Electrical conductive Cu/glass fibre composites prepared by electroless plating

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A simple and efficient method has been developed to create an electrical conductive copper shell on glass fibres. Instead of regular formaldehyde, the preferable reducing capacity of hydrazine hydrate served as the reducing agent for copper plating. On this basic condition, the effect of the bath temperature, the $Na_3C_6H_5O_7{\cdot}2H_2O$ and the $NH_3{\cdot}H_2O$ concentrations on the morphology and the conductivity of the Cu/glass fibre were explored. The morphology and the microstructure of the Cu/glass fibre particles were characterised by scanning electron microscopy, X-ray diffractometer techniques and the electrical conductivity was detected with the four-point probe method. The results showed that a compact and uniform copper layer was successfully deposited on the activated glass fibre, and the as-synthesised Cu/glass fibre composites exhibited a face centred cubic crystal structure and presented excellent electrical conductivity where the volume resistivity was 8.62×10^{-4} Ω cm.

1. Introduction: Recently, various conductive fillers have been used in electromagnetic shielding fabrication [1–5]. At present, the commonly-used metal fillers are highly conductive metals, such as silver, copper, nickel, cobalt and metal alloys. Silver has excellent electrical conductivity but the cost is high. Among various types of metals, copper is the optimum one owing to its better electrical conductivity which ranks only second to silver in terms of good thermal stability and low temperature coefficient of resistance [6]. The above micro or nanometal fillers exhibit good electrical conductivity and low cost as well, however they are too heavy to apply to modern electromagnetic shielding materials where demands for the 'thin, lightweight, wide and strong' characteristics have increased. According to this phenomenon, the low density core–shell structure composites might be the promising materials in the application of the electromagnetic shielding field.

It is well known that electroless plating with the advantages of low cost, simple process, excellent environment stability and other notable features is widely applied in the preparation of metal core–shell structure composites. A number of papers and reports about the core–shell structure composites synthesised by the electroless plating method have appeared in the literature in recent years. The choice of the core materials might be the key point here; according to the existing reports, polymer materials such as polyethylene terephthalate [7, 8], poly(glycidyl methacrylate) [9] and polystyrene [10], inorganic non-metal materials such as carbon fibre [11], graphite [12], carbon nanotubes [13, 14] and Al_2O_3 [15] were commonly used. In addition, Su *et al.* [16] developed a novel convenient method for electroless copper deposition on glass substrate. To obtain the metallisation core–shell structure materials, the electroless copper plating method might be the best choice.

Based on the above analysis, spherical fillers can be easily dispersed into the matrix; however the weight percentage is too high. The linear fillers can easily form conductive paths, which is attributed to the enhanced length–diameter ratio. Glass fibres are a kind of low-cost and low-density materials, which have found wide application in many fields [17, 18]. It can be expected that if the glass fibres were coated with a layer of metal, wider use would be developed in some fields, such as conducting glass fibre, which has some advantages of good conductivity, high intensity, low price and good combination with the polymeric matrix as they combine the properties of the glass fibre and the metal together. In 2012, Lien [19] successfully prepared a silver coated glass fibre with excellent conductivity. However, there are few reports about the copper coated glass fibre.

In the work reported in this Letter, we focused on developing a novel and convenient method for electroless copper plating on the surface of the glass fibre, where the preferable reducing capacity of hydrazine hydrate was regarded as a reducing agent. The main attention was paid to investing the effects of the solution compositions and the operation conditions of the plating process on the morphology and the electrical property of the synthesised composites. Another aim was to achieve a pure copper layer by using hydrazine hydrate as a reductant, which was verified by the XRD technology.

2. Experimental procedure: All the reagents were of analytical grade and used without further purification. The glass fibre was firstly degreased with 45 g/l NaOH aqueous solution at 65°C for 1 h, and then taken for vacuum filtration and dried for the following procedures. In a typical pretreated experiment, the degreased glass fibre was treated to produce catalytic activity through the following processes: coarsening, sensitisation and activation. The glass fibre was coarsened by using 42 g/l $K_2Cr_2O_4$, 85 ml/l H_2SO_4 solution at 40°C for 20 min, then sensitised in 35 g/l $SnCl_2$, 25 ml/l HCl solution for 15 min at 40°C, lastly the sensitised glass fibre was activated in 0.5 g/l $PdCl_2$, 5 ml/l HCl solution at 40°C for 30 min. To avoid the impurities from going into the next bath, the glass fibres were fully washed with distilled water after each step. The pretreated glass fibre was conducted in an electroless copper bath with the detailed composition and conditions listed in Table 1.

The morphology of the Cu/glass fibre was investigated by using scanning electron microscopy (Hitachi S-4800 scanning electron microscope). Structure analysis of the copper plating on the surface of the glass fibre was performed by an X-ray diffractometer (Bruker D8 focus diffractometer with Cu Kα radiation

Table 1 Composition and operation conditions of the electroless plating

Chemical	Concentration
$CuSO_4{\cdot}5H_2O$	25 g/l
$Na_3C_6H_5O_7{\cdot}2H_2O$	90 g/l
$NH_3{\cdot}H_2O$	100 ml/l
$N_2H_4{\cdot}H_2O$ (30 wt%)	50 ml/l
temperature	80°C
time	30 min

($\lambda = 0.15406$ nm) in the scanning angle ranging from 30° to 80°). The volume resistivity values were obtained by a SB 120 four-point probe instrument.

3. Results and discussion: Fig. 1*a* shows the SEM image of the glass fibre after electroless copper plating in the typical synthesis. It can be observed that the surface coatings were homogeneous, continuous and compact and there were fewer agglomerates, which indicated that the glass fibre dispersed uniformly in the solution during the electroless plating process. In addition, the diameter of the Cu/glass fibre was about 15 µm, whereas the length ranged from 40 to nearly 200 µm. From Fig. 1*b*, the extraordinarily compact surface microstructure of the Cu/glass fibre composites is clearly seen. What is more, the copper crystalline grain was about 300–500 nm. In consideration of its outstanding electrical conductivity, where the volume resistivity of 8.62×10^{-4} Ω cm was investigated from the four-point probe instrument, it is implied that a great potential conductive filler was comparable with the silver-coated particles in the electromagnetic shielding field.

X-ray diffraction measurement was performed to determine the chemical consistency of the as-obtained sample, presented in Fig. 2. Three sharpening diffraction peaks emerged at $2\theta = 43.5°$, 50.5° and 74.3°, which corresponded to the (111), (200) and (220) crystal planes of the cubic structure crystalline copper, respectively. It can be concluded that a layer of the copper coverage coating has deposited on the surface of the glass fibre by electroless

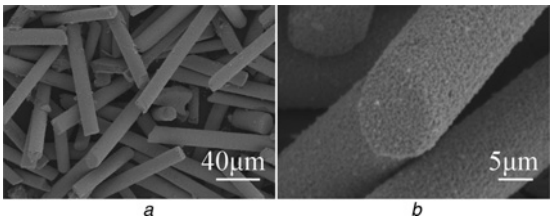

Figure 1 *SEM photo of the as-obtained Cu/glass fibre composites and the corresponding magnified image*
a SEM photo
b Magnified image

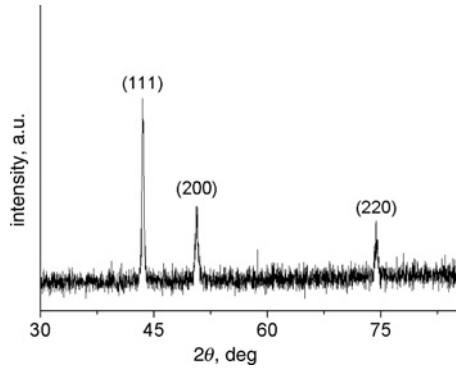

Figure 2 *XRD spectrum of the as-obtained Cu-coated glass fibre*

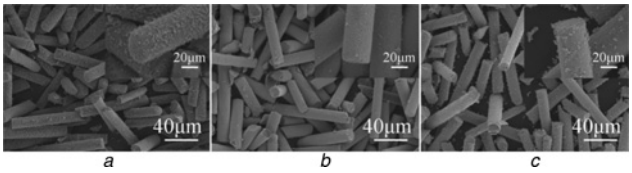

Figure 3 *SEM photos of the prepared Cu/glass fibre composites at different bath temperatures*
a 60°C
b 70°C
c 90°C
Insets of *a*, *b* and *c* are the magnified SEM images

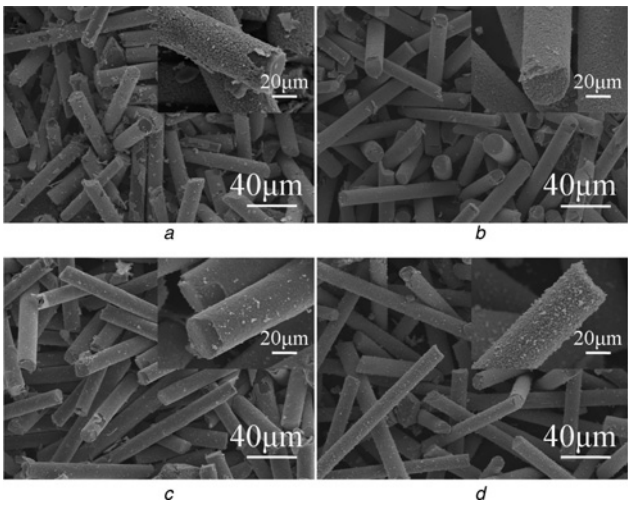

Figure 4 *SEM photos of the prepared Cu/glass fibre composites at different amounts of $Na_3C_6H_5O_7{\cdot}2H_2O$*
a 30 g/l
b 60 g/l
c 160 g/l
d 220 g/l
Insets of *a*, *b*, *c* and *d* are the magnified SEM images

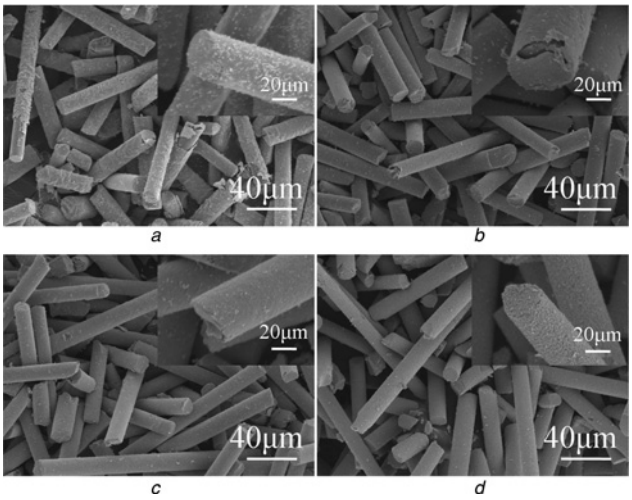

Figure 5 *SEM photos of the prepared Cu/glass fibre composites at different amounts of $NH_3{\cdot}H_2O$*
a 20 ml/l
b 60 ml/l
c 150 ml/l
d 200 ml/l
Insets of *a*, *b*, *c* and *d* are the magnified SEM images

Table 2 Volume resistivity (ρ_v) values of the Cu/glass fibre composites synthesised at different temperatures

Temperature, °C	50	60	70	80	90
ρ_v, Ω cm	—	—	9.87×10^{-3}	8.62×10^{-4}	2.12×10^{-3}

Note: — indicates ρ_v could not be obtained owing to the unstable current

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Table 3 Volume resistivity (ρ_v) values of the Cu/glass fibre composites synthesised with different $Na_3C_6H_5O_7{\cdot}2H_2O$ concentrations

$Na_3C_6H_5O_7{\cdot}2H_2O$, g l^{-1}	30	60	90	160	220
ρ_v, Ω cm	1.23×10^{-2}	1.21×10^{-2}	8.62×10^{-4}	9.16×10^{-4}	6.29×10^{-2}

Table 4 Volume resistivity (ρ_v) values of the Cu/glass fibre composites synthesised with different $NH_3{\cdot}H_2O$ concentrations

$NH_3{\cdot}H_2O$, ml l^{-1}	20	60	100	150	200
ρ_v, Ω cm	6.53×10^{-3}	5.31×10^{-3}	8.62×10^{-4}	9.74×10^{-4}	1.33×10^{-1}

plating, which processed the high crystallinity structure and the composition of the coating was pure copper without oxide.

Fig. 3 shows the SEM images of the prepared Cu/glass fibre composites at different bath temperatures. As we know, the essence of the electroless copper plating technique was redox reaction, which needed a certain energy to maintain the whole reaction. Here, the bath temperature was the main energy provider. Fig. 3*a* exhibits the sparse copper particles on the surface of the glass fibre. With the rising of the bath temperature, the copper grain was gradually formed into a film, however the adhesion between the copper shell and the glass fibre was very weak, resulting in the copper film being easily peeled off, as shown in Fig. 3*b*. At a higher temperature, the whole copper film has been coated around the surface of the glass fibre, however the surface of the copper film was rough, because of the high rate of the reaction at a high temperature. As shown in Fig. 3*c*, the bath temperature was 90°C.

The morphologies of the Cu/glass fibre composites at different concentrations of $Na_3C_6H_5O_7{\cdot}2H_2O$ were detected by the SEM, shown in Fig. 4. When the $Na_3C_6H_5O_7{\cdot}2H_2O$ content was 30 g/l, the copper film was formed on the surface of the glass fibre, as shown in Fig. 4*a*. However, the adhesion between the copper film and the glass fibre was too little to couple tightly owing to the fast plating rate. With the increasing amounts of $Na_3C_6H_5O_7{\cdot}2H_2O$, the copper film was gradually changed from sparse and thin to compact and uniform, as shown in Figs. 1 and 4*b* whereas the appropriate amounts of $Na_3C_6H_5O_7{\cdot}2H_2O$ was the key point for the perfect morphology of the synthesised composites. When the $Na_3C_6H_5O_7{\cdot}2H_2O$ contents exceeded 90 g/l, some excrescent copper particles of uneven size germinated on the uniform surface of the copper film (Fig. 4*c*), especially the amount of $Na_3C_6H_5O_7{\cdot}2H_2O$ was 220 g/l in the plating bath and the surface of the glass fibre became brushy. Since the $Na_3C_6H_5O_7{\cdot}2H_2O$ content was too much to grow into the other substance further study and characterisation are needed.

Fig. 5 exhibits the SEM images of the Cu/ glass fibre composites at different amounts of $NH_3{\cdot}H_2O$. It can be clearly seen that the copper film was changed from thin and fragile to even and dense with the increase of the $NH_3{\cdot}H_2O$ concentrations. This can be accounted for the following reasons. Firstly, the reduction agent $NH_3{\cdot}H_2O$ needs a strongly alkaline environment to make a difference. Secondly, $NH_3{\cdot}H_2O$ also can be regarded as a complexant in the copper plating process, which decreased the plating rate and was beneficial for the better microstructure of the copper coated glass fibre composites. However, an excess $NH_3{\cdot}H_2O$ dosage could easily decrease the electrical conductivity of the composites.

The above results have demonstrated that it was possible to control the morphology and the microstructure of the products by properly monitoring the process conductions and the components of the reaction system. Here, Tables 2–4 presented the further analysis of the electrical conductive properties of the Cu/glass fibre composites. Table 2 shows the relationship of the bath temperature and the electrical conductivity of the prepared particles. The volume resistivity varied obviously from 9.87×10^{-3} to 2.12×10^{-3} Ω·cm, and the lowest value was 8.62×10^{-4} Ω·cm at 80°C; it seemed that the suitable bath temperature was 80°C for excellent conductivity. In addition, the reaction failed to proceed when the bath temperature was lower than 60°C because of the insufficient energy. At the same time, Table 3 presents the volume resistivity of the Cu/glass fibre with different $Na_3C_6H_5O_7{\cdot}2H_2O$ concentrations. The results were in accordance with the SEM images; namely, the better morphology was beneficial to the electrical conductivity of the copper-coated glass fibre. When the amount of $Na_3C_6H_5O_7{\cdot}2H_2O$ was 90 g/l, the volume resistivity was the lowest, showing the best conductive property. Table 4 exhibits the volume resistivity of the Cu/glass fibre with different $NH_3{\cdot}H_2O$ dosages. It can be clearly seen that the volume resistivity was decreased firstly and then increased with the $NH_3{\cdot}H_2O$ dosages ranging from 20 to 200 ml/l and the electrical conductivity of the synthesised composites was the best when the amount of $NH_3{\cdot}H_2O$ was 100 ml/l. Based on the above analysis, both the SEM results and the electrical conductivity were affected by the process conductions and the components of the reaction system.

4. Conclusion: In summary, the excellent copper films assembled on the glass fibres were successfully synthesised for the first time via a facile and mild electroless copper plating procedure by using $N_2H_4{\cdot}H_2O$ as the reductant. The results demonstrated that it was possible to control the morphology and the microstructure of the products by properly monitoring the process conductions and the components of the reaction system. The as-obtained samples presented a compact and uniform surface morphology, the XRD map showed that the pure copper film was a face centred cubic crystal in that it was reduced by $N_2H_4{\cdot}H_2O$. We believe that such a synthetic route can also be adapted for the core–shell composites of the other metal. These core–shell composites may have some promising applications in lightweight conductive materials, sensors, catalysis and other fields.

5 References

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