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One-pot synthesis of ultra-small magnetite nanoparticles on the surface of reduced graphene oxide nanosheets as anode for sodium-ion batteries

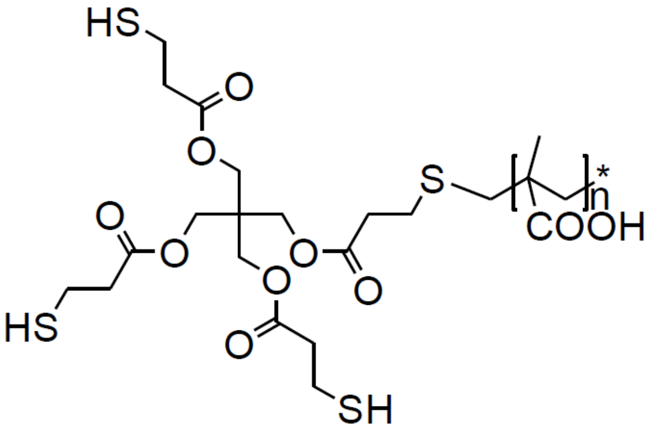
Shaohua Zhang,[a] Weijie Li,[a] Bien Tan,[c] Shulei Chou,[a] Zhen Li,[a,b,]* and Shixue Dou[a]

[a] Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Squires Way, North Wollongong, NSW 2500, Australia.

[b] School of Radiation Medicine and Radiation Protection, Collaborative Innovation Center of Radiological Medicine of Jiangsu Higher Education Institutions, Soochow University, 199 RenAi Road, Suzhou Industrial Park, Suzhou 215123, China.

[c] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

* Corresponding author: zhenl@uow.edu.au; Fax: +61-2-42215731; Tel: +61-2-42215163



Scheme S1. Molecular structure of multidentate polymer ligand poly(methacrylic acid) pentaerythritol tetrakis (3-mercaptopropionate) (PMAA-PTMP).

Part S1. Experimental Section

Materials

Iron (III) chloride hexahydrate ($FeCl_3·6H_2O$, 97%), iron (II) sulfate heptahydrate ($FeSO_4·7H_2O$, ≥99%), ammonium hydroxide solution ($NH_3·H_2O$, 28%), hydrochloric acid (HCl, 37%), anhydrous ethnol (99.5%), and acetone (99.9%) were purchased from Sigma-Aldrich and used as received without any purification. PMAA-PTMP was prepared as presented elsewhere.[1]

Synthesis of RGO/Fe_3O_4/ PMAA-PTMP nanocomposites (RGOF)

Graphene oxide (GO) nanosheets were synthesised from natural graphite powder by a modified Hummers method.[2] The composites were synthesized by using different volume of GO, i.e., 0.5 mL (~2.67 mg GO), 1 mL (~5.34 mg GO), and 1.5 mL (~8.01 mg GO), and are denoted as RGOF-1, RGOF-2, and RGOF-3 respectively. The typical synthesis is described as follows. 1 mL GO dispersion and PMAA-PTMP (0.1689 g, molecular weight (M_w) 5800 g mol^{-1}) was dissolved in Milli-Q water (50 mL) and purged with nitrogen to remove oxygen. The GO and polymer solution was then heated to 100 ℃ in an oil bath (130 ℃) to reflux. Meanwhile, $FeCl_3·6H_2O$ (0.1378 g, 0.51 mmol) and $FeSO_4·7H_2O$ (0.0701 g, 0.252 mmol) were dissolved in concentrated HCl (1 mL). Then, the mixture of iron precursors was quickly injected into the GO/polymer solution, followed by the addition of concentrated ammonia solution (15 mL, 28%). The solution became black immediately, and the resultant black solution was refluxed for 2 h. Then, 50 μL hydrazine solution was added into the mixture under vigorous magnetic stirring and kept refluxing for 3 h. The mixture was then cooled to room temperature naturally. The as-obtained black precipitates were washed thoroughly with deionized water and absolute alcohol several times, respectively, and finally dried in air at room temperature for further characterization. For comparison, bare RGO/Fe_3O_4 using 1 mL GO dispersion without PMMA-PTMP and Fe_3O_4/PMAA-PTMP using PMMA-PTMP without GO dispersion were also synthesized under the same procedure.

Structural and physical characterization

The morphology and microstructure of the as-prepared samples were examined by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM, JEOL 2011, 200 keV). The powder X-ray diffraction (XRD) patterns of the nanocomposites were obtained using Cu-Ka radiation (λ = 1.54056 Å) in the reflection geometry on a GBC-MMA instrument operating at 40 kV and 25 mA. Raman spectra were collected with a Jobin Yvon HR800 Raman spectrometer with a 10 mW He-Ne laser at 632.8 nm excitation. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific Sigma Probe instrument using Al Kα X-ray radiation and in fixed analyser transmission mode. Thermogravimetric analysis (TGA) was performed to analyse the weight ratios of the nanocomposites at a heating rate of 10 ℃ min^{-1} from room temperature to 700 ℃ under air and argon atmosphere respectively by using a thermogravimetric analyzer PerkinElmer TG/DTA 6300. Nitrogen adsorption-desorption measurements were were conducted at 77 K with a Quantachrome Autosorb iQ (USA). Before measurements, the samples were degassed under vacuum at 120 °C for 6 h. The Brunauer-Emmett-Teller (BET) specific surface area was calculated from the adsorption data in the relative pressure (P/P0) ranging from 0.05 to 0.35.

Electrochemical measurements

The nanocomposite-based electrodes were prepared by mixing 70% active materials, 10% carbon black, and 20% carboxymethyl cellulose (CMC) binder by weight to form an electrode slurry, which then was coated on copper foil, followed by drying in a vacuum oven overnight at 80 °C, and then pressing at 30 MPa. The loading mass for each electrode is about 2 mg. Sodium foil was cut by the doctor blade technique from a sodium bulk stored in mineral oil, which then was employed as both reference and counter electrode. The electrolyte was 1.0 mol/L $NaClO_4$ in an ethylene carbonate (EC) - diethyl carbonate (DEC) solution (1:1 v/v), with 5 vol.% addition of fluoroethylene carbonate (FEC). The cells were assembled in an argon-filled glove box. The electrochemical performances were tested on a Land Test System in the voltage range of 0-2 V (vs. Na^+/Na) at current density of 40 mA g^{-1}. The specific capacity of the electrode was calculated based on the total mass of composites (about 2 mg).

References

(1) Z. Li, P. W. Yi, Q. Sun, H. Lei, H. L. Zhao, Z. H. Zhu, S. C. Smith, M. B. Lan, G. Q. Lu, *Adv. Funct. Mater.*, 2012, **22**, 2387.

(2) D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano*, 2010, **4**, 4806.

Part S2. Figures

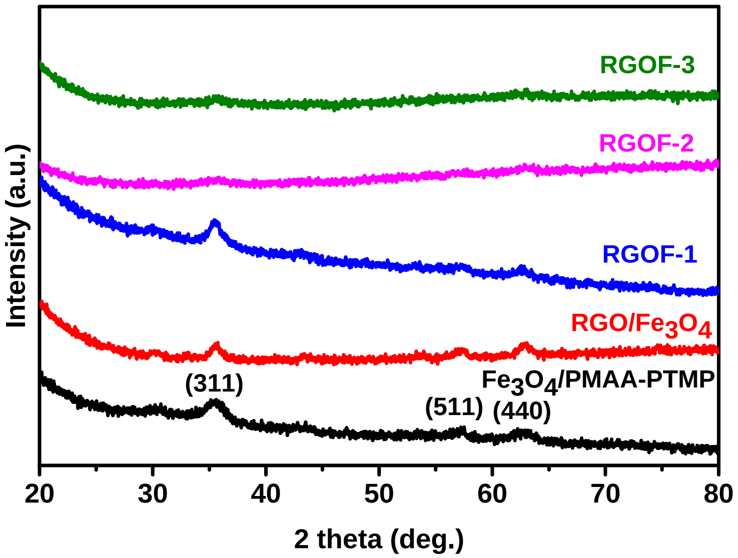


Figure S1. XRD patterns of Fe_3O_4/PMAA-PTMP, RGO/Fe_3O_4, and RGOF nanocomposites in the range of 20° to 80°.

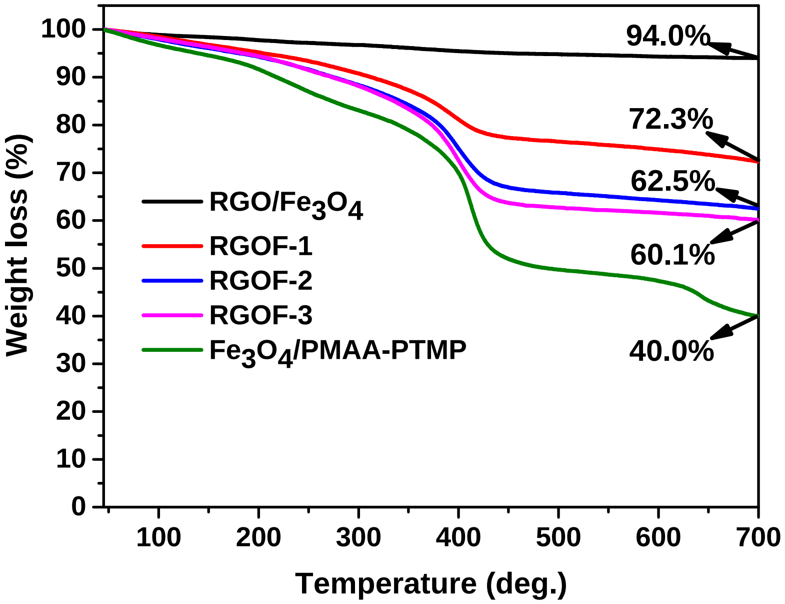


Figure S2. TGA curves for pristine Fe_3O_4/PMAA-PTMP, RGO/Fe_3O_4, and RGOF composites under argon atmosphere.

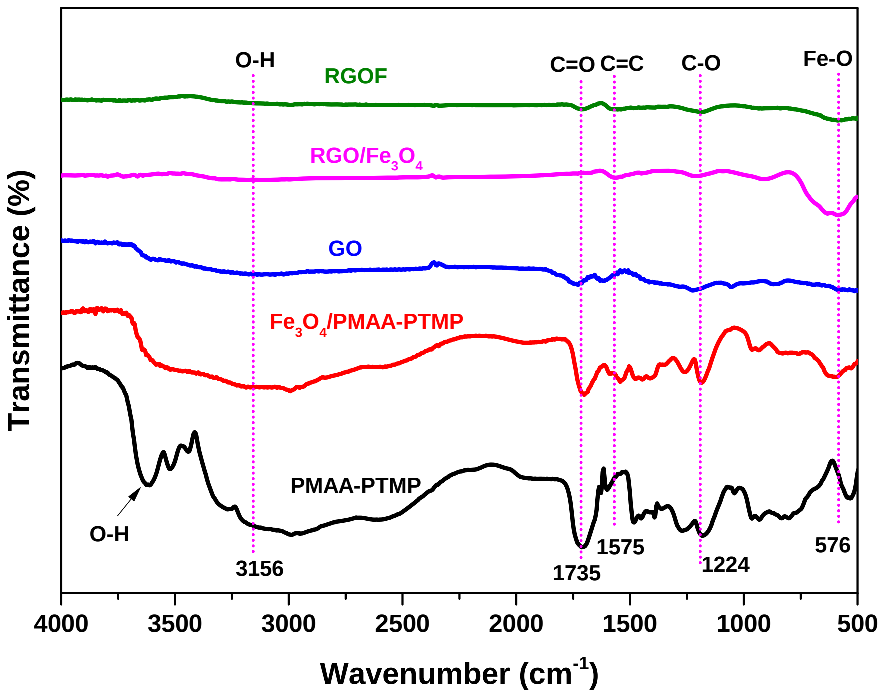


Figure S3. FT-IR spectra of pure PMAA-PTMP, Fe$_3$O$_4$/PMAA-PTMP, GO, RGO/Fe$_3$O$_4$, and RGOF.

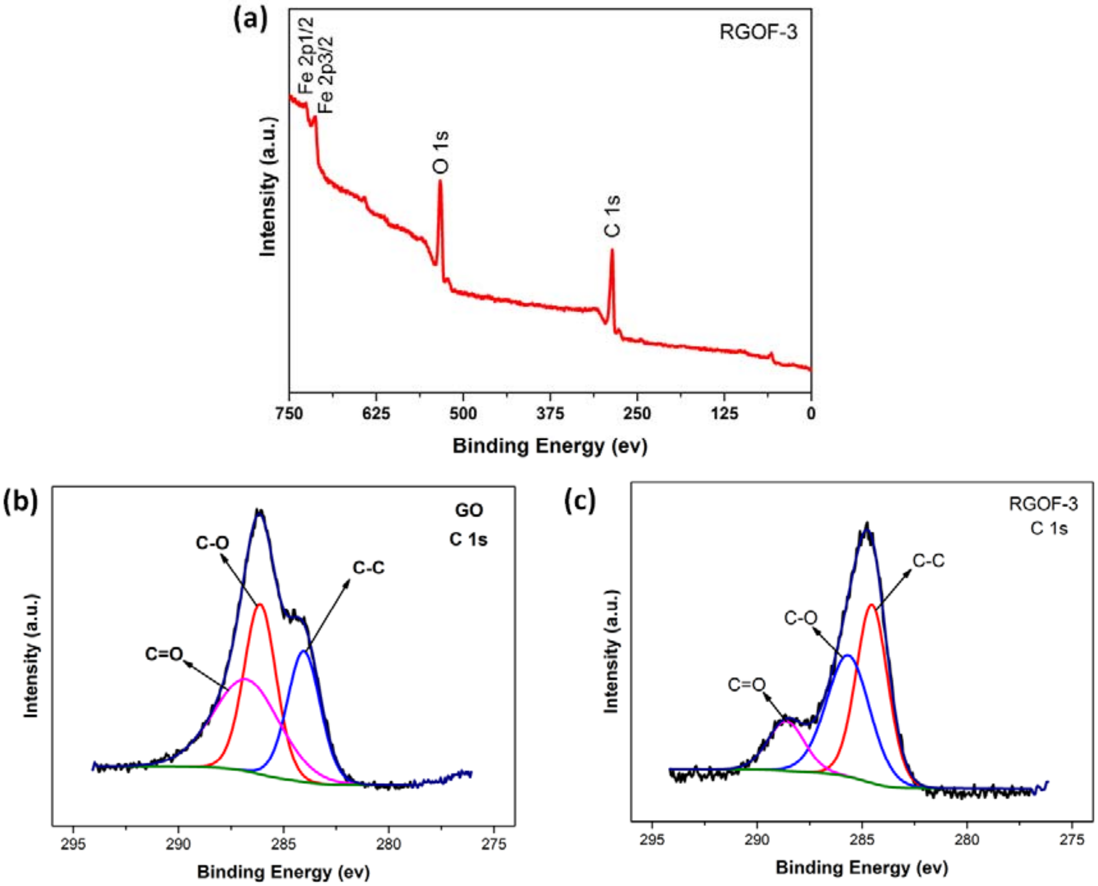
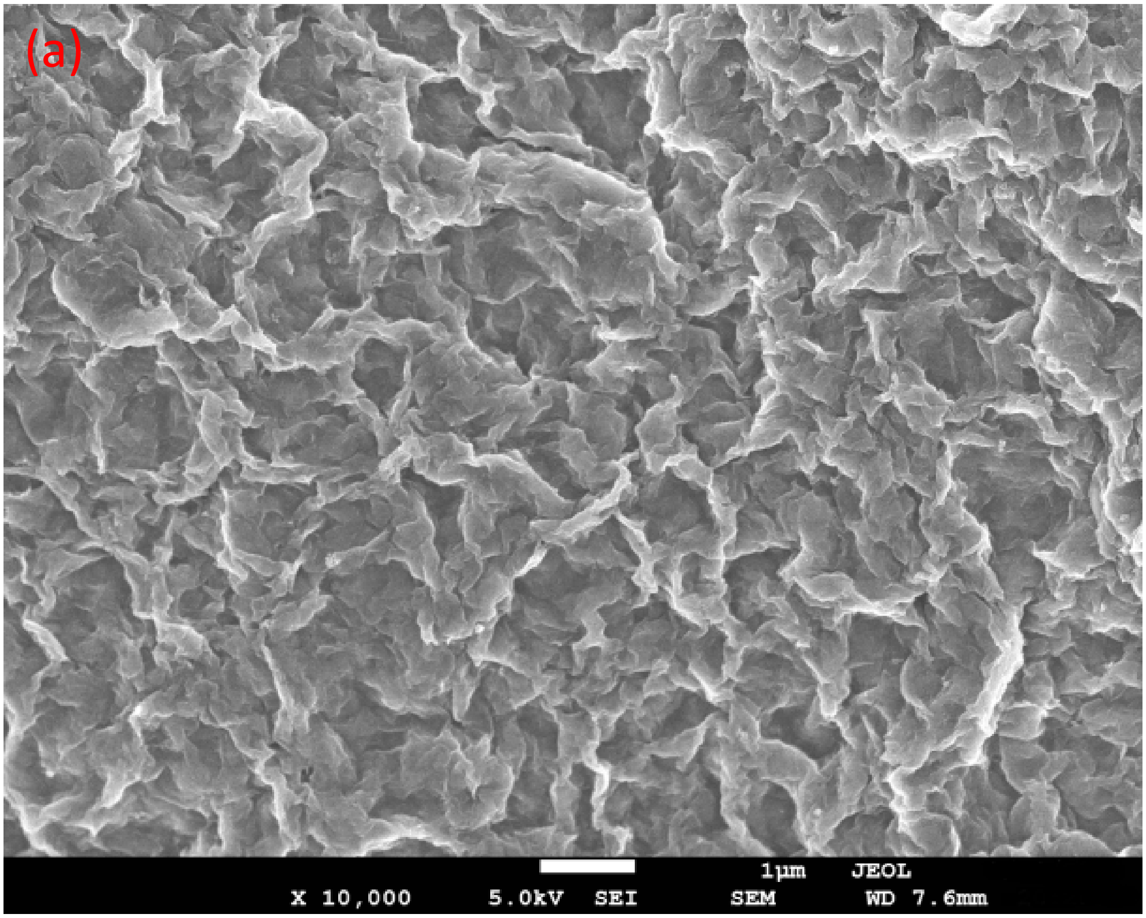
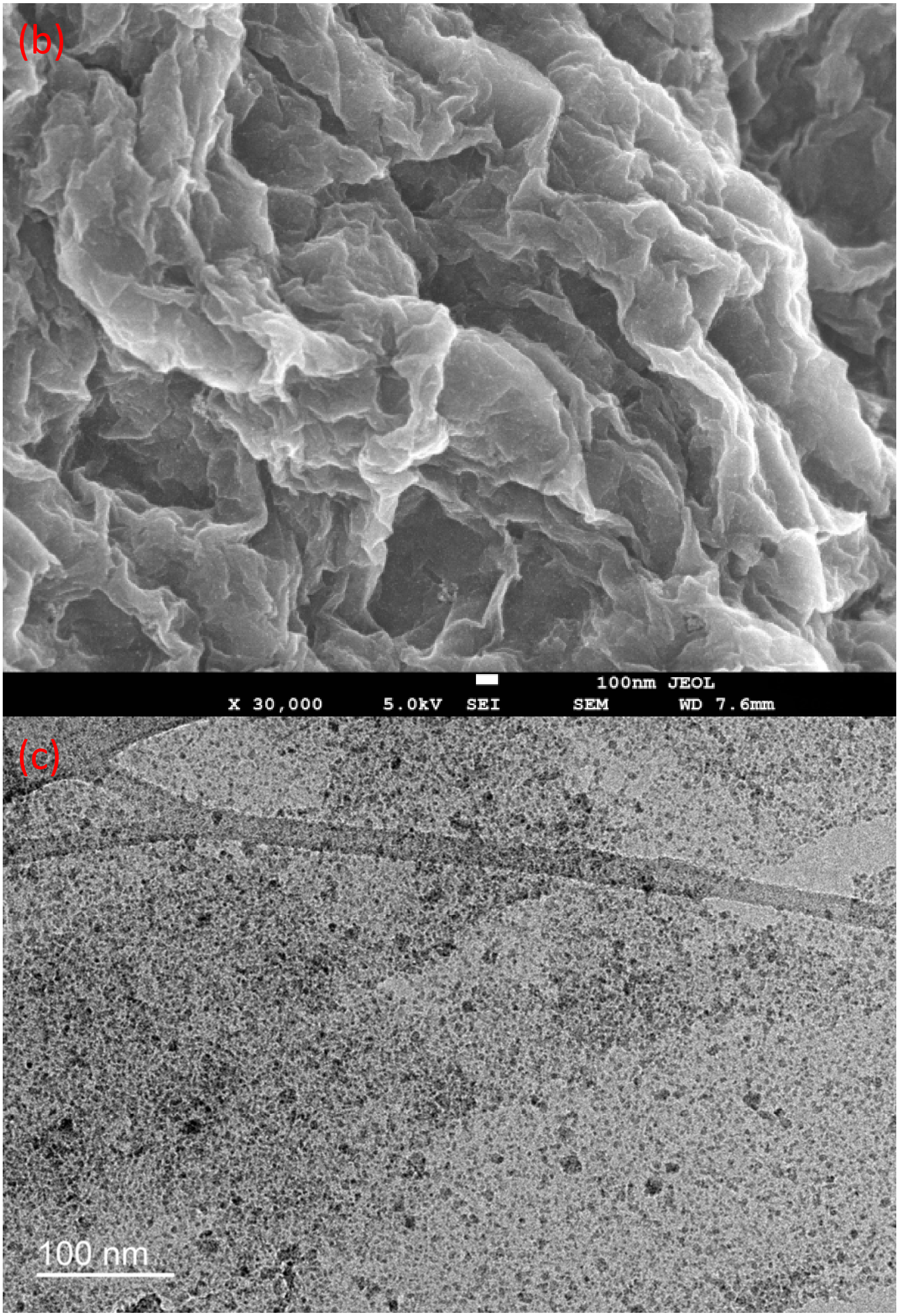


Figure S4. XPS spectra of RGOF-3 and GO: (a) survey scan of RGOF-3; C 1s spectra of (b) GO and (c) RGOF-3.


(a)
1µm JEOL
X 10,000 5.0kV SEI SEM WD 7.6mm


(b)
100nm JEOL
X 30,000
5.0kV
SEI
SEM
WD 7.6mm
(c)
100 nm

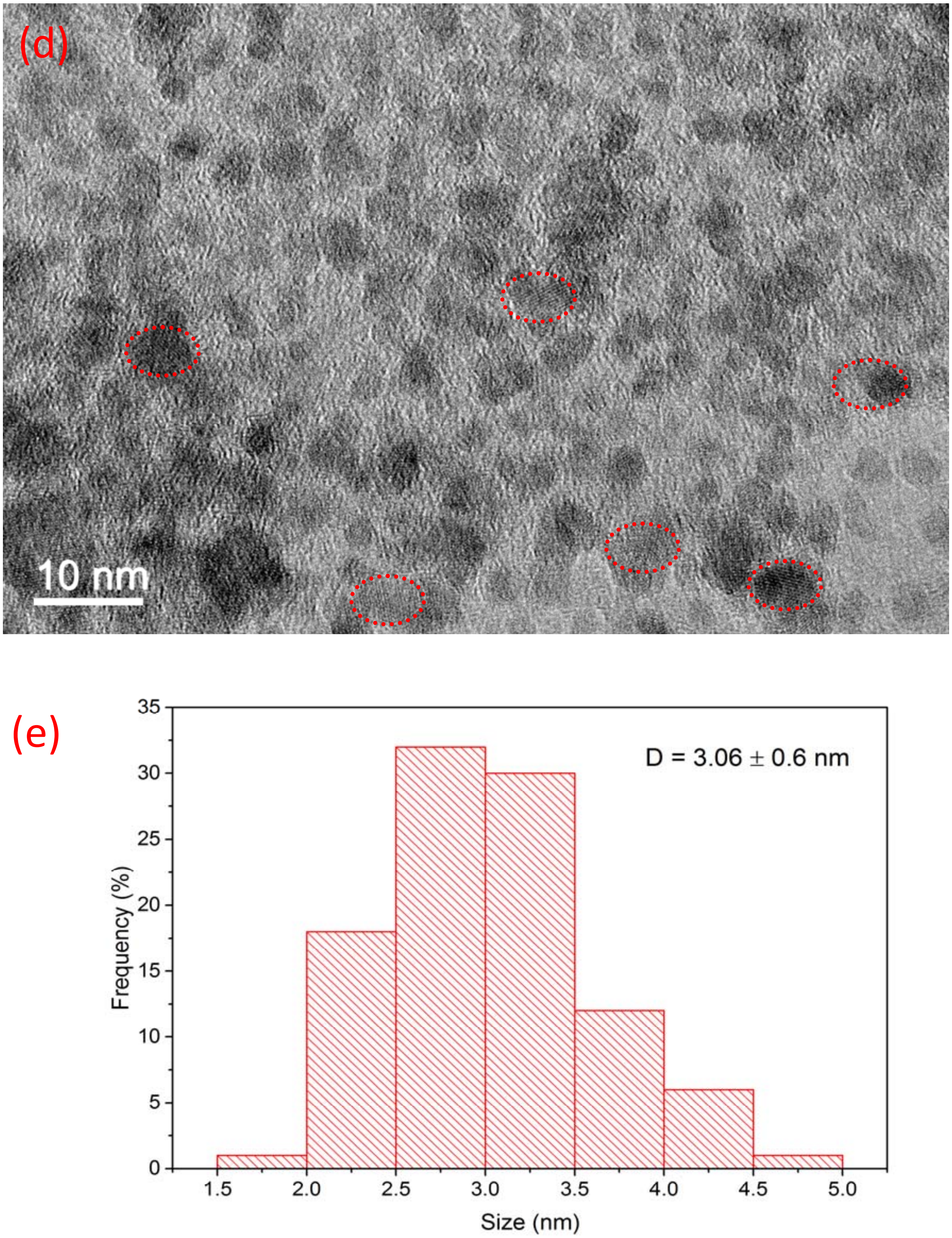
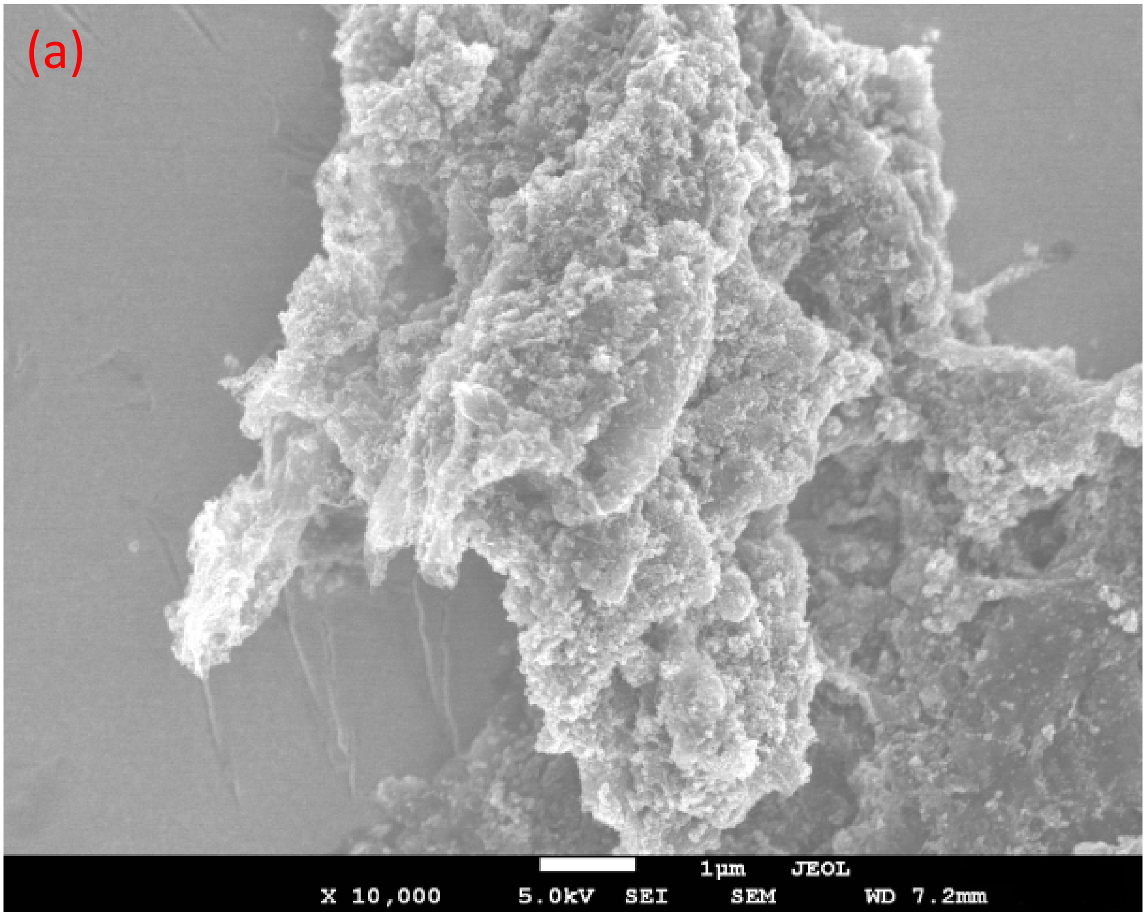


Figure S5. SEM (a, b) and TEM images (c, d) of RGOF-3 at different magnifications, and (e) its size distribution histogram of loaded Fe_3O_4 nanoparticles counted from 200 particles. The circled areas in (d) show the high crystallinity of Fe_3O_4 nanoparticles.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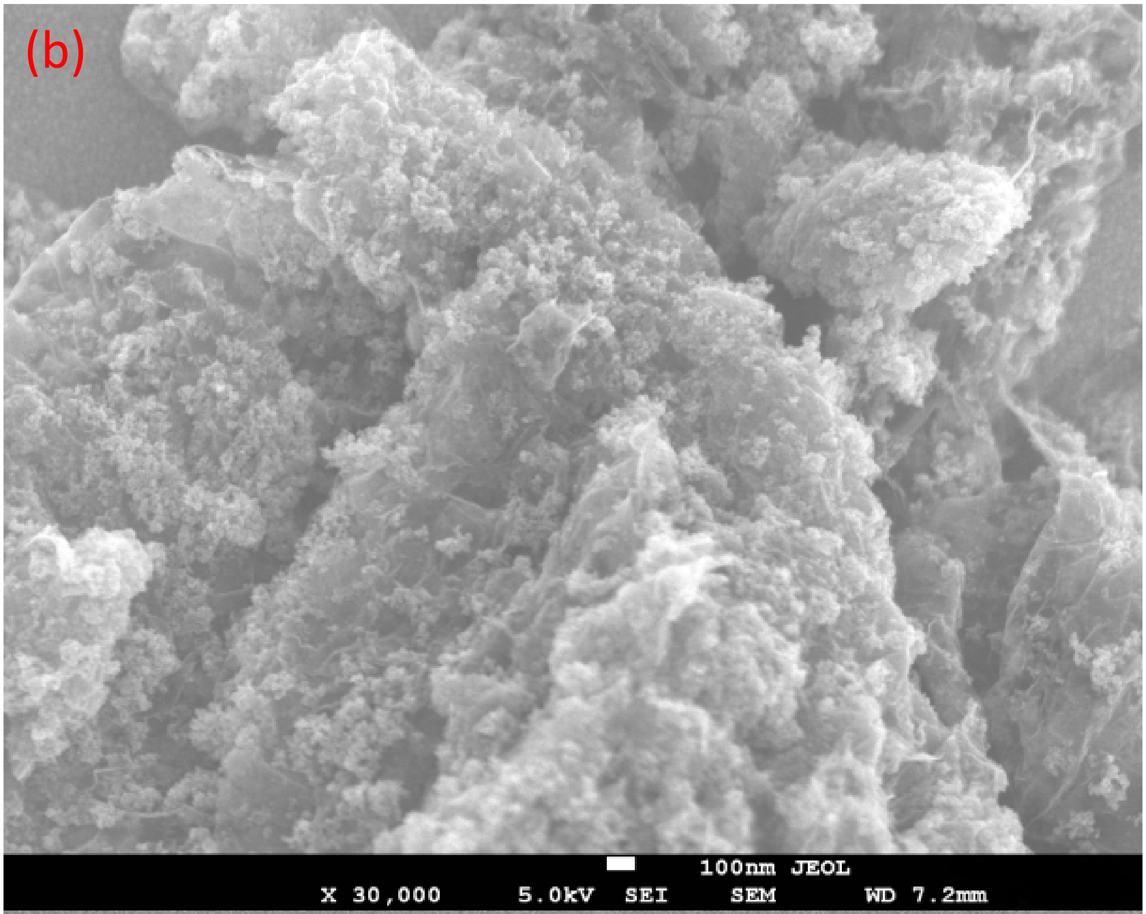
1µm JEOL
X 10,000 5.0kV SEI SEM WD 7.2mm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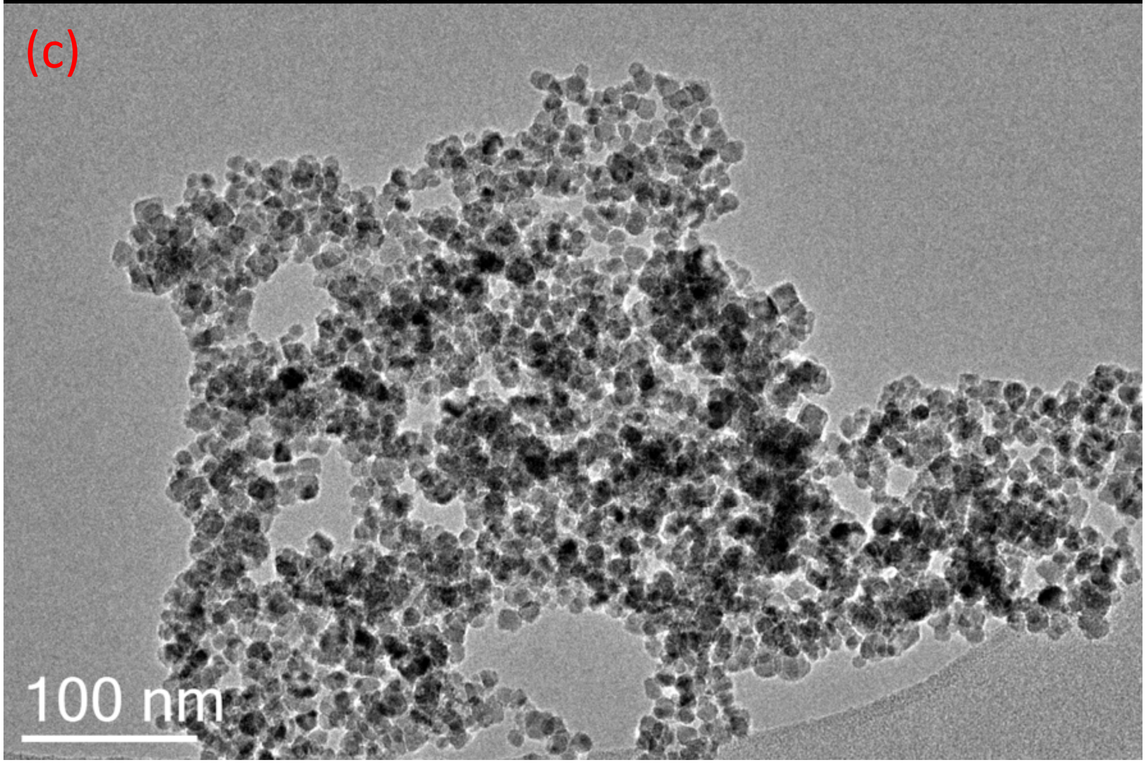
100nm JEOL
X 30,000
5.0kV
SEI
SEM
WD 7.2mm


(c)
100 nm

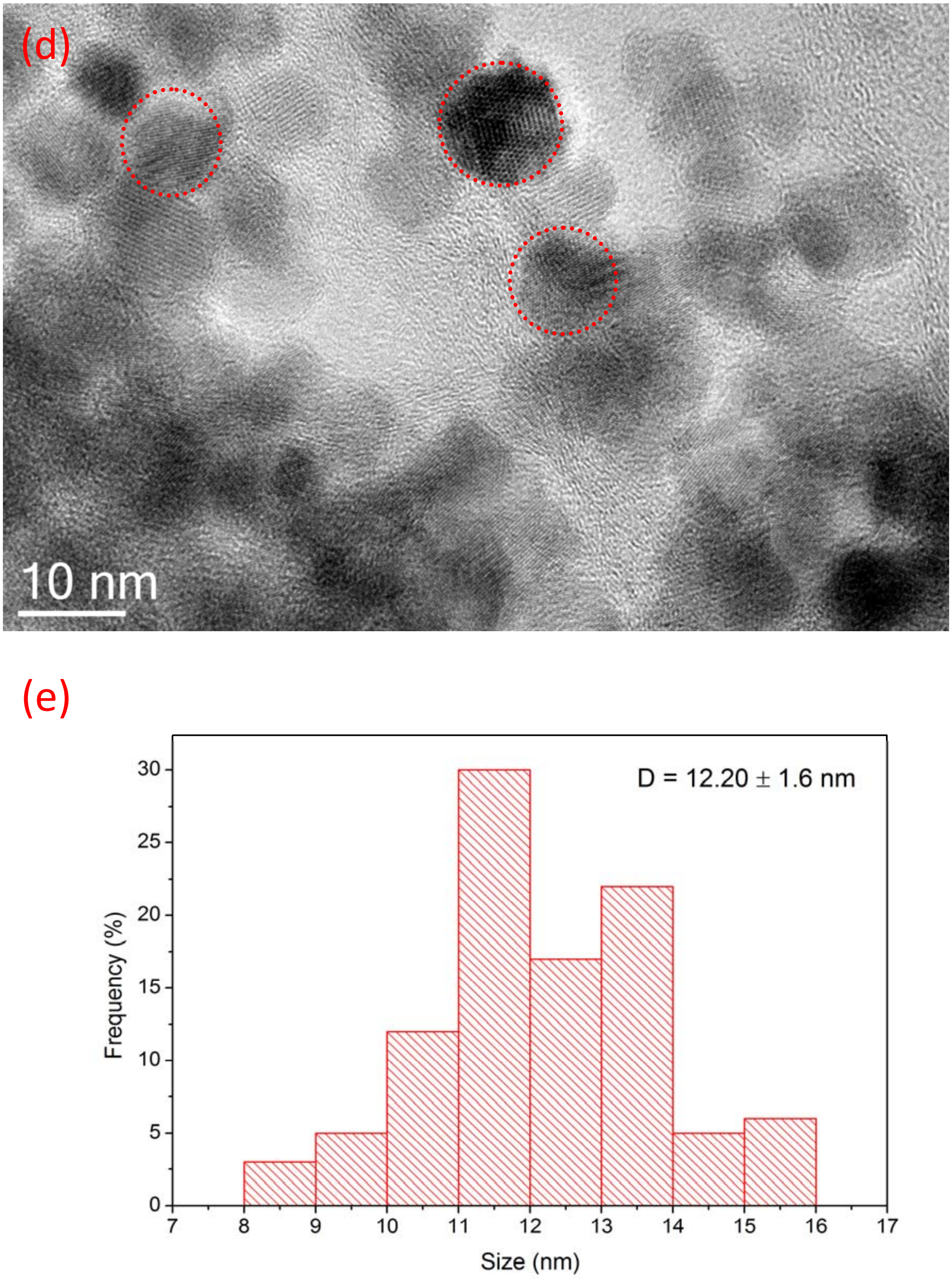


Figure S6. SEM (a, b) and TEM (c, d) images of RGO/Fe_3O_4 at different magnification and (e) its size distribution histogram of loaded Fe_3O_4 nanoparticles counted from 200 particles. The circled areas in (d) show the high crystallinity of Fe_3O_4 nanoparticles.

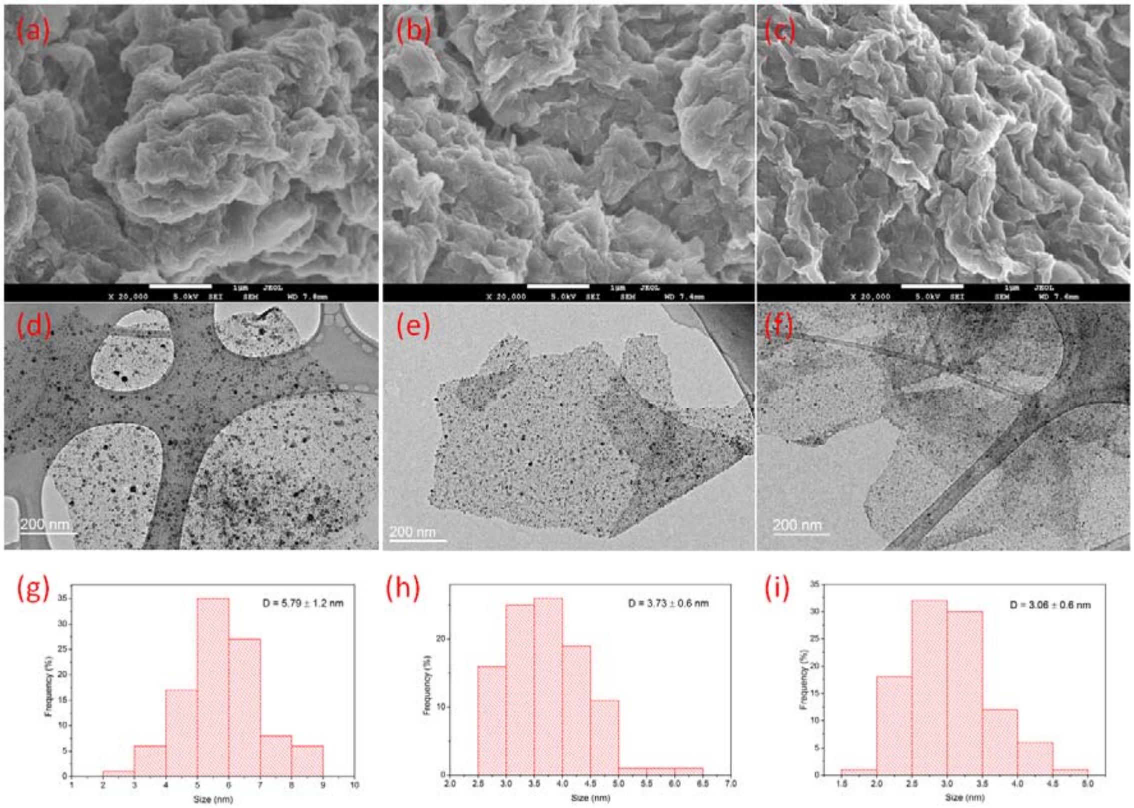


Figure S7. SEM (top) and TEM (middle) images, and size distribution histograms (bottom) of RGOF-1 (a, d, g), RGOF-2 (b, e, h) and RGOF-3 (c, f, i).

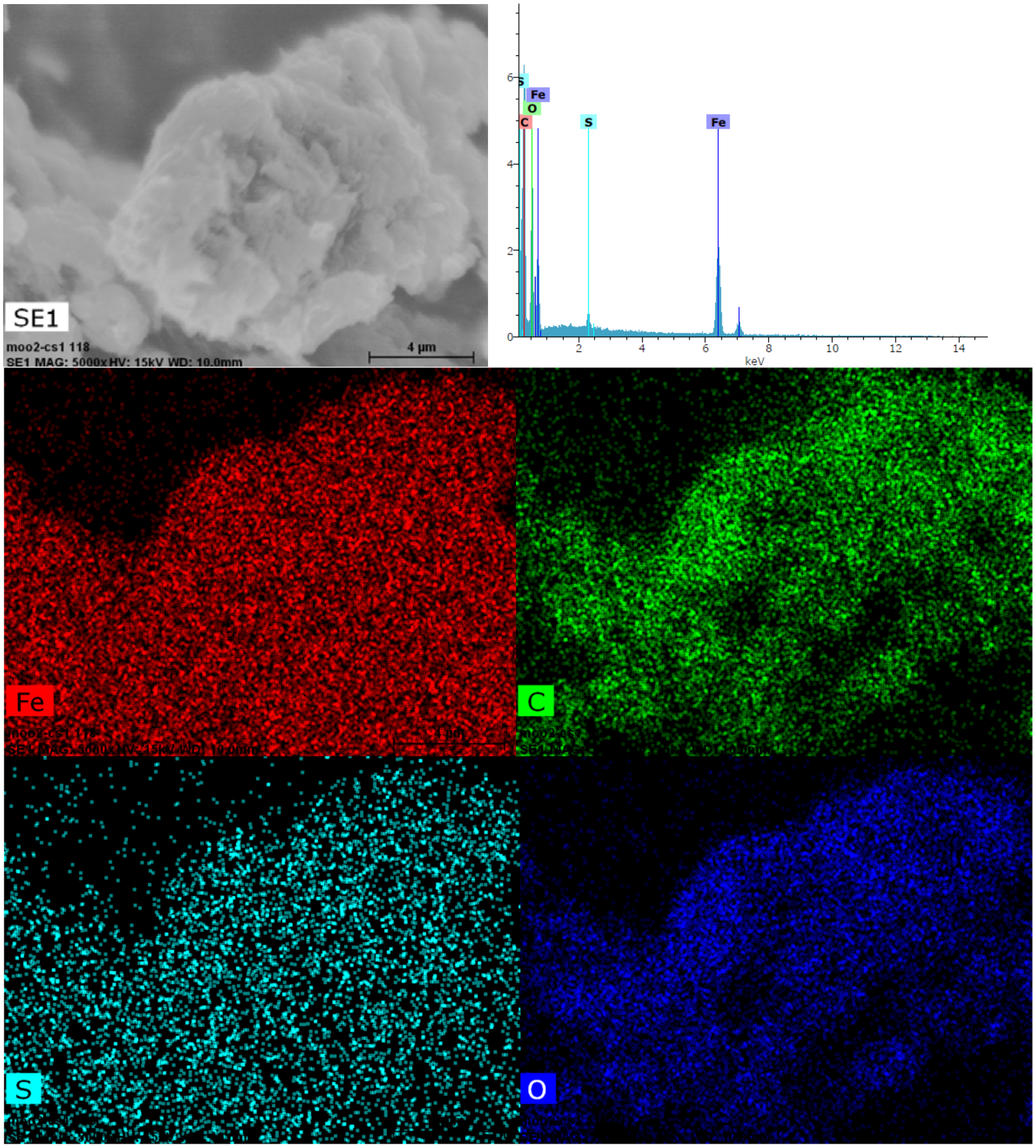


Figure S8. EDS elemental mapping of RGOF.

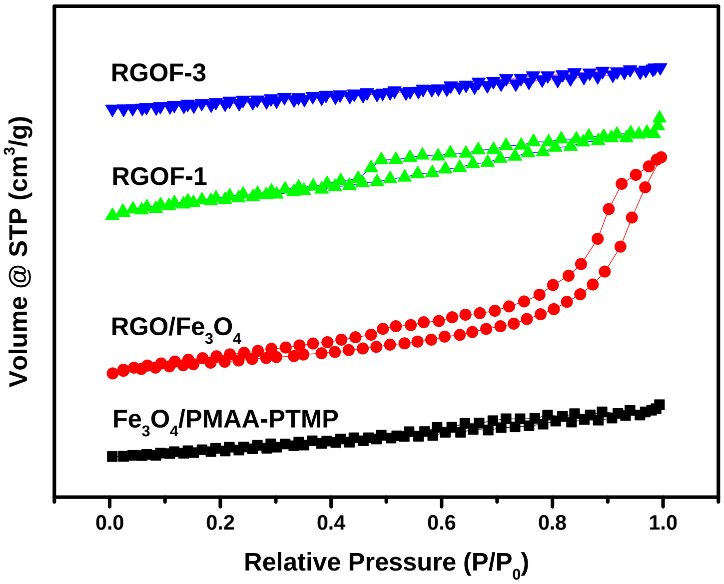


Figure S9. N_2 adsorption-desorption isotherms of different samples.

Table S1. BET surface areas and BJH pore volumes of different samples.

Sample	BET [m^2g^{-1}]	Total pore volume [cm^3g^{-1}]
Fe_3O_4/PMAA-PTMP	177.76	0.158
RGO/Fe_3O_4	147.67	0.608
RGOF-1	167.92	0.264
RGOF-3	137.34	0.124

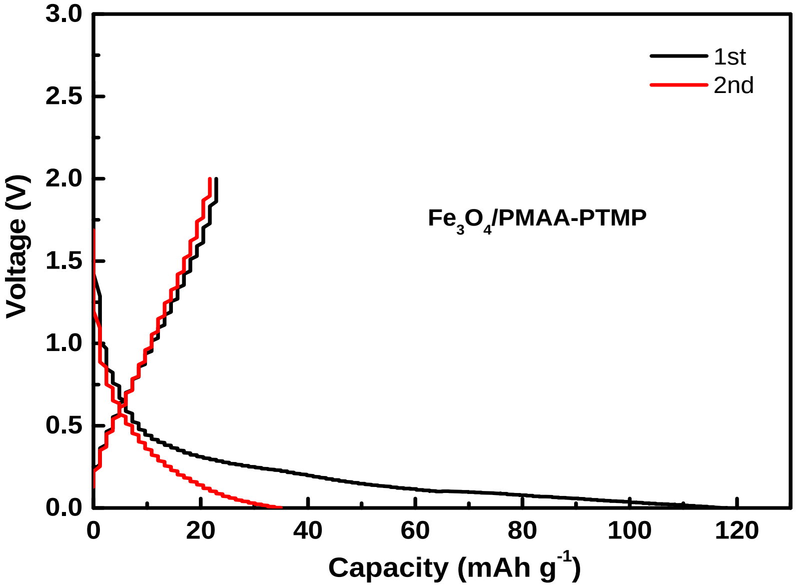


Figure S10. 1st and 2nd cycle discharge and charge profiles of electrode made from Fe_3O_4/PMAA-PTMP at a current density of 40 mAg^{-1}.

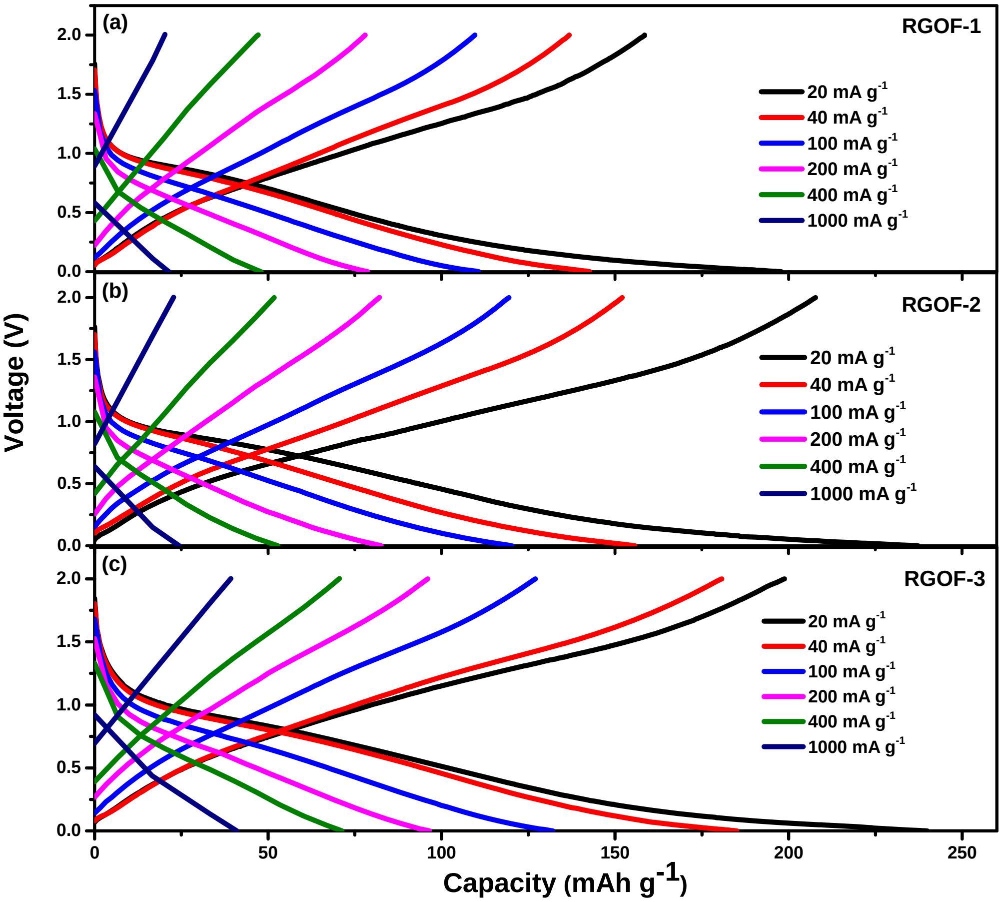


Figure S11. The charge-discharge curves of electrode made from RGOF-1(a), RGOF-2(b), RGOF-3(c) at a current density varied from 20 mAg^{-1} to 1000 mAg^{-1}.