surface treatment with an autocatalytic redox process, in which metal ions from the solution are reduced onto the substrate with the driving force of the reducing agent in solution instead of any electric current. It is extensively used in electronics manufacturing, corrosion protection and so on, because of the advantages of low cost, simple process, excellent environment stability and other notable features [1]. Recently, electroless copper plating has also been applied to the electromagnetic shielding field in order to achieve a high shielding efficiency of coatings on the polymer, especially plastics-based shells of electronic components [2–7]. In addition, electroless copper plating can also be employed to prepare coatings on resins [8], biomaterials [9], metallic materials [10] and inorganic non-metallic materials such as glass substrates [11]. Normally, the electroless copper plating bath contains copper salt, a complexing agent, a reducing agent and other additives. Various reducing agents including formaldehyde [12–14], dimethylamine boron [15, 16], borohydride [17], hypophosphite [18] and hydrazine hydrate [19] have been reported for electroless copper plating. Among them, the most widely used is formaldehyde because of its effectiveness and easy handling. However, it is toxic and non-environmentally friendly. The final products usually contain impurities of boron and phosphorus when dimethylamine boron, borohydride and hypophosphite are employed, and nickel ions are needed to catalyse the oxidation of hypophosphite in hypophosphite-reduced electroless plating systems [20]. It seems that hydrazine hydrate is a more promising reducing reagent for electroless copper plating because of the formation of clean nitrogen gas as the by-product.

The glass microsphere is a kind of inorganic non-metallic material with low density, low thermal conductivity, high dispersibility and thermal stability, which has been used in many fields, especially as fillers in elastomers and resins [21]. There have been many reports on depositing metals on the surface of glass microspheres. However, work seldom focused on pure copper coating deposited on the surface of glass microspheres via an electroless plating method using hydrazine hydrate as the reducing agent. In the work reported in this present Letter, Cu-coated glass microspheres were fabricated through the hydrazine hydrate reduction route, and the coating microstructure and volume resistivity of such microspheres were greatly influenced by some synthetic

factors including the concentration of copper salt, volume of aqueous ammonia and the bath temperature. Finally, we also extended this method to fabricate Ag- and Co-coated glass microspheres with excellent conductivity. These metal-coated glass microsphere composites may have applications in the electromagnetic shielding field. Presently, the common fillers of conductive silicon rubber were mainly focused on metallic materials including silver and nickel. However, these kinds of electromagnetic shielding materials were too heavy to be applied into some special fields. The as-prepared copper-coated glass microsphere composites with light weight and excellent conductivity could be regarded as one of the new conductive fillers, and the matrix materials might be rubber, resin or plastic.

2. Experimental procedure
2.1. Raw materials: The diameter of the glass microspheres ranges from 20 to 50 μm. For the electroless copper plating bath, copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) were used as the copper source and complexing agent, respectively. Hydrazine hydrate was employed as the reducing agent, and the base media was controlled by aqueous ammonia. All chemical agents were of analytical grade and used as received without further purification.

2.2. Preparation of Cu-coated glass microspheres: The Cu-coated glass microspheres were prepared by a multistep process, which included surface etching, sensitising, activating pretreatment and electroless copper plating. First, 3 g of glass microspheres was dispersed in 100 ml of aqueous solution which contained 3 g of potassium dichromate ($K_2Cr_2O_7$) and 6 ml of sulphuric acid (H_2SO_4, 98 wt%), stirred for 15 min at 30°C, and then the glass microspheres were filtered off. Subsequently, the glass microspheres were sensitised in 100 ml of solution containing 2 g of tin (II) chloride ($SnCl_2 \cdot 2H_2O$) and 1 ml of hydrochloric acid (HCl, 37 wt%), accompanied by stirring for 15 min at 30°C, then the glass microspheres were filtered off for the activating treatment. Namely, the glass microspheres collected from the sensitising step were re-dispersed in 100 ml of solution composed of 0.01 g of palladium (II) chloride ($PdCl_2$) and 0.1 ml of HCl (37 wt%), and also stirred for 15 min at the same temperature. The activated spheres were rinsed three times with distilled water,

and collected for electroless copper plating. Typically, 100 ml of an aqueous solution was prepared by dissolving 4 g of $CuSO_4 \cdot 5H_2O$ and 10 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ in distilled water, and then 12 ml of $NH_3 \cdot H_2O$ (25 wt%) and the as-activated glass microspheres were added into the above solution in sequence. After that, the bath was heated to 80°C for 10 min and accompanied by vigorous stirring. At this temperature, 3 ml of $N_2H_4 \cdot H_2O$ (30 wt%) was introduced and the reaction proceeded for 50 min. Finally, the product was rinsed and dried for characterisation. The controlled experiments were carried out by changing the concentration of $CuSO_4 \cdot 5H_2O$, volume of $NH_3 \cdot H_2O$ and bath temperature, respectively, while the other parameters were kept constant. For the fabrication of Ag- and Co-coated glass microspheres, all the procedures were the same, and just by changing some raw materials.

2.3. Characterisations: The X-ray diffraction (XRD) pattern was recorded on a Bruker D8 focus diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm) with the 2θ angle ranging from 20° to 100°. Scanning electron microscope (SEM) images were taken by a Hitachi SU-1500 SEM with secondary electrons, and the volume resistivity values were obtained by an SB120 four-point probe instrument.

3. Results and discussion: The phases present in the copper coating was determined by XRD and the XRD pattern is presented in Fig. 1. Five diffraction peaks at $2\theta = 43.3°$, 50.5°, 74.1°, 89.9° and 95.3° could be indexed to the (111), (200), (220), (311) and (222) crystal planes of face-centred cubic (fcc) copper, respectively, consistent with the reported data (JCPDS File No. 04–0836). No peaks of other impurities or the amorphous signals for glass microsphere were detected, which indicated that continuous copper coating was successfully deposited on the surface of the glass microspheres via the electroless plating method.

Fig. 2a shows the panoramic SEM image of the Cu-coated glass microspheres obtained in the typical synthesis. All the copper coatings on the glass microspheres were compact and continuous, and no broken position was seen. Hence, it was difficult to evaluate the thickness of the copper layer. From the magnified view in Fig. 2b, it can be clearly seen that the copper coating was composed of many smaller particles of size 300–500 nm, and therefore the surface was not smooth as that of the glass microspheres. The volume resistivity of the sample was measured by an SB120 four-point probe instrument, and followed by calculation using the formula

$$\rho_v = \frac{\pi \cdot U \cdot d}{K \cdot I} \tag{1}$$

where ρ_v is the volume resistivity value, K is the conductive coefficient, U is the voltage, I is the electric current and d is the thickness of the sample incused under a pressure of 10 MPa by the specified mould. The value was calculated to be 4.28×10^{-4} $\Omega \cdot cm$, which shows excellent conductivity.

Fig. 3 displays the SEM images of the Cu-coated glass microspheres prepared from different concentrations of Cu^{2+} cations. It
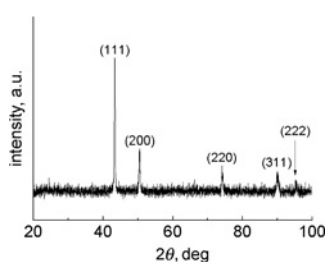
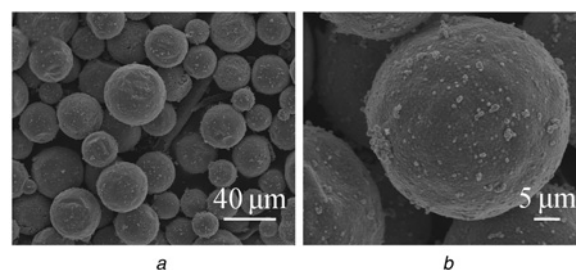**Figure 1** *XRD pattern of the as-obtained Cu-coated glass microspheres*

Figure 2 *SEM images of the as-obtained Cu-coated glass microspheres*
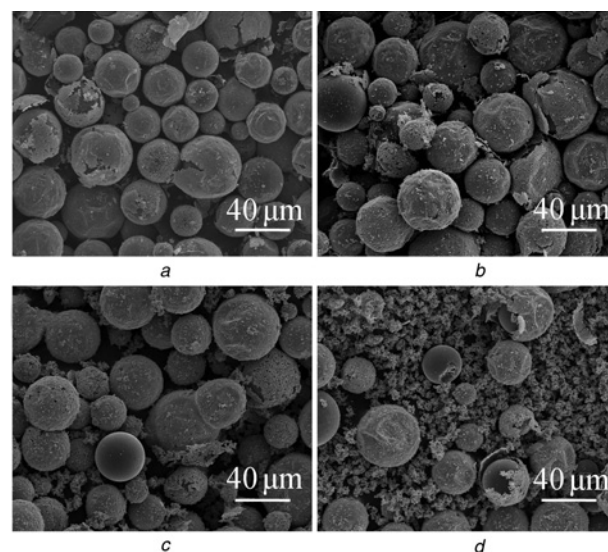*a* Low magnification
b High magnification

Figure 3 *SEM images of Cu-coated glass microspheres prepared with different concentrations of $CuSO_4 \cdot 5H_2O$*
a 15 g·l^{-1}
b 30 g·l^{-1}
c 70 g·l^{-1}
d 90 g·l^{-1}

could be seen that the deposited copper layer with low concentrations of copper salt was loose and cracked (Figs. 3a and b), and it seemed that the copper layer was easy to be peeled off from the surface of the glass microspheres. The thickness observed from the cracked position was approximately 1–2 µm. With the concentration of copper sulphate increasing, many isolated copper particles were produced instead of being deposited on the surface of the glass microspheres (Figs. 3c and d). This was because the reaction was greatly accelerated with higher concentrations of raw materials, and the initially formed copper seeds did not have enough time to move to the surface for coating growth. Another important point might be that the nitrogen gas as the by-product was released from the intense reaction and destroyed the growth of copper film. The volume resistivity values of the Cu-plated glass microspheres synthesised with different Cu^{2+} concentrations are listed in Table 1. The minimum ρ_v value was confirmed with the initial $CuSO_4 \cdot 5H_2O$ concentration of 40 g·l^{-1}, and such excellent conductivity was attributed to the perfect copper coating.

Table 1 Volume resistivity (ρ_v) values of the Cu-coated glass microsphere composites synthesised from different $CuSO_4 \cdot 5H_2O$ concentrations

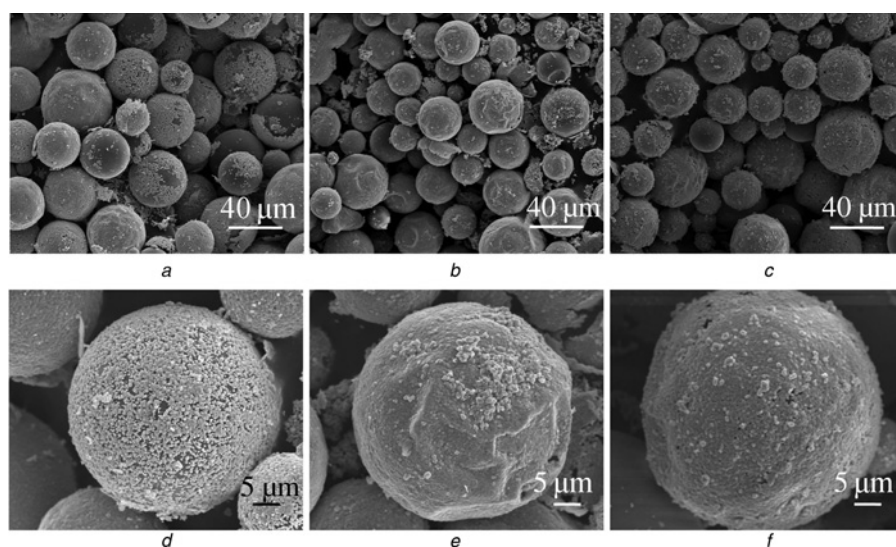| $CuSO_4 \cdot 5H_2O$, g·l^{-1}	15	30	40	70	90
ρ_v, $\Omega \cdot cm$	1.11×10^{-3}	5.63×10^{-4}	4.28×10^{-4}	7.16×10^{-4}	7.35×10^{-4}

Figure 4 *SEM images of Cu-coated glass microspheres prepared at different temperatures*
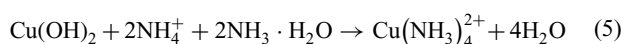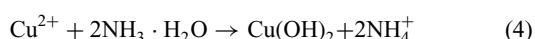*a* 60°C
b 70°C
c 90°C
d–f Corresponding higher magnification views

Apart from the significant effect of the copper salt, bath temperature also played a key role in the formation of copper coating. The chemical reaction did not take place when the temperature was below and equal to 50°C, and hence, no copper was generated. Figs. 4*a* and *d* show that the coating deposited at 60°C was thin and the copper particles on the surface of the glass microspheres were scattered and discontinuous. The reason was that only a small amount of copper was produced in a given time. With increasing temperature, more energy was supplied for the reaction and the copper coating became packed (Figs. 4*b* and *e*). However, the copper film seemed to possess a porous structure when the experiment was carried out at 90°C, and many redundant particles were on the surface (Figs. 4*c* and *f*). It was supposed that the redox reaction for copper deposition needed sufficient energy, and therefore, a high temperature was required. On the other hand, higher temperature greatly accelerated the plating process, and the release of nitrogen gas became more intense. The volume resistivity values of the composite particles prepared with temperature as a synthetic parameter are shown in Table 2. As the temperature increased from 60 to 90°C, the values decreased at first, and then showed a slight tendency to improve. The best electrical conductivity occurred at 80°C, and higher values at other temperatures were owing to the discontinuous copper coatings.

The concentration of aqueous ammonia was another important factor. It can be clearly confirmed from Fig. 5 that the copper coatings changed from rough to smooth and continuous with increasing concentrations of $NH_3 \cdot H_2O$. Herein, $NH_3 \cdot H_2O$ offered the base media and the reducing ability of hydrazine hydrate was greatly enhanced. In addition, it could combine with Cu^{2+} to form a complex and the quantities of free Cu^{2+} in solution were reduced, which resulted in the slow generation of copper atoms. The reaction mechanism was expressed as follows

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^- \qquad (2)$$

$$2Cu^{2+} + N_2H_4 \cdot H_2O + 4OH^- \rightarrow 2Cu + N_2 + 5H_2O \qquad (3)$$

$$Cu^{2+} + 2NH_3 \cdot H_2O \rightarrow Cu(OH)_2 + 2NH_4^+ \qquad (4)$$

$$Cu(OH)_2 + 2NH_4^+ + 2NH_3 \cdot H_2O \rightarrow Cu(NH_3)_4^{2+} + 4H_2O \qquad (5)$$

The volume resistivity values of the composites were further determined and are listed in Table 3. The electrical conductivity was excellent when the concentration of $NH_3 \cdot H_2O$ was equal to or higher than 80 ml·l^{-1}, and little variation occurred with increasing concentrations of $NH_3 \cdot H_2O$. However, an excess amount of aqueous ammonia could lead to instability of the plating solution.

Table 2 Volume resistivity values of the Cu-coated glass microsphere composites synthesised with different temperatures

Temperature, °C	50	60	70	80	90
ρ_v, Ω·cm	—	3.12×10^{-3}	1.53×10^{-3}	4.28×10^{-4}	7.34×10^{-4}

Note: — indicates ρ_v could not be obtained owing to the failure of the copper film to form on glass microspheres
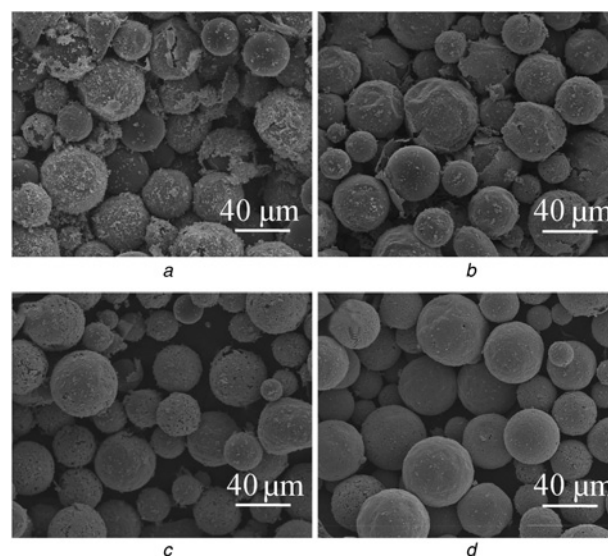

Figure 5 *SEM images of Cu-coated glass microspheres prepared with different concentrations of $NH_3 \cdot H_2O$*
a 40 ml·l^{-1}
b 80 ml·l^{-1}
c 160 ml·l^{-1}
d 240 ml·l^{-1}

The current versatile method can be applied to deposit other metals (e.g. silver, cobalt, nickel etc.) on glass microspheres by just changing some raw materials. It was necessary that some synthetic parameters should be slightly tuned to obtain the most excellent conductivity and continuous coatings. Fig. 6 presents the SEM images and XRD patterns of Ag- and Co-coated glass microspheres, respectively. The silver coating was glossy and tight for the Ag-coated glass microspheres (Fig. 6a), and the XRD pattern (Fig. 6c) indicated the perfect fcc phase of silver from the four diffraction peaks of (111), (200), (220) and (311) at 38.1, 44.3, 64.4 and 77.5°, respectively [22]. Hence, the silver coating on the glass microspheres possessed high crystallinity, and it had a more excellent conductivity of 3.14×10^{-4} $\Omega \cdot$cm compared with copper coatings. Similarly, continuous and uniform cobalt film could be also formed on the Pd-activated glass microspheres (Fig. 6b) via the current electroless plating (Fig. 6b). The corresponding XRD pattern (Fig. 6d) indicated the hexagonal close-packed (hcp) phase of cobalt (JCPDS 05-0727). Herein, the volume resistivity of the as-prepared Co-coated glass microspheres was calculated to be 3.50×10^{-3} $\Omega \cdot$cm. Compared with other similar reports, the excellent conductivity of as-obtained copper-coated microspheres was one of the features herein. Moreover, it was challenging to use hydrazine hydrate as a reducing agent because the reducing capacity of hydrazine hydrate was so strong that the copper particles were difficult to form the film or the film was loose and easily peels off. As far as the other conventional reducing agent HCHO is concerned, it had been recognised as a kind of toxic reagent that was bad for human health and environment. Another common reducing agent was sodium hypophosphite, that had been widely used in electroless cobalt or nickel plating process, but the products often contained Co-P or Ni-P. In addition, if we choose sodium hypophosphite as the reducing agent in electroless copper plating, a certain amount of Ni^{2+} must be added to the system as the active metal ions. Therefore, hydrazine hydrate was chosen to reduce copper ions, and the coating quality of the as-obtained composites was improved under a suitable amount of complexing agent and pH

value. All these metal-coated glass microspheres might have potential application as shielding electromagnetic materials, because of their characteristics of light weight and excellent conductivity.

4. Conclusion: Cu-coated glass microsphere composite particles with uniform and compact coatings were successfully prepared by electroless plating with hydrazine hydrate as the reducing reagent. The morphology and conductivity of the synthetic particles could be controlled by the plating solution parameters. The as-prepared composites exhibited a perfect fcc crystal structure, which indicated that a uniform and compact copper layer was successfully covered on the surface of glass microspheres. In addition, the volume resistivity of the obtained composite particles was 4.28×10^{-4} $\Omega \cdot$cm, showing excellent conductivity. This method could also be applied to fabricate Ag- and Co-coated glass microspheres, and all these composite particles possessed excellent electrical conductivity, and therefore they may be used as fillers in the preparation of shielding electromagnetic materials.

Table 3 Volume resistivity values of the Cu-coated glass microsphere composites synthesised from different $NH_3 \cdot H_2O$ concentrations

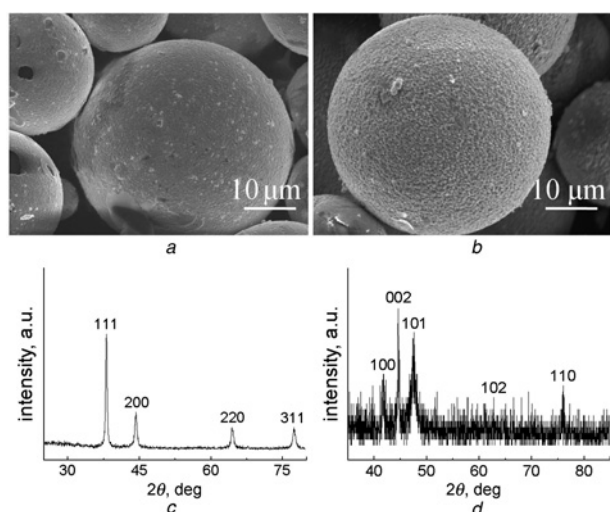| $NH_3 \cdot H_2O$, ml·l^{-1}	40	80	120	160	240
ρ_v, $\Omega \cdot$cm	4.30×10^{-3}	5.98×10^{-4}	4.28×10^{-4}	7.61×10^{-4}	7.79×10^{-4}

Figure 6 SEM images
a Ag-coated microspheres
b Co-coated microspheres
c and d Their corresponding XRD patterns

6   References

[1]   Sudagar J., Lian J.S., Sha W.: 'Electroless nickel, alloy, composite and nano coatings – a critical review', *J. Alloys Compd.*, 2013, **571**, pp. 183–204

[2]   Liu X.L., Jiang Z.H., Guo Y.W., Zhang Z.H., Ren L.Q.: 'Fabrication of super-hydrophobic nano-sized copper films by electroless plating', *Thin Solid Films*, 2010, **518**, pp. 3731–3734

[3]   Yang W.B., Fu Y.Y., Xia A., Zhang K., Wu Z.: 'Microwave absorption property of Ni-Co-Fe-P-coated flake graphite prepared by electroless plating', *J. Alloys Compd.*, 2012, **518**, pp. 6–10

[4]   Lu Y.X.: 'Improvement of copper plating adhesion on silane modified PET film by ultrasonic-assisted electroless deposition', *Appl. Surf. Sci.*, 2010, **256**, pp. 3554–3558

[5]   Garcia A., Berthelot T., Viel P., Polesel-Maris J., Palacin S.: 'Microscopic study of a ligand induced electroless plating process onto polymers', *ACS Appl. Mater. Inter.*, 2010, **2**, pp. 3043–3051

[6]   Liao Y.C., Kao Z.K.: 'Direct writing patterns for electroless plated copper thin film on plastic substrates', *ACS Appl. Mater. Inter.*, 2012, **4**, pp. 5109–5113

[7]   Yu W.X., Hong L., Chen B.H., Ko T.M.: 'A study on the interfacial composition of the electroless-copper-plated BPDA-PDA polyimide sheet', *J. Mater. Chem.*, 2003, **13**, pp. 818–824

[8]   Wang Y., Bian C., Jing X.L.: 'Adhesion improvement of electroless copper plating on phenolic resin matrix composite through a tin-free sensitization process', *Appl. Surf. Sci.*, 2013, **271**, pp. 303–310

[9]   Lu P., Shi Z.W., Walker A.V.: 'Selective electroless deposition of copper on organic thin films with improved morphology', *Langmuir*, 2011, **27**, pp. 13022–13028

[10]   Wang Z.W., Li Q., She Z.X., Chen F.N., Li L.Q.: 'Low-cost and large-scale fabrication method for an environmentally-friendly super-hydrophobic coating on magnesium alloy', *J. Mater. Chem.*, 2012, **22**, pp. 4097–4105

[11]   Su W., Yao L.B., Yang F., Li P.Y., Chen J., Liang L.F.: 'Electroless plating of copper on surface-modified glass substrate', *Appl. Surf. Sci.*, 2011, **257**, pp. 8067–8071

[12]   Xu L.N., Zhou K.C., Xu H.F., *ET AL.*: 'Copper thin coating deposition on natural pollen particles', *Appl. Surf. Sci.*, 2001, **183**, pp. 58–61

[13]   Jusys Z., Pauliukaité R., Vaškelis A.: 'EQCM study of the effect of ligands on the rate of Cu^{II} reduction by formaldehyde', *Phys. Chem. Chem. Phys.*, 1999, **1**, pp. 313–318

[14]   Hanna F., Hamid Z.A., Aal A.A.: 'Controlling factors affecting the stability and rate of electroless copper plating', *Mater. Lett.*, 2004, **58**, pp. 104–109

[15]   Liao Y., Zhang S.T., Dryfe R.: 'Electroless copper plating using dimethylamine borane as reductant', *Particuology*, 2012, **10**, pp. 487–491

[16]   Kulyk N., Cherevko S., Chung C.H.: 'Copper electroless plating in weakly alkaline electrolytes using DMAB as a reducing agent for

metallization on polymer films', *Electrochim. Acta*, 2012, **59**, pp. 179–185

[17] Vaškelis A., Juškènas R., Jačiauskienè J.: 'Copper hydride formation in the electroless copper plating process: *in situ* X-ray diffraction evidence and electrochemical study', *Electrochim. Acta*, 1998, **43**, pp. 1061–1066

[18] Gan X.P., Zhou K.C., Hu W.B., Zhang D.: 'Role of additives in electroless copper plating using hypophosphite as reducing agent', *Surf. Coat. Technol.*, 2012, **206**, pp. 3405–3409

[19] Yagi S., Nakanishi H., Matsubara E., ET AL.: 'Formation of Cu nanoparticles by electroless deposition using aqueous CuO suspension', *J. Electrochem. Soc.*, 2008, **155**, pp. 474–479

[20] Gan X.P., Wu Y.T., Liu L., Shen B., Hu W.B.: 'Electroless plating of Cu-Ni-P alloy on PET fabrics and effect of plating parameters on the properties of conductive fabrics', *J. Alloys Compd.*, 2008, **455**, pp. 308–313

[21] Zhang Q.Y., Wu M., Zhao W.: 'Electroless nickel plating on hollow glass microspheres', *Surf. Coat. Technol.*, 2005, **192**, pp. 213–219

[22] Hu Y.J., Zhang H.Y., Cheng X.L., Li F., Chen T.L.L.: 'Electroless plating of silver on cenosphere particles and the investigation of its corrosion behavior in composite silicon rubber', *Appl. Surf. Sci.*, 2011, **257**, pp. 2813–2817