Supplementary Information

Facile preparation of high-quality copper layer on epoxy resin via electroless plating for applications in electromagnetic interference shielding

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1. The optimization study of the Ag^+ concentration in $AgNO_3/C_2H_5OH$ solution

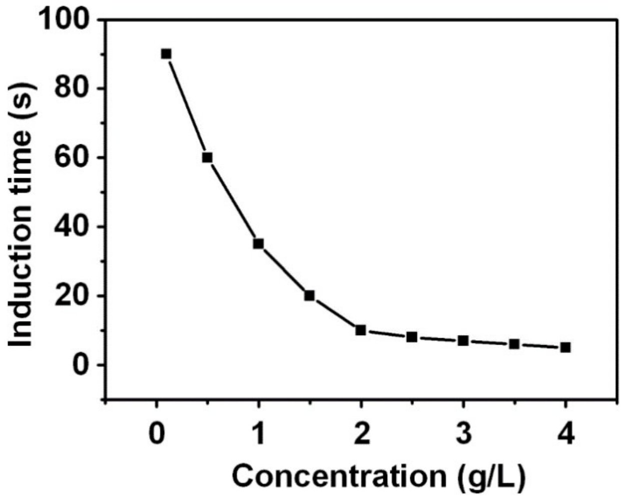

Fig. S1 Induction time versus silver nitrate concentrations.

Induction time is the time before Ag triggers the ECP. To reduce the deposition time and improve conductance of the copper layer, induction time should be reduced as far as possible. We tested the induction time of $AgNO_3/C_2H_5OH$ solution with silver nitrate concentrations of 0.1 g/L, 0.5 g/L, 1 g/L, 1.5 g/L, 2 g/L, 2.5g/L, 3 g/L, 3.5 g/L, 4 g/L by electrochemistry. As the Fig. S1 shows, induction time comes to be almost stable while the concentration reaches 2g/L. Therefore, we used 2g/L as the final concentration for the balance of induction time and the cost.

2. XPS spectra of S in modified epoxy resin substrate

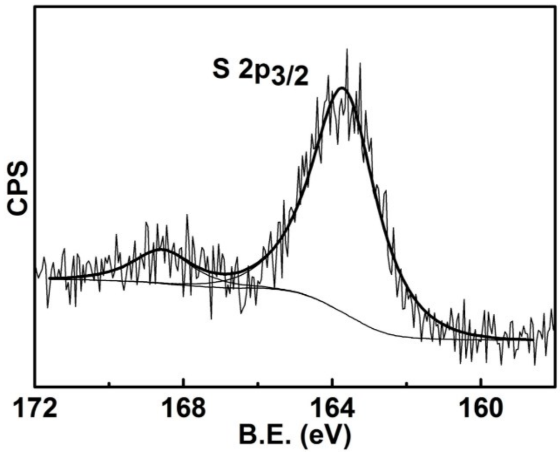

Fig. S2 XPS spectra of and S.

Corresponding data of the S element (Fig. S3) can be found in the database from the National Institute of Standards and Technology (NIST).[1]

3.The SEM and EDS images of pristine and modified epoxy resin substrate soaked in $AgNO_3/C_2H_5OH$ solution even after ultrasonic washing

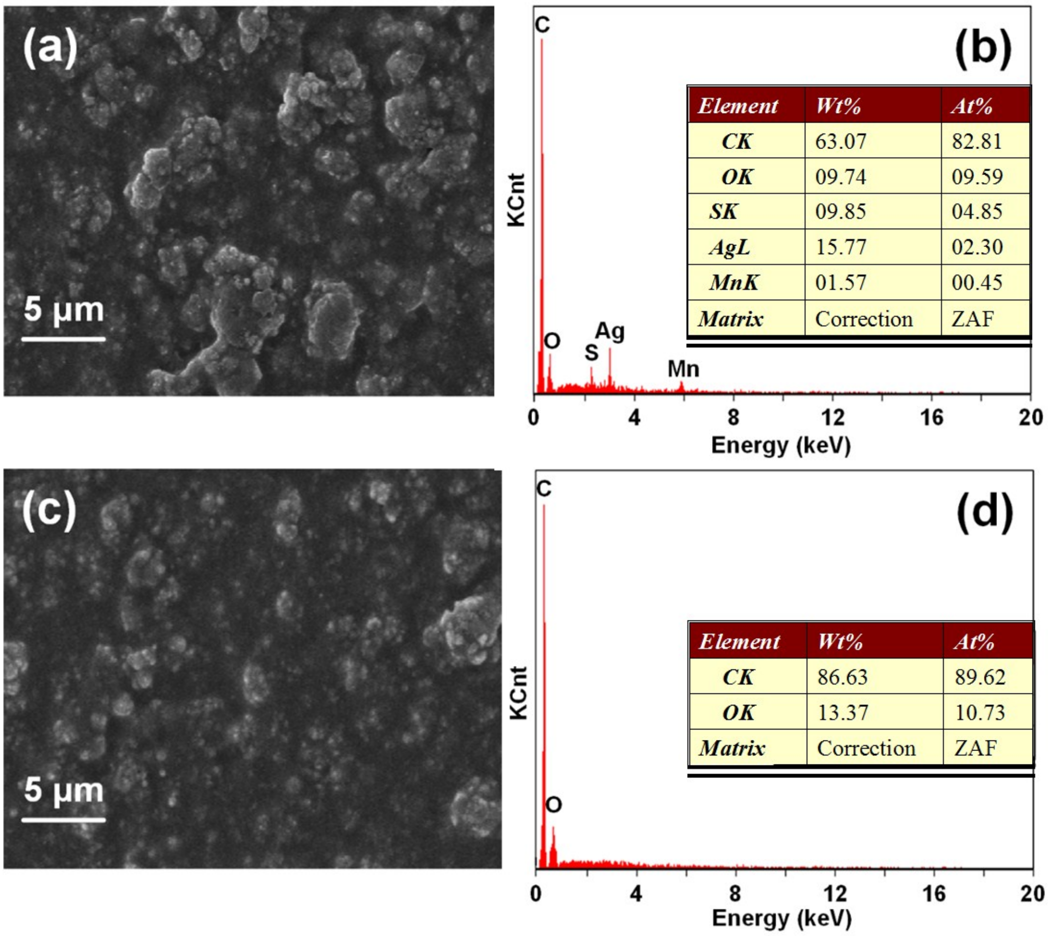

Fig. S3 SEM images and EDS spectra of (a), (b) modified and (c), (d) pristine substrate after immersing $AgNO_3/C_2H_5OH$ solution and ultrasonic washing.

Fig. S3 shows the modified substrate (Fig. S3a, b) and pristine substrate (Fig. S3c, d) with immersing in $AgNO_3/C_2H_5OH$ solution and ultrasonic cleaning. The result shows that the silver is only found on the modified epoxy resin substrate after ultrasonic washing. It indicates that the catalytic silver ions can be attached tightly on the modified epoxy resin substrate even after ultrasonic washing.

4. The electroless copper plating on modified epoxy resin with 50 min

Fig. S4 Optical image of ECP on modified epoxy resin with 50 min.

Fig. S4 shows that the copper layer starts to deteriorate adhesion with frothy surface when ECP tine exceeds 40 min.

5. The copper layer fabricated on pristine epoxy resin substrate

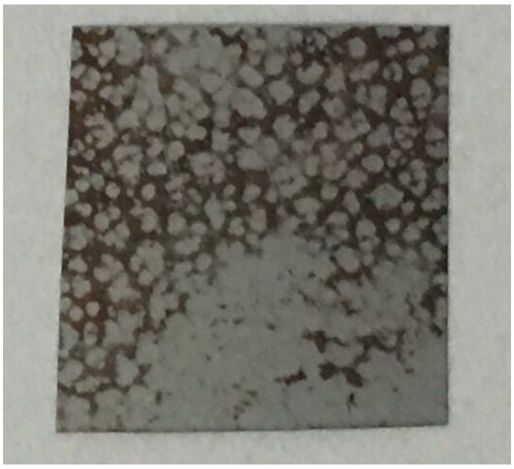

Fig. S5 Optical image of ECP on pristine epoxy resin.

6. The tape test on deposited copper layer

Fig. S6 Tools used to test adhesion of copper patterns.

The set of tools used to test adhesion of the deposited copper layer include a sharp blade with 11 edges in equidistance, a brush, a magnifier and a transparent tape (Cat. 600, 3M) (Fig. S6). The test method for measuring adhesion by tape test was operated following the ASTM standard D3359.[2]

Reference：

1 The NIST XPS Database, http://srdata.nist.gov/xps/Default.aspx, (accessed June 2017).

2 ASTM International, http://www.astm.org/cgi-bin/resolver.cgi?D3359, (accessed July 2017).

7. The relationship between dielectric properties with the measured frequency.

The relative permittivity of the medium is[3-5]

$$\varepsilon_r = 1 + \frac{NZe^2}{m\varepsilon_0\left(\omega_0^2 - \omega^2 - ir\omega\right)} \qquad (1)$$

where, ε_r is relative permittivity of the medium, NZ is the number of electrons per unit volume, m is mass, ω_0 is electric natural frequency, ε_0 is vacuum dielectric constant, ω is frequency of external electric field, and r is damping coefficient. At high frequency, assuming that there are the amount of electron (f_j) in each molecule with the fetter frequency (ω_f) and the damping coefficient (r_0), then $\omega >> \omega_f$, $\omega >> r_0$, the electrons in the metal are free and the damping is negligible, and the effect of the metal on the electromagnetic waves is similar to plasma. Suppose there are some free electrons (f_0) in each molecule, then

$$\therefore\ \varepsilon_r = 1 - \frac{Ne^2}{m\varepsilon_0}\sum\frac{f_j}{\omega^2} - \frac{Ne^2 f_0}{m\varepsilon_0\omega^2} \qquad (2)$$

$$\because\ \sum f_j = Z - f_0 \qquad (3)$$

$$\therefore\ \varepsilon_r = 1 - \frac{NZe^2}{m\varepsilon_0\omega^2} \qquad (4)$$

If $\omega_p^2 = \frac{NZe^2}{m\varepsilon_0}$ (5)

$$\therefore\ \varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2} \qquad (6)$$

Where, ω_p is the plasma frequency of conducting electric.

If $\omega < \omega_p$, then $\varepsilon_r < 0$, and $n = \sqrt{\varepsilon_r}$ is a purely imaginary number, the electromagnetic wave enters the metal very shallow, and it is almost completely reflected back.

If $\omega > \omega_p$, then $\varepsilon_r > 0$, and $n = \sqrt{\varepsilon_r}$ is a real number, the electromagnetic wave can pass freely through the metal; for copper, the number of electrons per unit volume $NZ = 8.5 \times 10^{23}\left(\frac{1}{m^3}\right)$, so ω_p is

$$\omega_p = \sqrt{\frac{8.5 \times 10^{28} \times (1.6 \times 10^{-19})^2}{9.1 \times 10^{-31} \times 8.85 \times 10^{-12}}} \approx 10^{16}\frac{1}{s} \quad (7)$$

So, when $\omega > 10^{16}$ 1/s (10^{16} Hz = 10^7 GHz), electromagnetic waves can pass through copper. However, we measured EMI shielding effectiveness of deposited copper layer of ECP with different time on modified epoxy resin from 4 GHz to 18 GHz (far less than 10^7 GHz), electromagnetic waves cannot pass through copper. The descriptive discussion above has been added into the revised manuscript, please find the change highlighted in the revised manuscript.

3 X. Chen, J. Chen, F. Meng, L. Shan, M. Jiang, X. Xu, J. Lu, Y. Wang, Z. Zhou, Compos. Sci. Technol., 2016, **127**, 71-78.

4 P. Xu, X. J. Han, C. Wang, D. H. Zhou, Z. S. Lv, A. H. Wen, X. H. Wang, B. Zhang, J. Phys. Chem. B, 2008, **112**, 10443-10448.

5 E. Vazquez, M. Prato, ACS Nano, 2009, **3**, 3819-3824.

8. The measured EMI shielding effectiveness of deposited copper layer on

pristine epoxy resin.

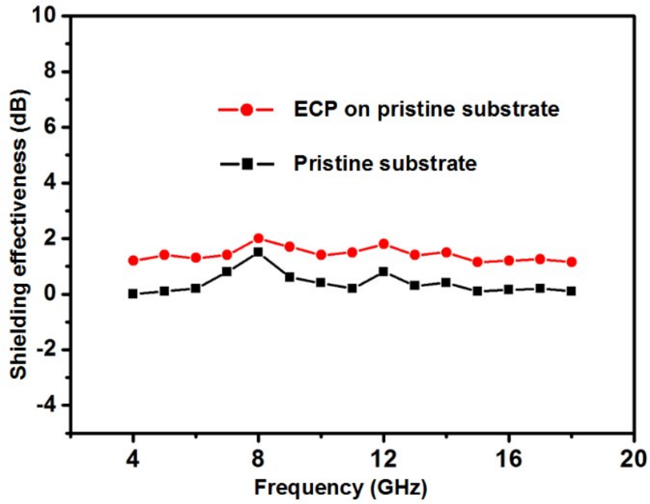

Fig. S8 The variation in EMI shielding effectiveness of pristine and ECP on pristine epoxy resin substrate range from 4 GHz to 18GHz.

Fig. S8 shows the measured EMI shielding effectiveness of pristine and deposited copper layer of ECP on pristine epoxy resin. The pristine epoxy resin cannot exhibit any wave shielding. Meanwhile, the value of EMI shielding effectiveness of deposited copper layer of ECP on unprocessed epoxy resin is about 1-2 dB. The results represent that deposited copper layer of ECP on pristine epoxy resin cannot shield any electromagnetic waves at high frequencies.