

Electronic Supplementary Information

Surfactant-Free Hybridization of Transition Metal Oxide Nanoparticles with Conductive Graphene for High-Performance Supercapacitor

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A representative TEM and the corresponding electron diffraction (ED) images of Fig. S1 show the exfoliated pristine graphene from expanded graphite. The surface of pristine exfoliated graphene is very smooth and flat, and the corresponding ED pattern clearly reveals the typical six-fold symmetric diffraction pattern (Fig. S1 inset). TEM image also indicated that durative and powerful sonication in N-methyl pyrrolidone (NMP) solvent could mechanically break the expanded graphite sheets into smaller stacks with dimensions between 0.3 and 3 μm .

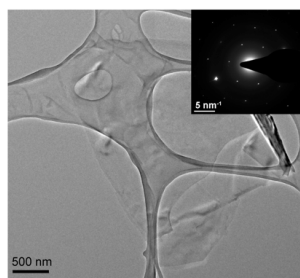


Fig. S1 TEM image of exfoliated pristine graphene and ED pattern.

High-resolution XPS spectra of the exfoliated pristine graphene and a graphene/ Fe_3O_4 composite were collected using the large area analysis mode, since XPS is very sensitive to Fe^{2+} versus Fe^{3+} cations.³⁰ These spectra are shown in Fig. S2. For the pristine exfoliated graphene (Fig. S2a), the binding energy (284.5 eV) and peak shape of the C 1s peak are consistent with hexagonal graphite. The atomic percentage of carbon and oxygen is 97.9 at% and 2.1 at%. For the sample of graphene/ Fe_3O_4 composite, carbon, oxygen and iron were detected on the surface. The atomic percentage is 54.9 at%, 34.2 at% and 10.9 at%, respectively. Fig. S2b-e shows the expanded C 1s, Fe 2p, Fe 3p and O 1s regions, respectively. The Fe 2p region displays two peaks, at 710.8 and 724.3 eV – for $\text{Fe}_{2p1/2}$ and $\text{Fe}_{2p3/2}$ – and is consistent with pure Fe_3O_4 ^{30,31} (Fig. S2c). The Fe 3p peak at 55.8 eV also corresponds to Fe_3O_4 ^{30,31} (Fig. S2b) as does the dominant O 1s peak at a binding energy of 530.2 eV.

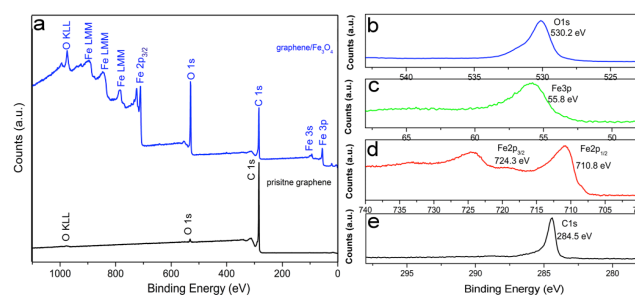


Fig. S2 (a) XPS spectra of pristine exfoliated graphene and graphene/Fe₃O₄ composite samples. (b-e) detailed spectrum of specific regions shown in S1a.

In order to measure the sheet resistance of graphene, we collected the supernatant of the exfoliated graphene in NMP which was centrifuged at 1000 rpm for 20 min; then was filtered through a 0.45 μm polytetrafluorethylene (PTFE) membrane and washed several times with ethanol and acetone to remove the residual. Finally, the graphene sheets were transferred from the PTFE membrane to a Si substrate with a 300 nm-thick SiO₂ layer. We measured the sheet resistance of the exfoliated graphene sheet by a four-probe instrument, and the resistance was about 850 Ω/sq , as shown in Fig. S3.

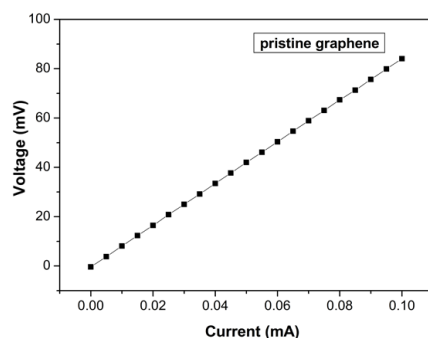


Fig. S3 Sheet resistance of a single exfoliated graphene.

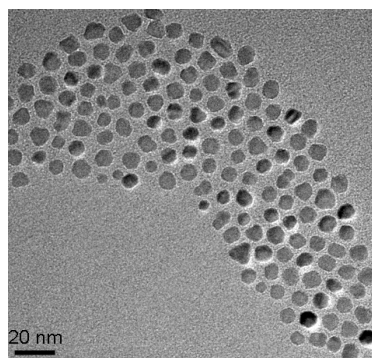


Fig. S4 Pure Mn₃O₄ nanoparticles prepared at 200°C for 8h, using Mn(acac)₃ as precursor without graphene as substrate.