Supporting Information

Efficient heat dissipation by ion-mediation assembled reduced graphene oxide

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Cross-linking agent of IMA-GO structure

GO sheets in IMA-GO structure are primarily interconnected by metal ions rather than π -π stacking and hydrophobic interactions. To prove the adhesion force caused by metal ions, IMA-GO was immersed in 2 wt% ethylenediaminetetraacetic acid (EDTA) solution. EDTA strongly coordinates with metal ion forming a metal-EDTA complex, which breaks the coordination between metal ion and GO sheets.[1] Fig. S1 shows that IMA-GO was completely dispersed in EDTA solution with gentle shaking, implying that cross-linking between GO sheets in IMA-GO structure arises from the coordination between metal ion and GO sheets. Meanwhile, IMA-GO structure was entirely removed from the copper substrate. It means that metal ion plays a role as a bridge between a substrate and IMA-GO structure.
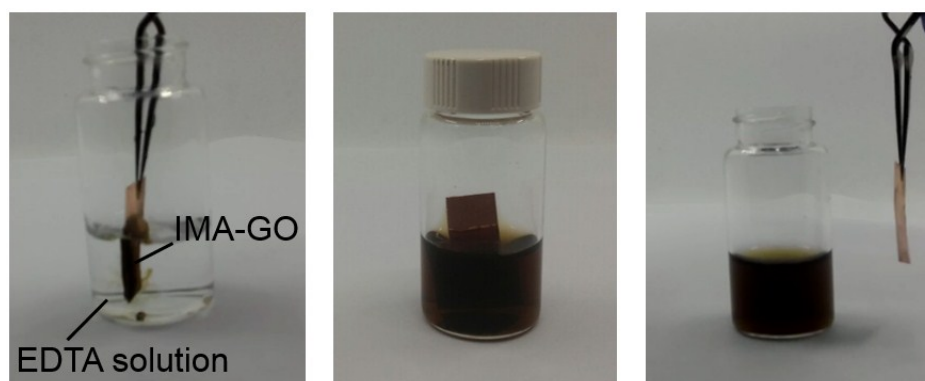

Fig. S1 Behavior of IMA-GO structure immersed in EDTA solution.

Porosity and surface area of IMA-rGO structure

The porosity and pore diameter of IMA-rGO were measured using a mercury porosimetry (AutoPore IV 9500) as shown in Fig. S2. Porosity was estimated to be 90.8% implying that considerable space of IMA-rGO remained empty. Average pore diameter was 12.1 µm which is consistent with that measured from SEM images. The surface area of IMA-rGO was measured using methylene blue adsorption.[2] It has been well known that each methylene blue molecule adsorbed on graphitic materials represents 1.35 nm^2 of surface area.[3] After immersing a known mass of IMA-rGO in methylene blue aqueous solution, the solution was stirred at a rate of 500 rpm for a day to reach maximum adsorption of methylene blue molecules. The solution was centrifuged to completely settle IMA-rGO, thereby leaving unabsorbed methylene blue molecules in supernatant. The methylene blue concentration was determined through UV-vis spectroscopy analysis as shown in Fig. S3. Star mark indicates the concentration of methylene blue in supernatant. Considering initial methylene blue concentration, the mass of IMA-rGO and initial solution, the surface area for IMA-rGO was calculated to be 144.5 m^2 g^{-1}. Meanwhile, the density of IMA-rGO structure was measured to be 12.3±0.8 mg cm^{-3}. Therefore, 85 µm thick IMA-GO structure has the surface area of 151 cm^2 for the apparent area of 1 cm^2.
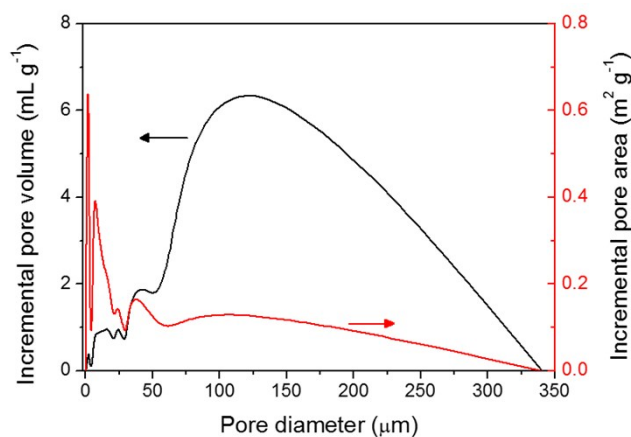

Fig. S2 Dependence of pore volume and pore area of IMA-rGO on pore diameter.
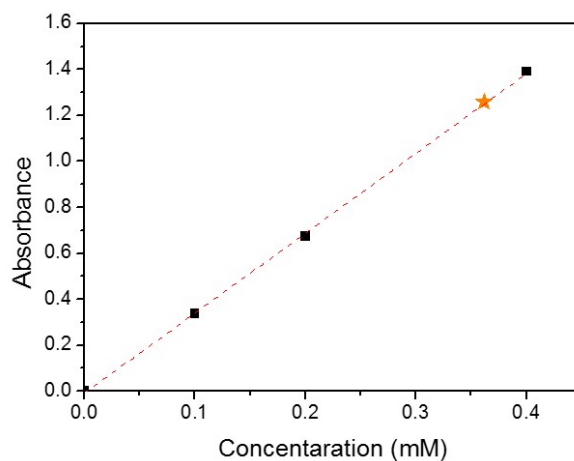
**Fig. S3** Dependence of absorbance of methylene blue solution on its concentration.

Ion-mediated assembly (IMA) and electrophoretic deposition (EPD)

Both IMA and EPD of GO are performed in a same experimental setup in which target electrode is anode and counter electrode is cathode. A major difference between them is whether or not the anodic dissolution of target metal occurs. Various metals, including Cu, Fe, Cr, Ti, and Al which can dissolve divalent or trivalent ions, were used as electrodes. As shown in Fig. S4, thick and uniform GO foams were formed on Cu and Fe electrodes with 1 mg mL^{-1} GO solution, applied voltage of 5 V, and process time of 5 sec. However, Cr, Ti, and Al made thin and irregular GO films on their surface due to their corrosion resistance that hindered anodic dissolution. The formation of GO films on these metals is attributed to the effect of EPD rather than IMA.
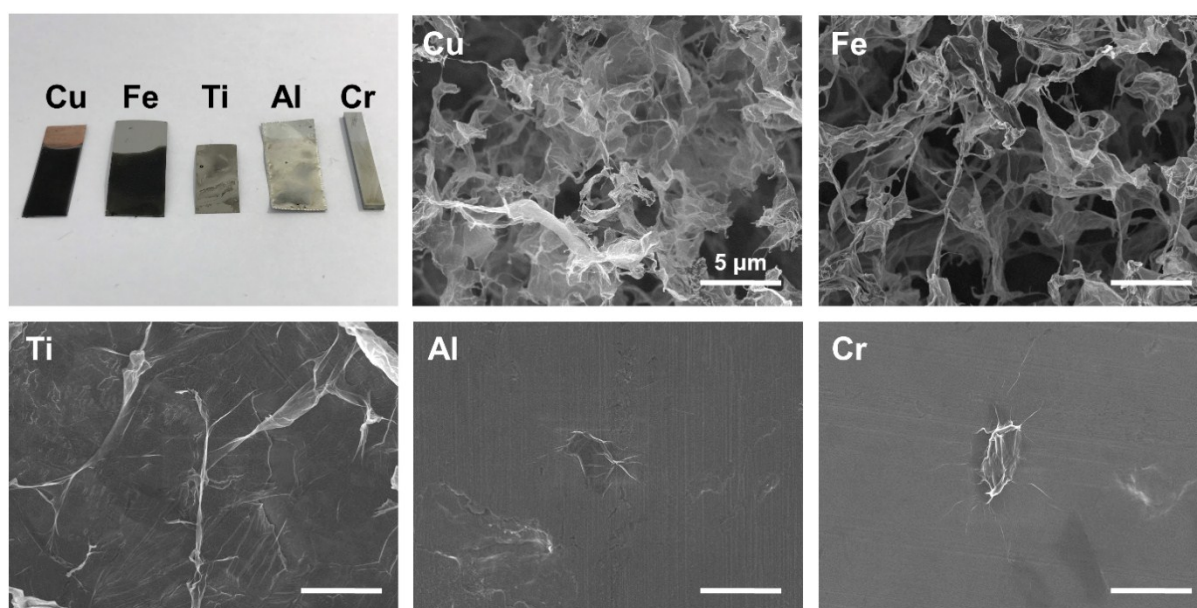

**Fig. S4** Optical, SEM images of GO structures on the various metals.

Another difference between IMA and EPD is the content of metal ions that interconnect GO sheets. While EPD is based on the migration of negatively charged GO under an electric field, IMA exploits the anodic dissolution of a metal substrate and uses dissolved metal ion as a cross-linker interconnecting GO sheets. Therefore, GO foam made by IMA should contain metal ions dissolved from the metal substrate. We measured the content of metal ions in GO foam made on Cu electrode. A GO foam detached from the electrode was attached on an Au substrate to avoid the detection of the electrode. A scanning electron microscope (Carl Zeiss, SUPRA 55VP) equipped with energy dispersive spectrometer (EDS) was used to detect metal ions as shown in Fig. S5. The content of Cu ions ranges from 3.7 to 5.3 at% influenced by process variables such as applied voltage and GO concentration, implying that GO foams we used here were fabricated by IMA process. Sulfur peak came from organosulfate groups located at the basal plane and edge of GO.[4]
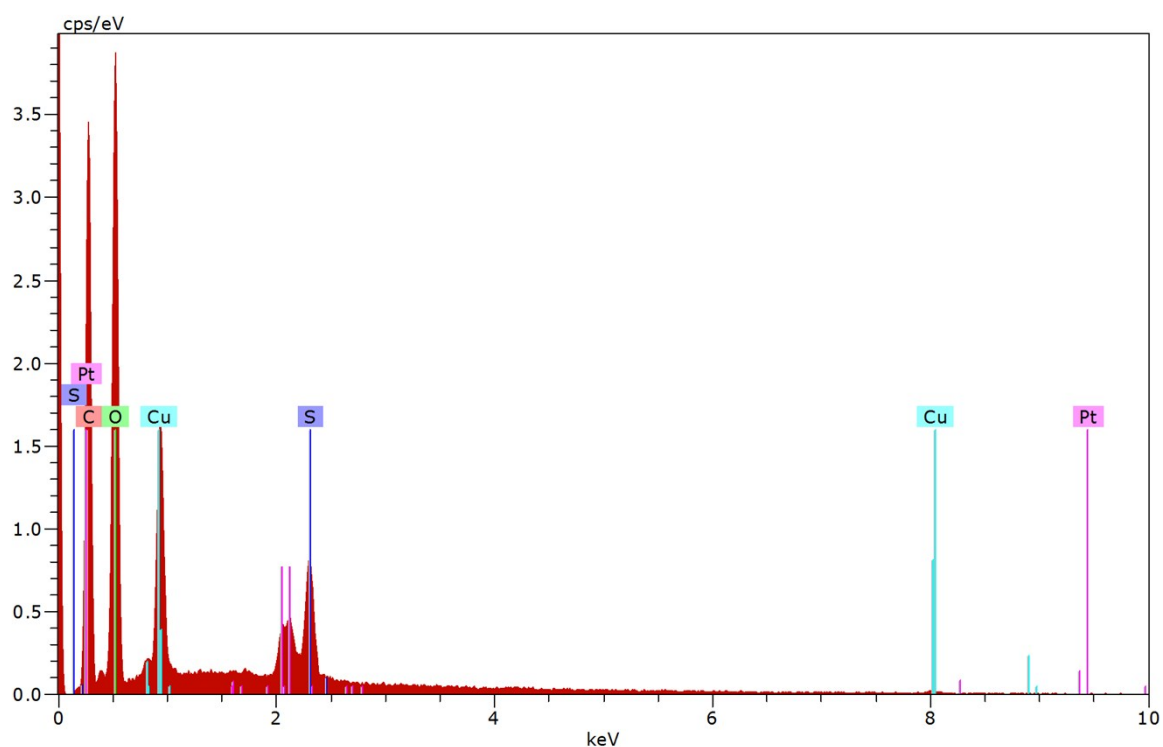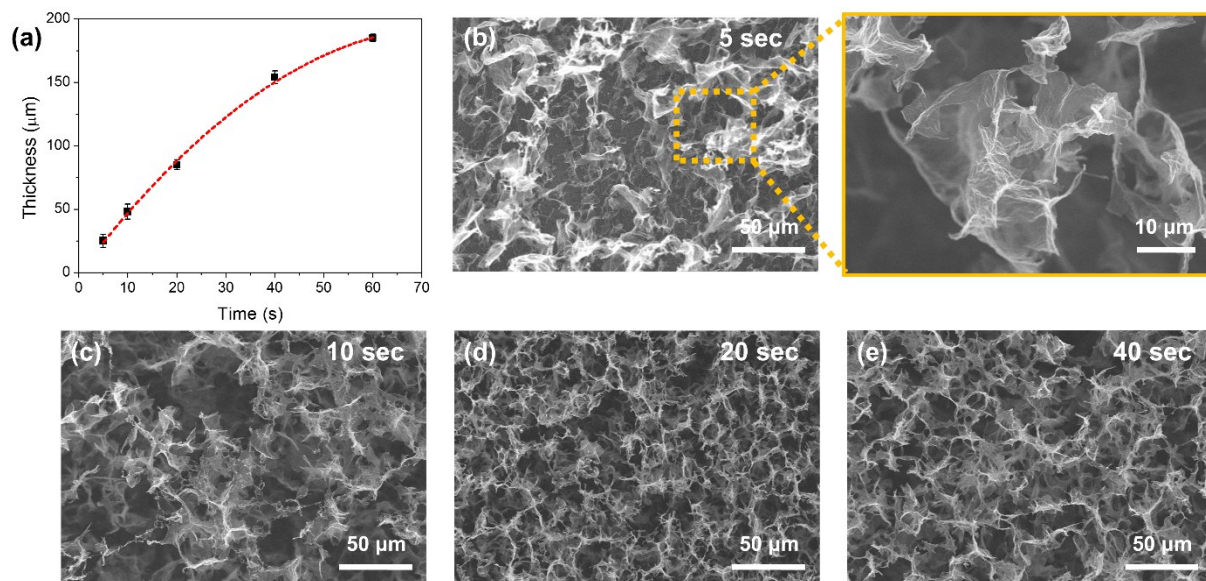

**Fig. S5** EDS spectrum of GO foam made by IMA.
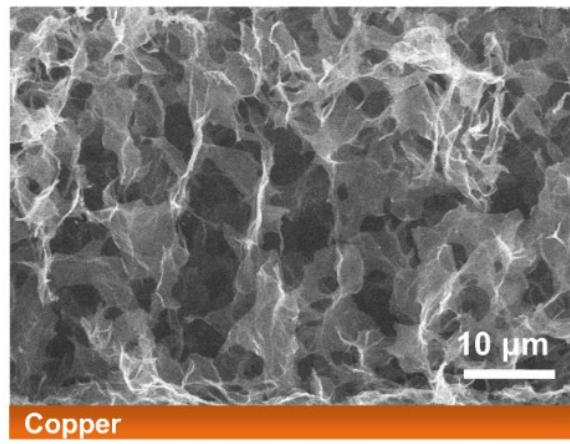
Fig. S6 The cross-section SEM image of IMA-rGO structure with vertical directionality.
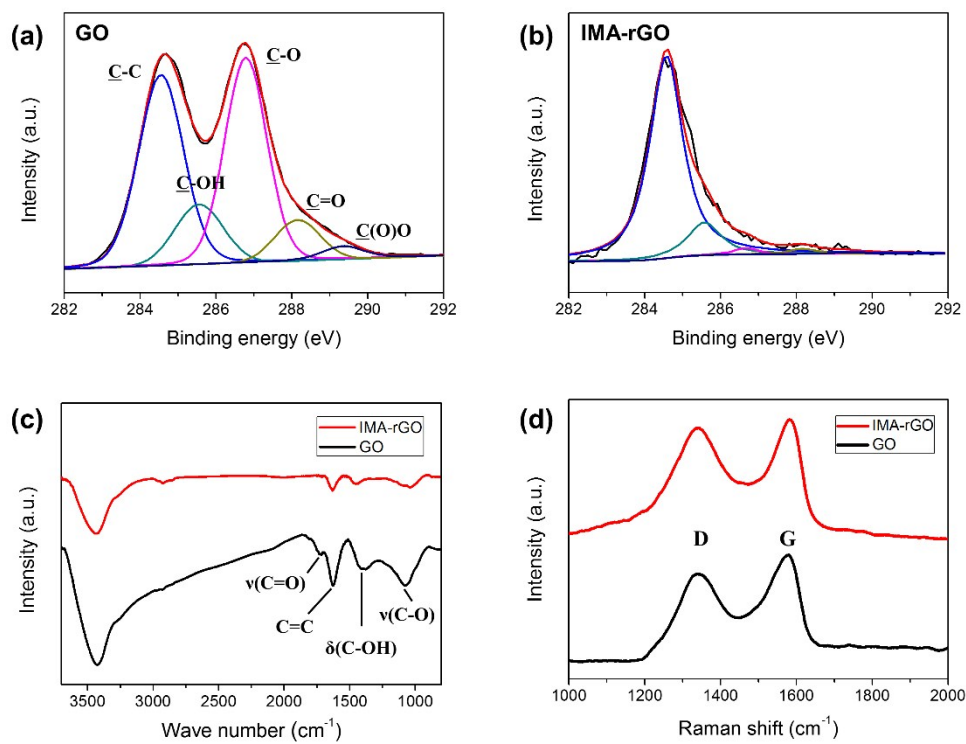
Fig. S7 XPS spectra of (a) GO and (b) IMA-rGO. (c) FT-IR spectra of GO, IMA-rGO annealed at 200 ℃. (d) Raman spectra of GO and IMA-rGO.
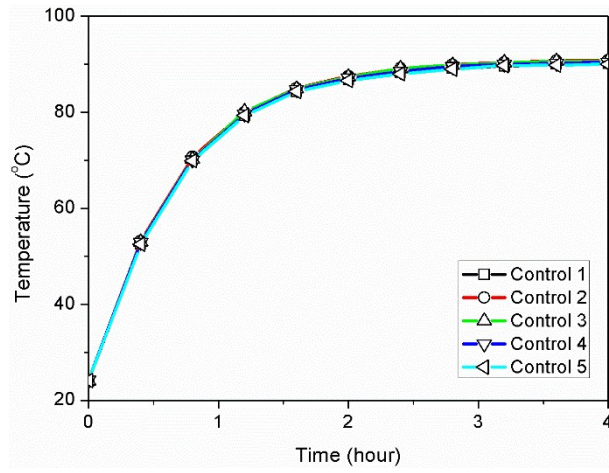
Fig. S8 Influence of IMA process time on IMA-rGO structure. (a) Influence of process time on the thickness of IMA-rGO structure. (b-e) Low- and high-resolution SEM images of the IMA rGO structure.
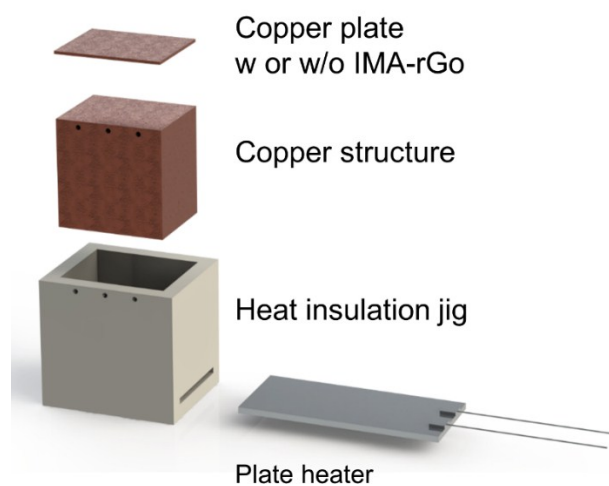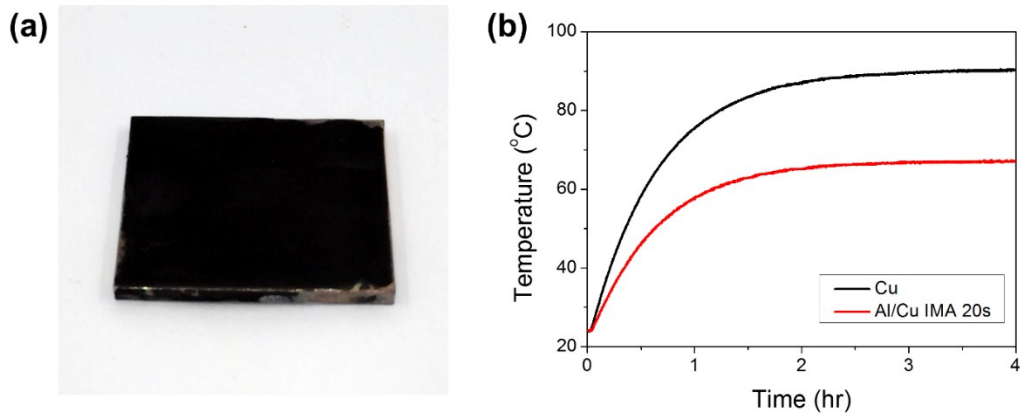
Fig. S9 The setup of heat dissipation test, which consists of plate heater, heat insulation jig, copper structure and copper plate with or without IMA-rGO.
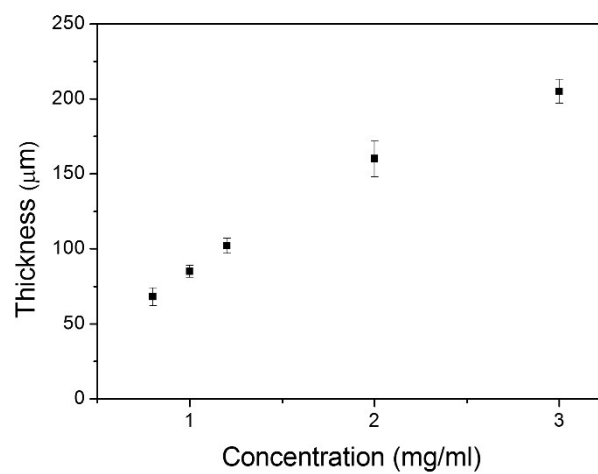
Fig. S10 Heat dissipation performance of 5 different bare copper plates.

Fig. S11 (a) The optical image of IMA-rGO on copper layer deposited on aluminum plate. (b) Heat dissipation performance of IMA-rGO on copper layer deposited on aluminum plate (Al/Cu IMA 20s).

Fig. S12 Influence of concentration on the thickness of IMA-rGO structure.

References

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