Electronic Supplementary Material (ESI) for RSC Advances.

The effect of rigid phenoxyl substituent on the NH_3-sensing properties of tetra-α-(4-*tert*-butylphenoxyl)-metallophthalocyanine/reduced graphene oxide hybrids

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Preparation of GO

The GO was synthesized from natural graphite powder (99.95%).Briefly, 3.0 g of graphite, 2.5 g of $K_2S_2O_8$, and 2.5 g of P_2O_5 were added into 12 mL of concentrated H_2SO_4 under strong stirring at 80 °C for 4.5 h. After the solution was cooled down to room temperature naturally, 0.5 L of deionized (DI) water was added into the above solution and was then aged for 12 h. The suspension was filtered, washed, and dried to obtain the black solid.The black solid was mixed with 120 mL of concentrated H_2SO_4 and 15 g of $KMnO_4$ in an ice bath below 20 °C and was then transferred to a water bath and magnetically stirred at 35 °C for 2 h. The resultant dark-brown paste was diluted with the slow addition of 250 mL of DI water and then stirred for another 2 h; 20 mL (30 wt %) of H_2O_2 was slowly added to quench the solution to produce a golden-brown solution. After the product was centrifuged, the sample was washed with HCl (1:10) and DI water, respectively, until the pH of the washed solution was ca. 6. Finally, the product was dried at 40 °C in vacuum to obtain the GO sample. The GO aqueous solution (0.05 wt%) was prepared by ultrasonic dispersion of GO sample in DI water for 2 h to obtain a stable and homogeneous GO aqueous solution.

Preparation of TBPOMPc (M= Cu, Ni, Pb)

TBPOMPc was synthesized by refluxing (p-*tert*-butylphenoxyl)-phthalonitrile with DBU and anhydrous $CuCl_2$, $NiCl_2$, $PbCl_2$ in anhydrous iso-pentanol, followed by column chromatography separation according to an established procedure.[41] Fig. S1A shows the schematic interaction process for the preparation of TBPOMPc.

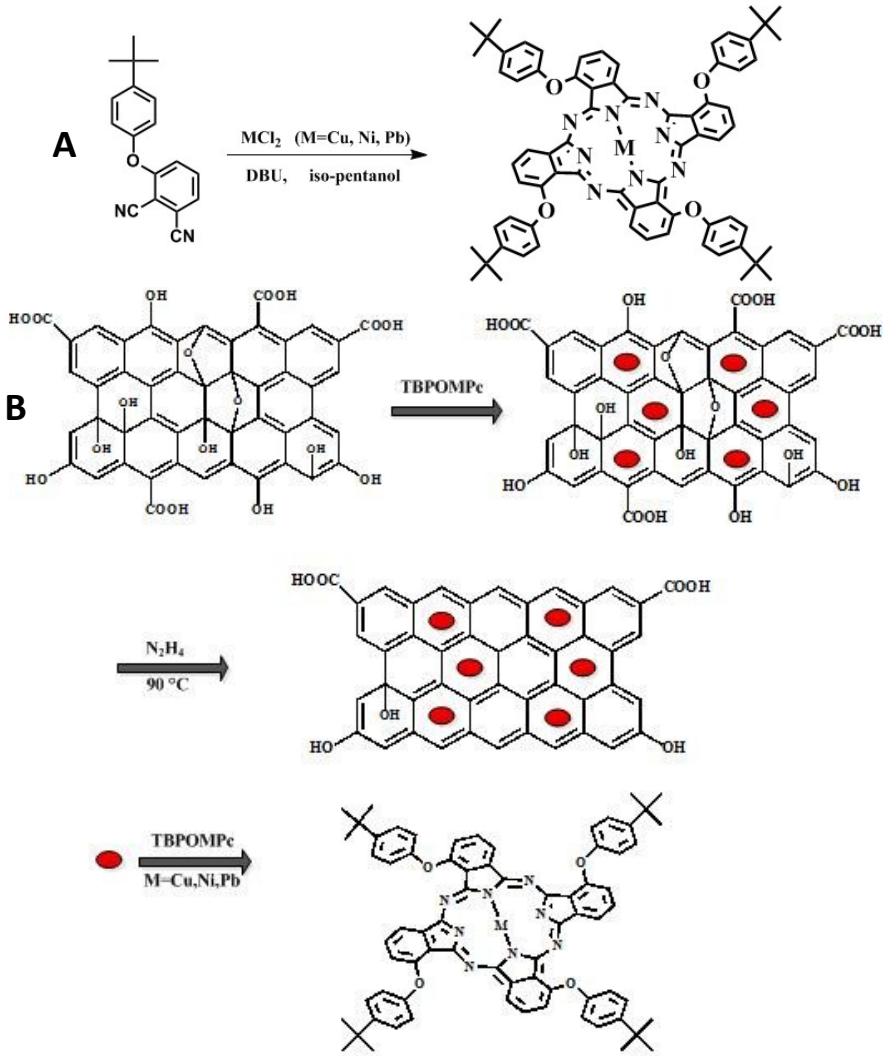

Fig. S1. The schematic interaction process for the preparation of (A) TBPOMPc and (B) RGO/TBPOMPc hybrids.

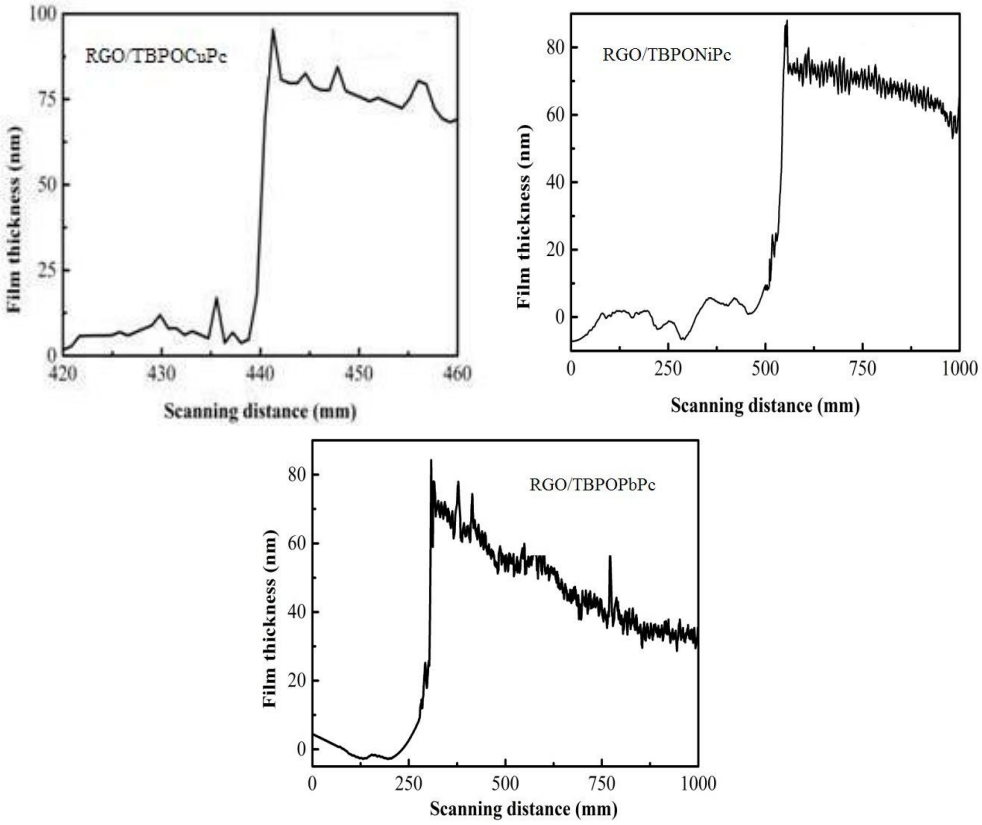

Fig. S2. Film thicknesses of RGO/TBPOMPc (M= Cu, Ni, Pb) placed on the electrodes.

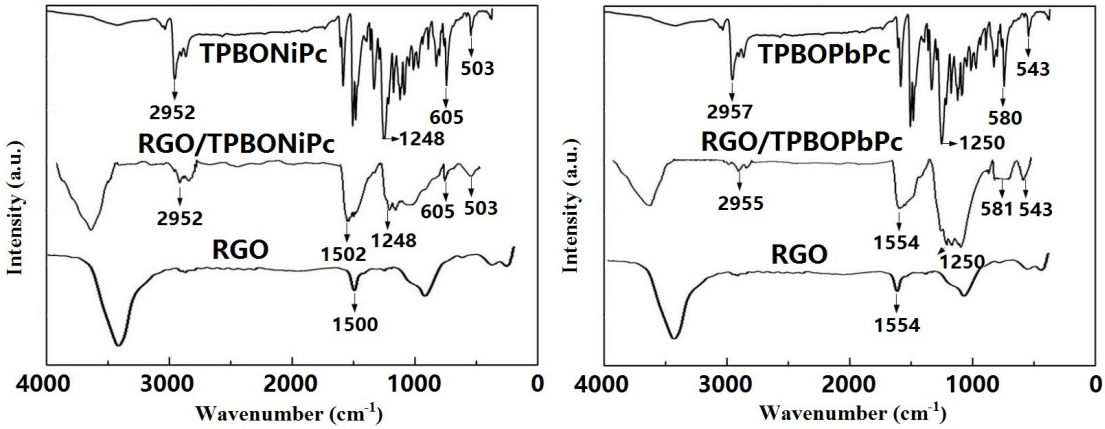

Fig. S3. FTIR spectra of RGO, RGO/TBPOMPc and TBPOMPc (M= Ni and Pb).

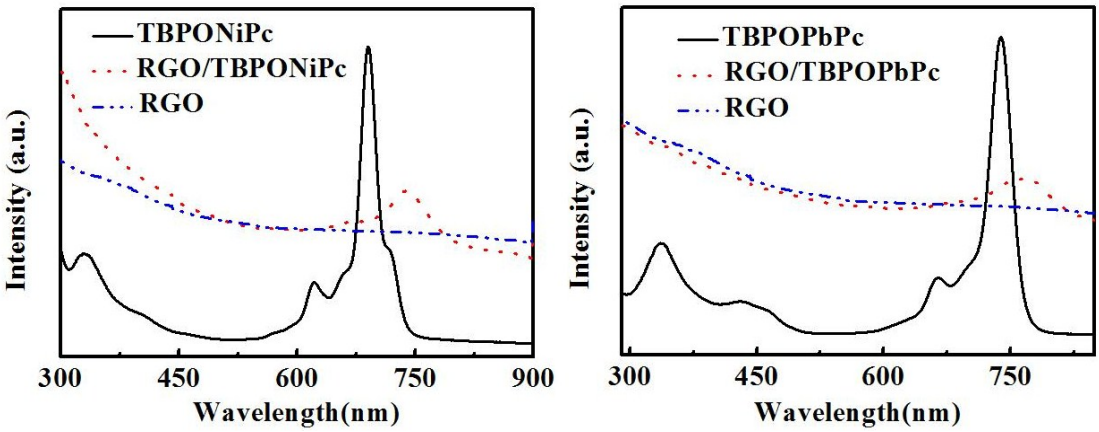

Fig. S4. Absorption spectra of RGO, RGO/TBPOMPc and TBPOMPc (M= Ni and Pb).

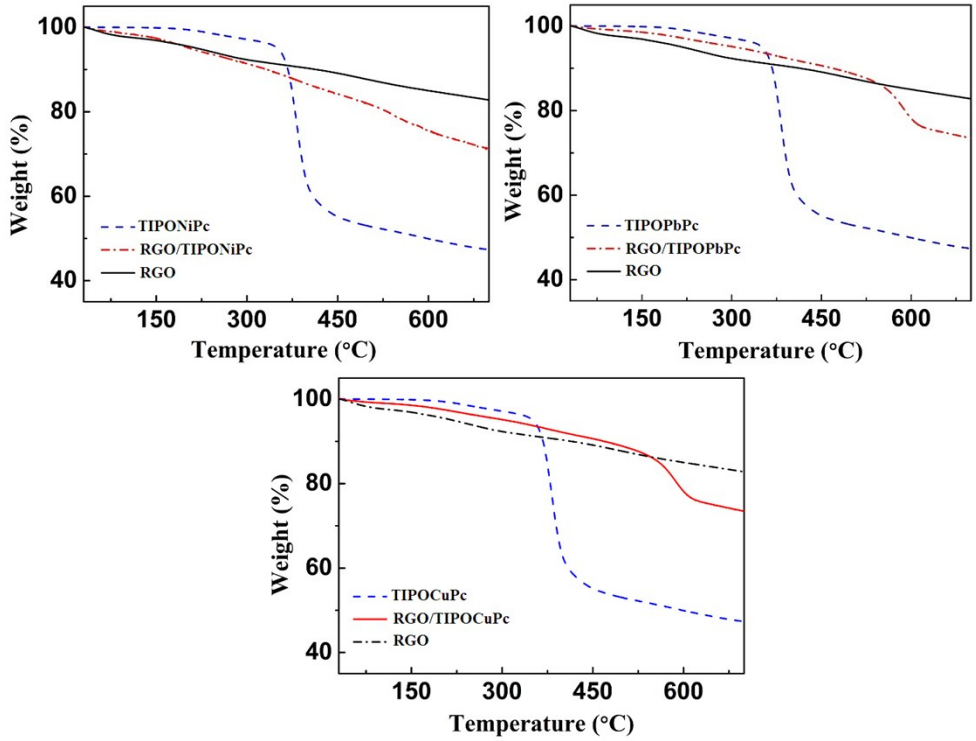

Fig. S5. Thermo gravimetric analysis of RGO, TIPOMPc and RGO/TIPOMPc hybrids.

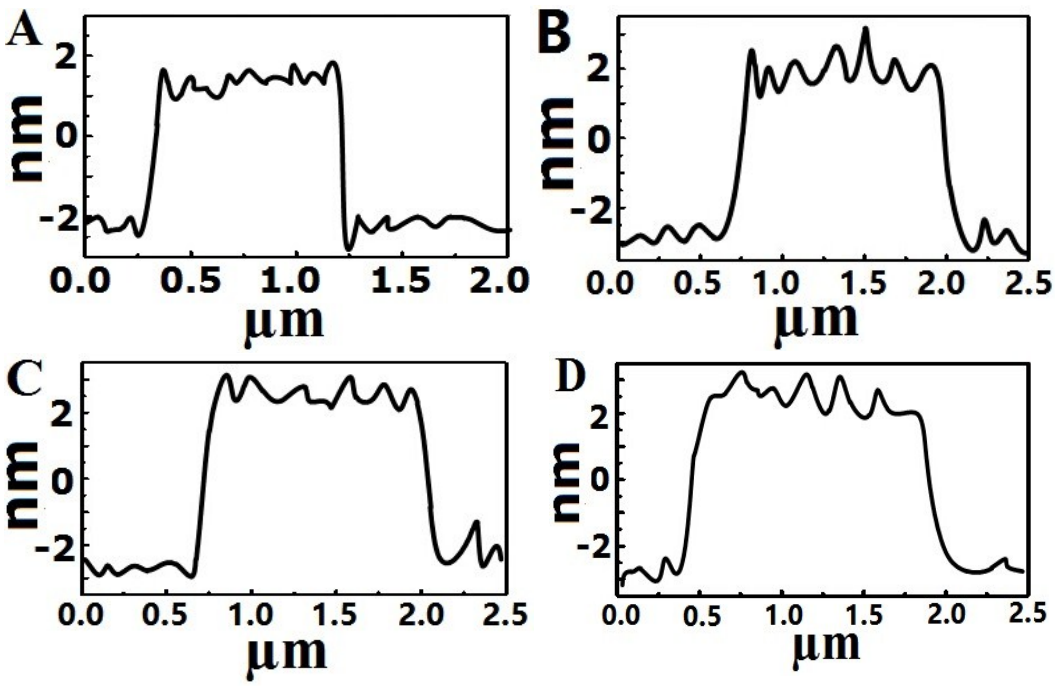

Fig. S6. Cross-section analysis of RGO (A), RGO/TBPOCuPc (B), RGO/TBPONiPc (C) and RGO/TBPOPbPc (D).

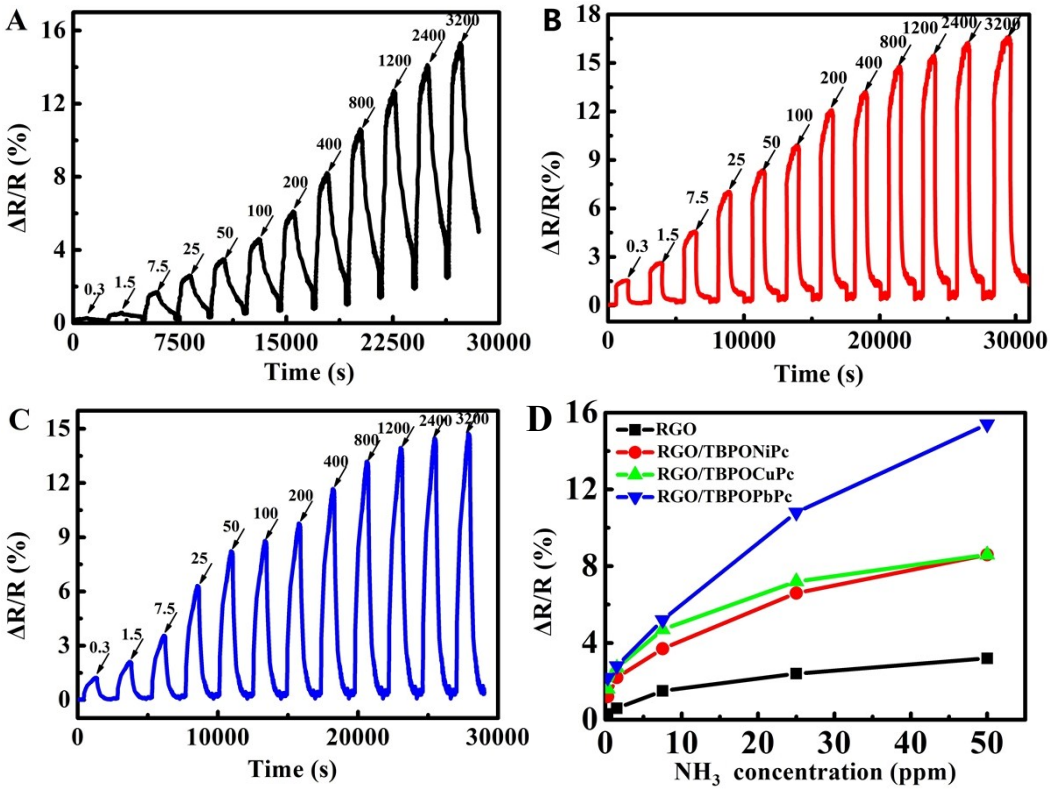

Fig. S7. Dynamic sensing response ($\Delta R/R$) to different concentration of NH_3 at room temperature. A: RGO; B: RGO/TBPOCuPc; C: RGO/TBPONiPc; D: the linear fitting of ($\Delta R/R$) to C.

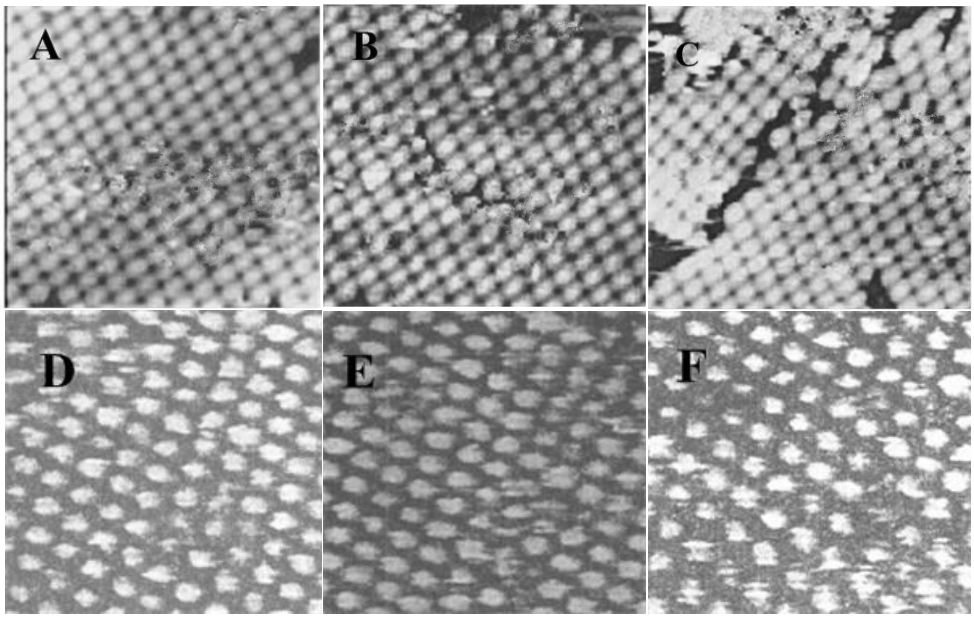

Fig. S8. Large-scale STM images of RGO/TIPOMPc (M= Cu, Ni, Pb, A, B, C) and RGO/TBPOMPc (M= Cu, Ni, Pb, D, E, F), 40 nm×40 nm; Tunnel Current: 200 pA; Sample Bias: 1.8 V

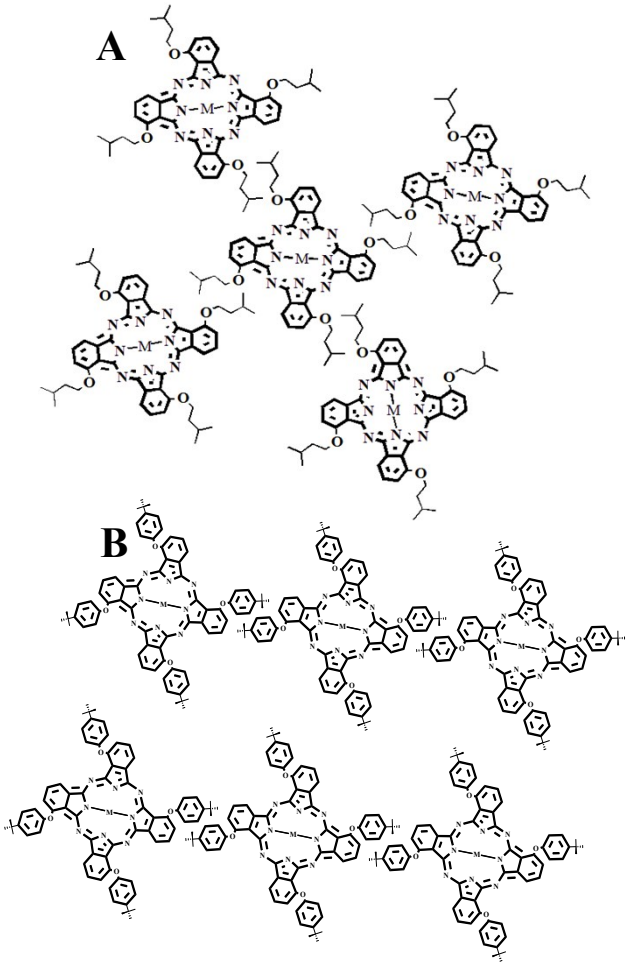

Fig. S9. The molecular structure model of TIBOMPc aggregation (A) and TBPOMPc aggregation (B).

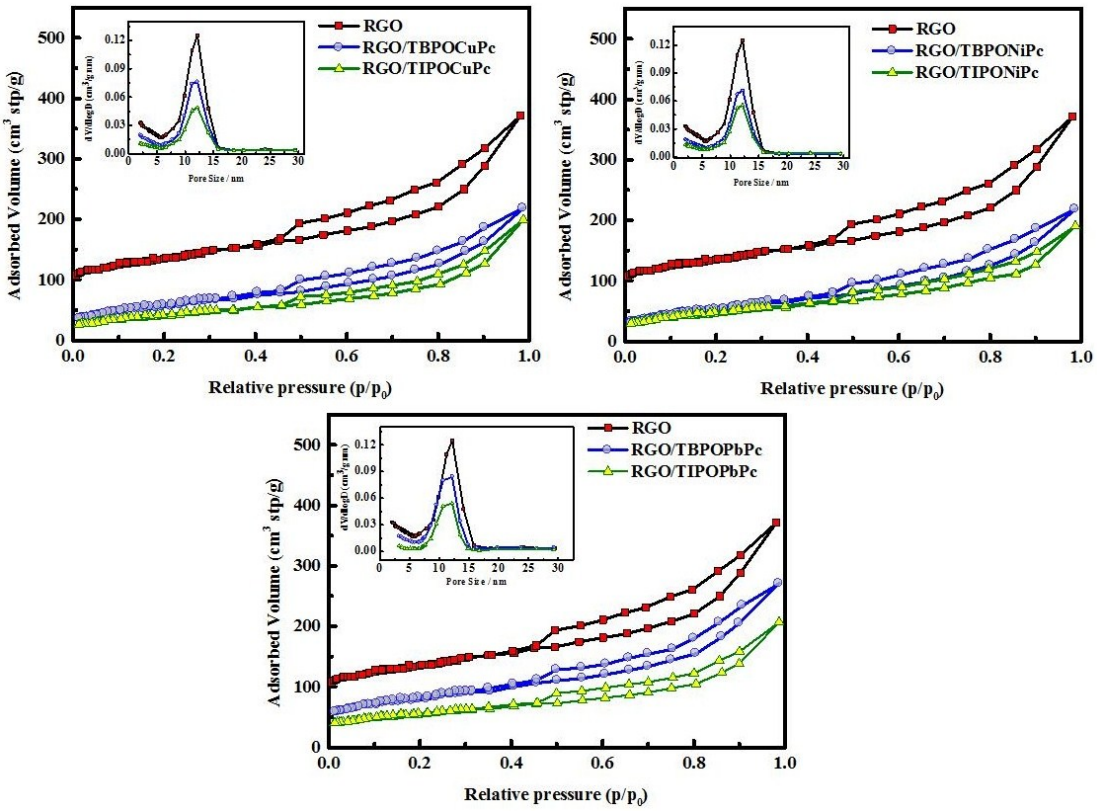

Fig. S10. N_2 adsorption-desorption isotherms of RGO, RGO/TIBOMPc, RGO/TBPOMPc.

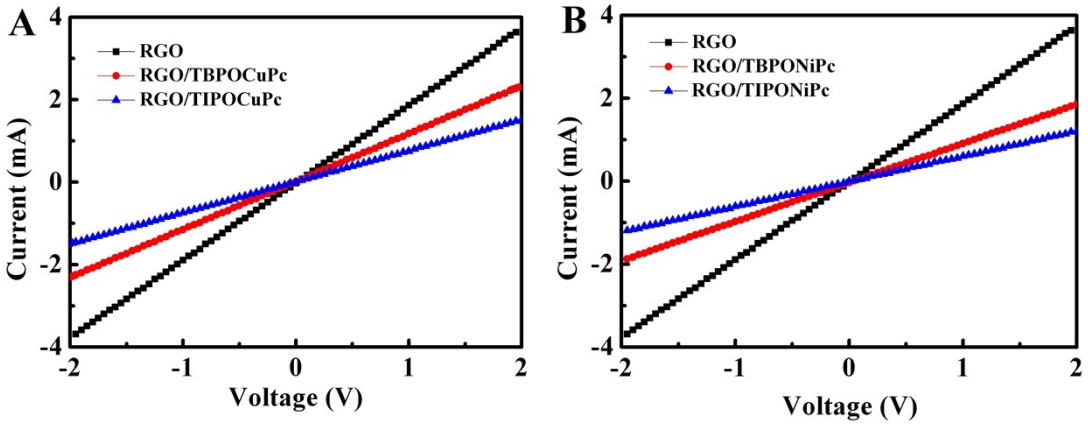

Fig. S11. I–V curves of RGO, RGO/TBPOMPc and RGO/TIPOMPc (M= Cu and Ni) hybrids.

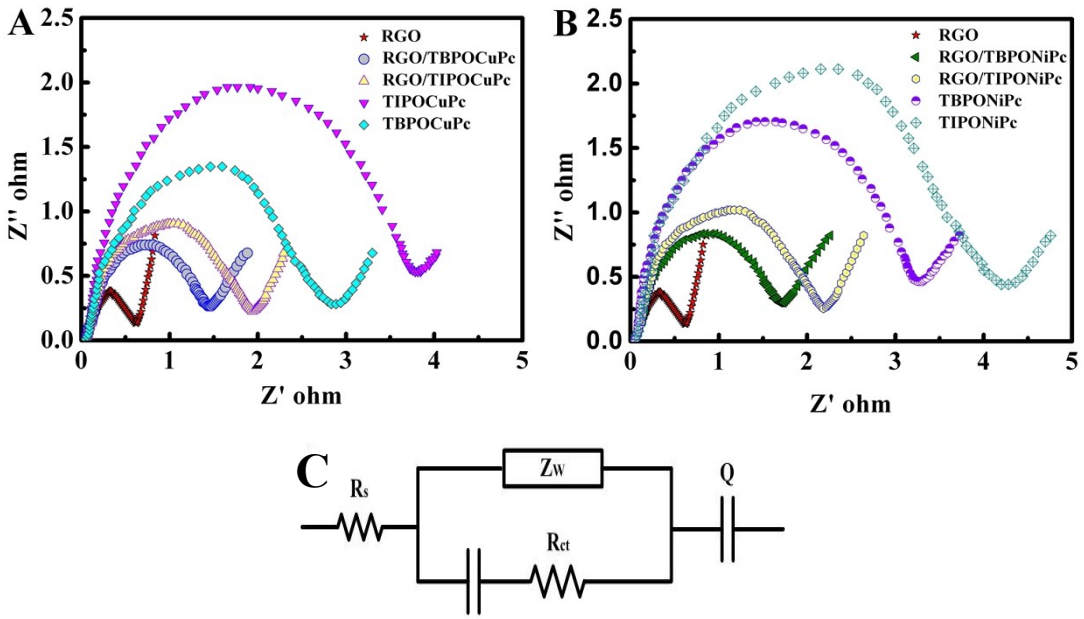

Fig.S12. EIS measurements of RGO, RGO/TIPOMPc, RGO/TBPOMPc, TIPOMPc and TBPOMPc (M= Cu and Ni) electrodes in 6 M KOH aqueous solution (A-B); (C) shows the corresponding electrical equivalent circuit.