

ESI:

**Formation of metal coatings on magnesium using a galvanic
replacement reaction in ionic liquid**

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Experimental details

BMP–DCA IL was prepared and purified following a published method [D.R. MacFarlane, S.A. Forsyth, J. Golding and G.B. Deacon, *Green Chem.*, 2002, **4**, 444.]. The IL was washed with dichloromethane (99 wt.%, SHOWA), filtered to remove precipitates, and then vacuum-dried at 100 °C for 12 h before use. The water content of the IL, measured with a Karl Fisher titrator, was ~80 ppm by mass. To prepare the plating solutions for replacement reactions, 0.1 M CuCl, NiCl₂, TiF₄, and ZnCl₂ were respectively dissolved in the BMP–DCA IL to provide the metal ion precursors. Each mixture was continuously stirred by a magnetic paddle for 24 h to ensure uniformity. Mg with a purity of above 99.9 wt.% was used in this study. Prior to use, the Mg samples were ground using successively finer abrasive papers to a grit of #4000. The galvanic replacement reactions were performed at 25 °C by immersing the Mg electrodes in the ILs with various metal ions for 24 h. All the chemicals and electrodes were handled and tested in an argon-filled glove box (Innovation Technology Co. Ltd.), where both the moisture content and oxygen content were maintained at below 1 ppm (by weight).

For electrochemical measurements in the IL, the reference electrode was a Pt wire placed in a fritted glass tube filled with ferrocene/ferrocenium (Fc/Fc⁺=50/50 mol.%) containing a butylmethylpyrrolidinium–bis(trifluoromethanesulfonyl)imide IL; therefore, all the potential values reported in the IL are related to this electrode. The open-circuit potentials (OCPs) of the electrodes were monitored by an AUTOLAB potentiostat. To examine the replacement reactions, in-situ X-ray absorption spectroscopy (XAS) was employed. In the analysis, 1 ml of the metal-ion-containing IL was dropped on a 1-cm² Mg sample, and XAS spectra were recorded as a function of time. The XAS experiments were performed on beamline 17 C at the National

Synchrotron Radiation Research Center (NSRRC) in Taiwan. The storage ring was operated with an electron energy of 1.5 GeV and a current of between 100 and 200 mA. A Si (111) double-crystal monochromator was employed for energy selection. X-ray diffraction (Bruker D8 Advance) with a Cu target was used to analyze the crystal structure of the obtained samples. The X-ray detector was scanned in a 2θ range of 20° to 80° at a speed of $1^\circ/\text{min}$. The surface morphologies and chemical compositions were analyzed using a scanning electron microscope (SEM, Hitachi S-4700I) and its auxiliary energy-dispersive X-ray spectrometer, respectively.

Corrosion resistances of various samples were evaluated by potentiodynamic polarization tests, which were performed with a potential sweep rate of 5 mV/s toward the anodic direction in 0.1 M Na_2SO_4 aqueous solution. A three-electrode electrochemical cell controlled by an AUTOLAB potentiostat was adopted. In this measurement, a Pt wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively.

Table S1 Corrosion potentials (E_{corr}) and anodic current densities (i) at -1.2 V_{Ag/AgCl} of Mg electrodes coated by various metal films measured in 0.1 M Na₂SO₄ aqueous solution.

| | Cu@Mg | Ni@Mg | Zn@Mg | Ti@Mg | Bare Mg |
|---|-------|-------|-------|-------|---------|
| E_{corr} (V _{Ag/AgCl}) | -1.35 | -1.25 | -1.40 | -1.45 | -1.60 |
| i (mA/cm ²) | 0.33 | 0.27 | 0.59 | 7.83 | 19.0 |

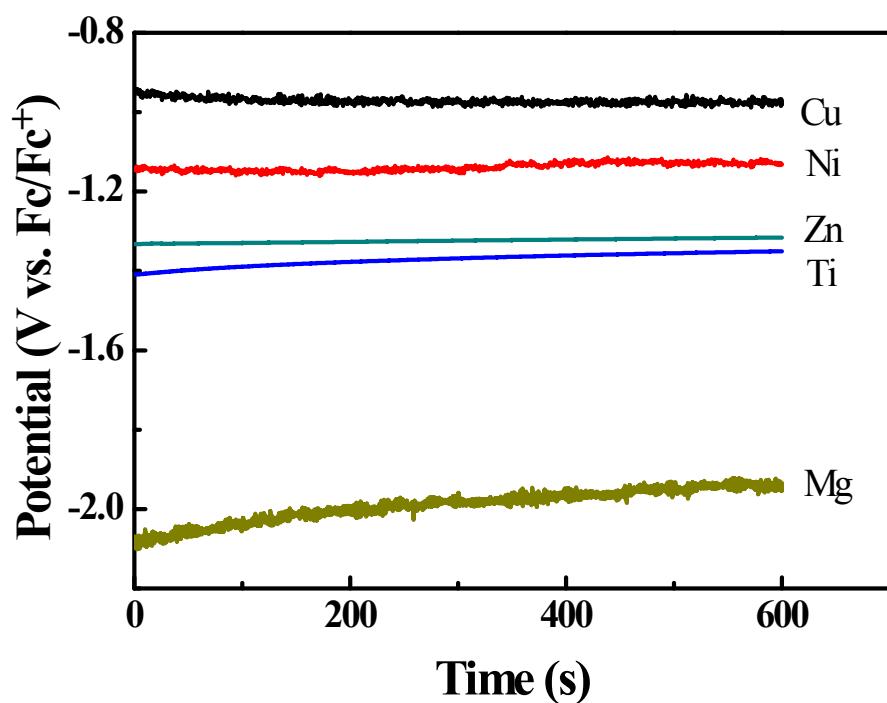


Fig. S1 Open-circuit potentials versus time for various metal electrodes measured in neat BMP–DCA IL.

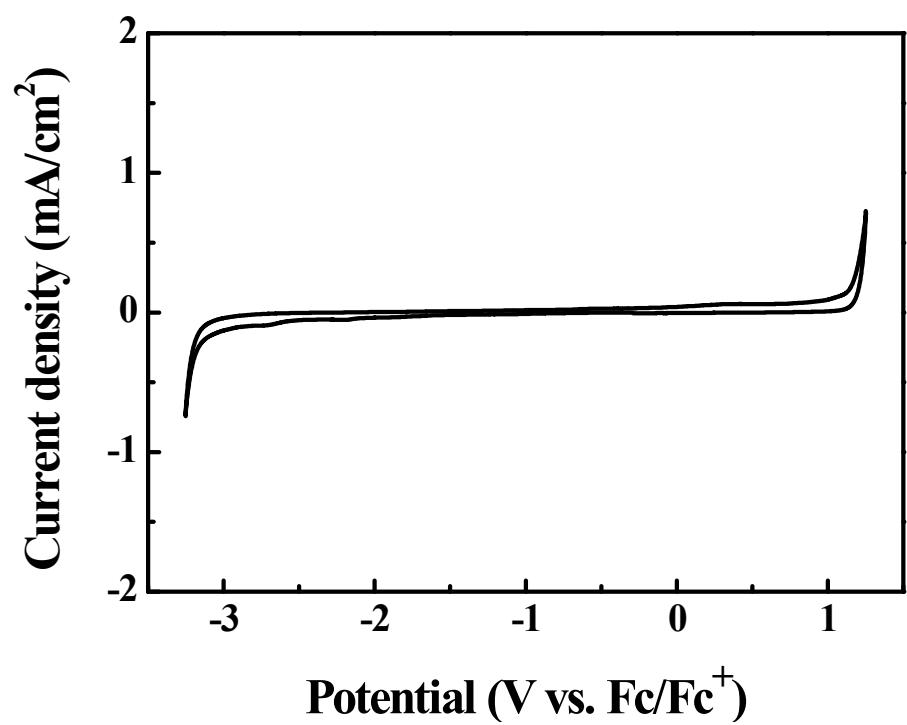


Fig. S2 Cyclic voltammogram of an inert glassy carbon electrode recorded in BMP–DCA IL at a potential sweep rate of 50 mV/s.

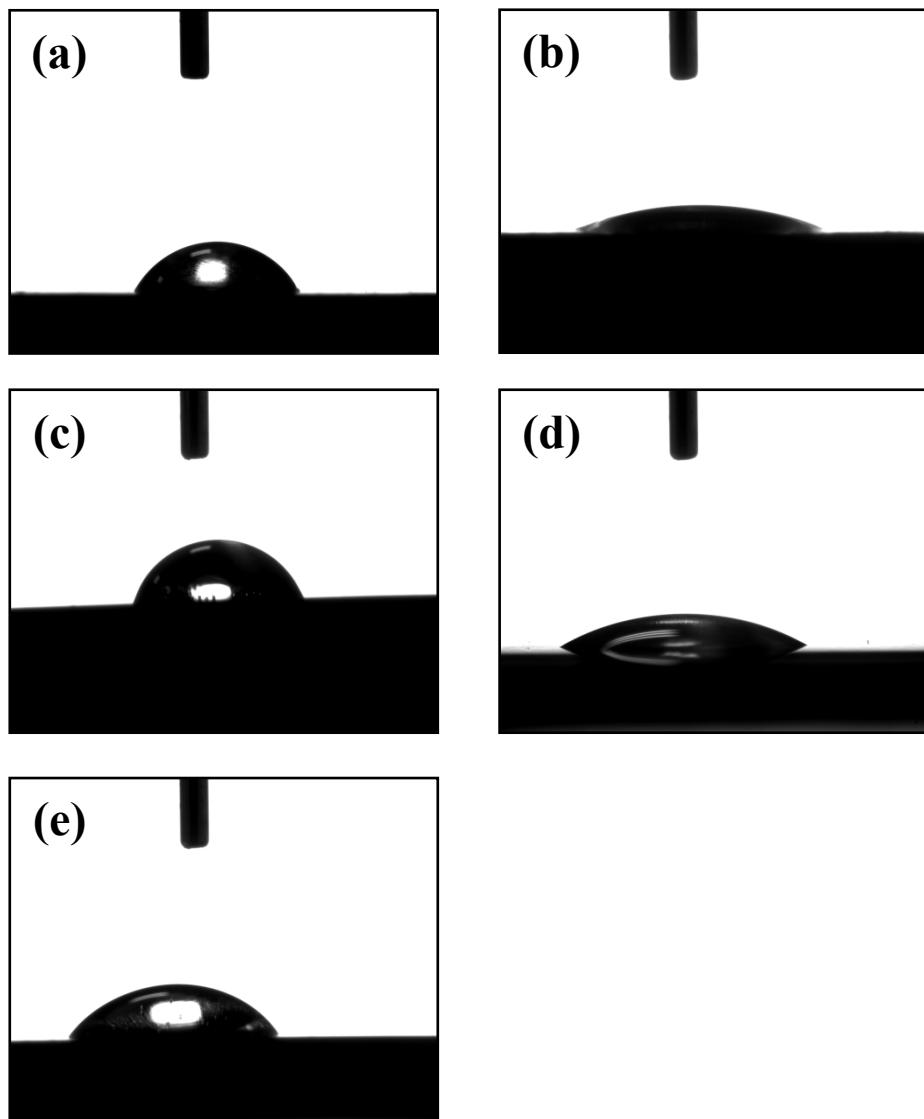


Fig. S3 Water wettability at (a) Cu-coated, (b) Ni-coated, (c) Zn-coated, (d) Ti-coated, and (e) bare Mg samples.

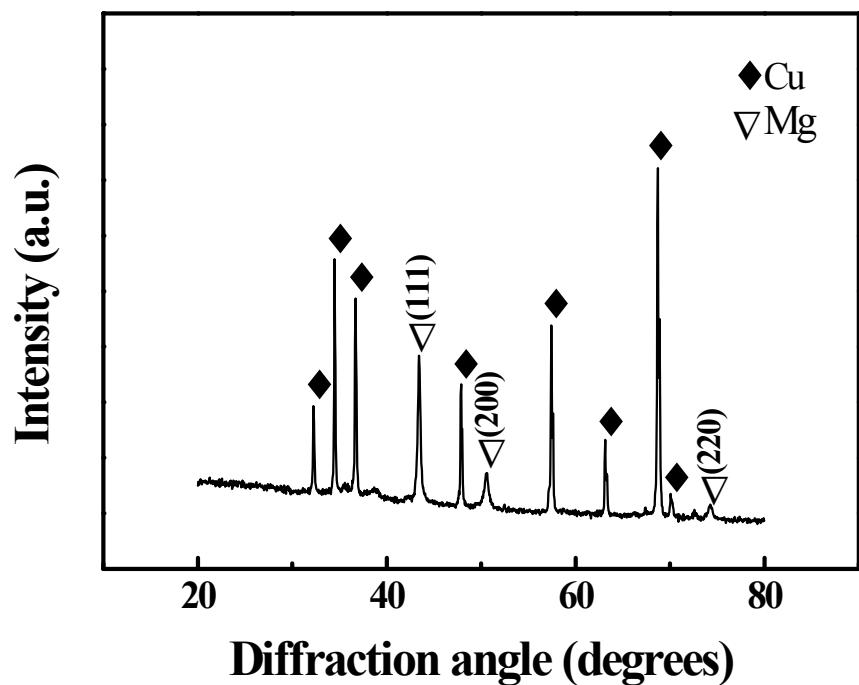


Fig. S4 X-ray diffraction pattern of Cu-coated Mg sample obtained via a replacement reaction in Cu⁺-containing IL for 24 h.

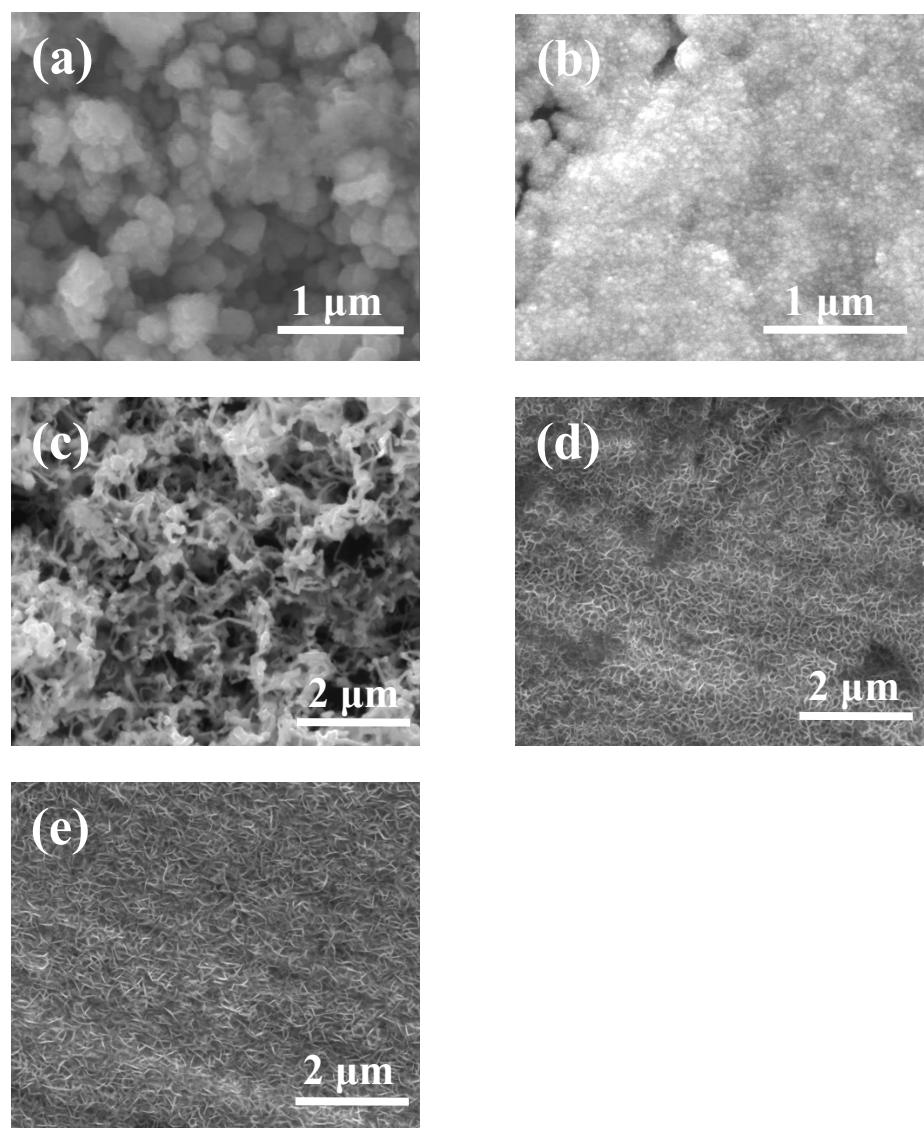


Fig. S5 SEM micrographs of (a) Cu-coated, (b) Ni-coated, (c) Zn-coated, (d) Ti-coated, and (e) bare Mg samples after being immersed in 0.1 M Na_2SO_4 aqueous solution for 1 h.