Electronic Supplementary Information for

Solvent-directed Solgel Assembly of 3-dimensional Graphene-tented Metal Oxides and Strong Synergistic Disparities in Lithium Storage

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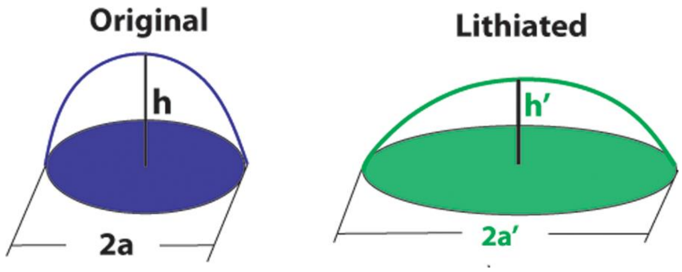
Spherical-cap model

Based on our TEM measurements, we find that the average diameter of the nanoparticles in the lithiation state increases by a factor of 2.5 compared to that in the delithiated state. As the volume of a spherical particle is given by $V=4/3\pi(D/2)^3$, where D is the particle size (i.e., diameter) measured under TEM. This would project a volume expansion of nearly 1560%, which is unlikely. We recognize, however, that the Fe_2O_3 nanoparticles are nucleated on and thus interfaced with the graphene, which most likely adopt a spherical-cap shape with a height (h) and the base diameter (2a) (see the left-hand side scheme); the ratio of h/a defines the particle shape; i.e., h/a=1 (hemisphere); h/a=2 (sphere). The volume of the spherical-cap is given by $V = \frac{\pi h}{6}(3a^2 + h^2)$. After the lithiation, the height and base radius become h′ and a′. Assuming a volume expansion of ~96% for Fe_2O_3,[1] we numerically solve h′ based on the measured 2a and 2a′ from TEM. **Fig. S11** shows the calculation results. In all the cases, we observe a reduction of height during the lithiation; i.e., nanoparticles preferentially spread over the graphene surface during the lithiation process. The calculation is the basis of the schematic presentation in the main figure, Fig. 4D.



Graphene surface coverage during the lithiation

To estimate the graphene surface area that is covered by the lithiated Fe_2O_3 particles in a graphene/γ-Fe_2O_3 hybrid electrode sample with 56 wt.% Fe_2O_3 load, we make the following assumptions:

1) Uniform particle sizes.

2) Pristine Fe_2O_3 particles have a hemispherical shape.

3) After lithiation, the contact area between particles and graphene sheets is circular.

4) Graphene surface is flat.

The following parameters are employed in our calculations:

γ-Fe_2O_3 density: ρ_{FO} = 4.89 g/cm^3

pristine Fe_2O_3 particle size: d_{FO} = 8.1 nm (from TEM)

lithiated Fe_2O_3 particle size: D_{FO} = 20.6 nm (from TEM)

specific surface area of GMA: a_{GMA} = 1500 m^2/g

weight fraction of Fe_2O_3 in the hybrid sample: f = 0.56.

The number of Fe_2O_3 particles in 1 g of graphene/γ-Fe_2O_3 hybrid is

$$N_{FO} = \frac{f}{\rho_{FO}(1/12)\pi d_{FO}^3} = 8.2\times10^{17}$$

After full lithiation, the graphene surface area covered by a Fe_2O_3 is

$$a_{FO} = \pi D_{FO}^2/4 = 333\ \mathrm{nm}^2$$

The surface area covered by all Fe_2O_3 particles is

$$A_{FO} = N_{FO}a_{FO} = 270\ \mathrm{m}^2$$

On the other hand, the total graphene surface area per gram of the composite is

$$A_{GMA} = (1-f)a_{GMA} = 660\ \mathrm{m}^2$$

The graphene surface coverage by the lithiated Fe_2O_3 particles is thus $\Gamma = A_{FO}/A_{GMA} = 41\%$.

If assuming the ratio of particle sizes in the lithiated and delithiated states is a constant, i.e., $D_{FO}/d_{FO}=\lambda$, one has

$$\Gamma = \frac{3f\lambda^2}{(1-f)a_{GMA}\rho_{FO}d_{FO}} \propto \frac{1}{d_{FO}}$$

i.e., the surface coverage is inversely proportional to the particle size.

Table S1. A summary of our sample information and electrochemical performances of graphene/Fe_2O_3 as anodes for Lithium-ion batteries.

Sample (wt. %)	**Pristine Particle Size**	**Lithiated Particle Size**	**Recipe for electrode**	**Thickness**	**Performance**
α+γ-Fe_2O_3/graphene (56%)	~15 nm	48.9 ± 14.6 nm	No carbon additive, no binder	250 µm	853 mAh/g @ 100 mA/g after 30 cycles (based on hybrid)
α+γ-Fe_2O_3/graphene (40%)	12.5 ± 5.5 nm	--	No carbon additive, no binder	250 µm	1166 mAh/g @ 100 mA/g after 30 cycles (based on hybrid)
γ-Fe_2O_3/graphene (56%)	8.1 ± 1.2 nm	20.6 ± 7.5 nm	No carbon additive, no binder	250 µm	880 mAh/g @ 100 mA/g (based on hybrid)

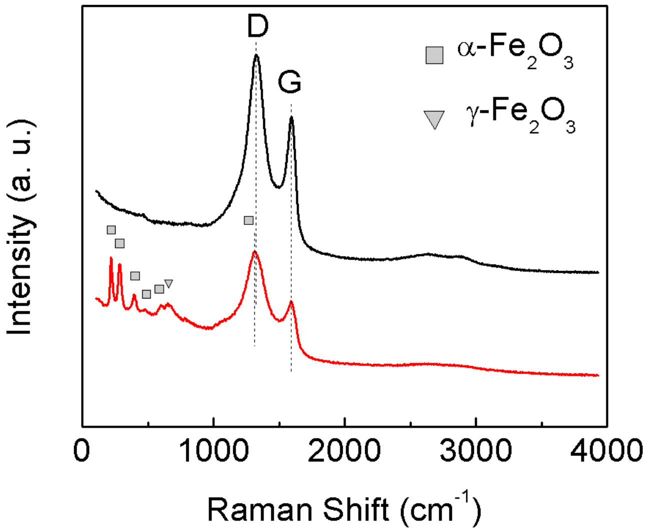


Fig. S1. Raman spectra of the 3D graphene and a Fe_2O_3/graphene hybrid sample (containing both α- and γ-Fe_2O_3).

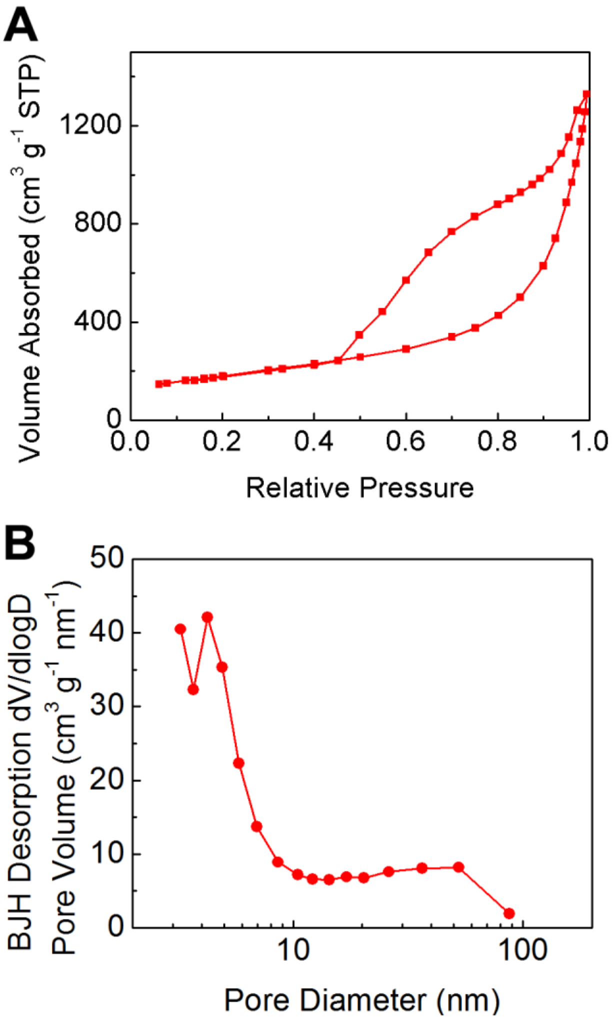


Fig. S2. (**A**) Nitrogen adsorption/desorption isotherms and (**B**) pore size distribution for Fe_2O_3/graphene nanocomposites.

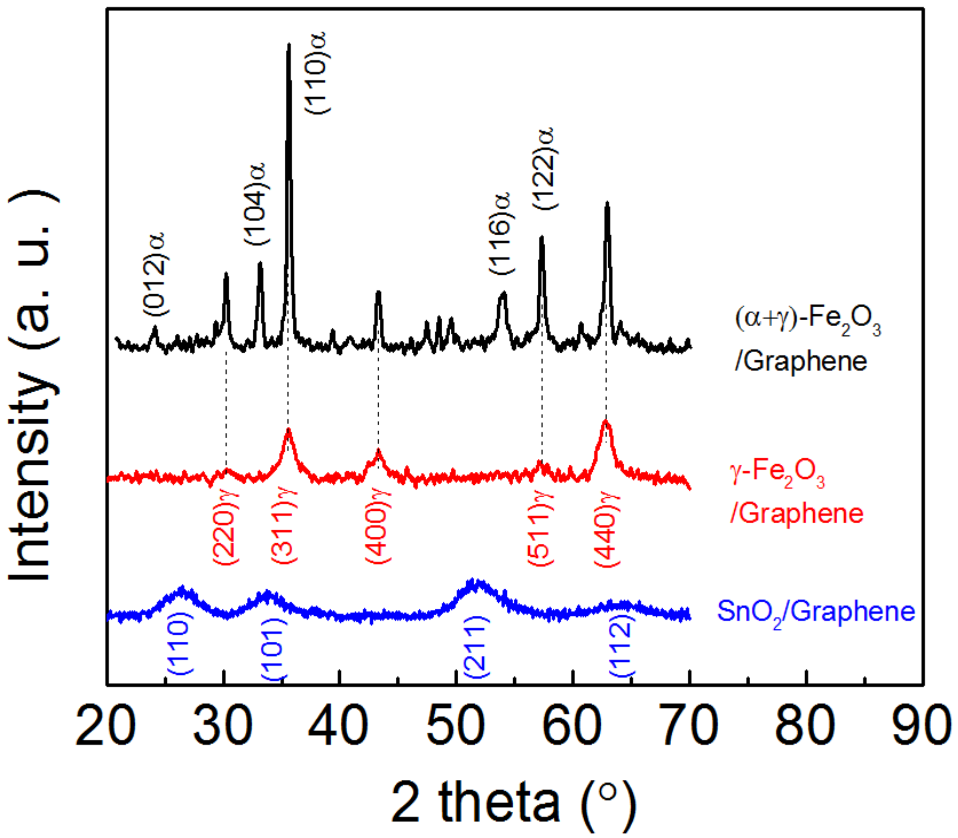


Fig. S3. XRD patterns of two representative Fe_2O_3/graphene and one SnO_2/graphene samples. One contains α- and γ-Fe_2O_3 phases, and the other has 100% γ-Fe_2O_3. The peaks are indexed according to JCPDS cards: PDF#00-033-0664 and PDF#00-039-1346.

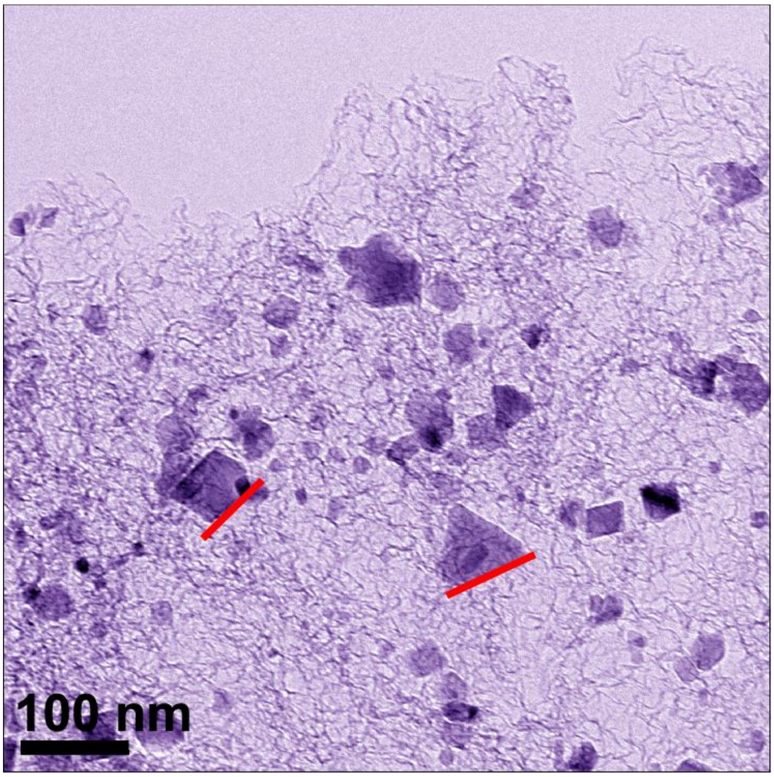


Fig. S4. An additional TEM image of (α+γ)-Fe_2O_3/graphene (40 wt.%), indicating the faceted nature of as-grown particles as manifested by the rather straight edges in 2D projection.

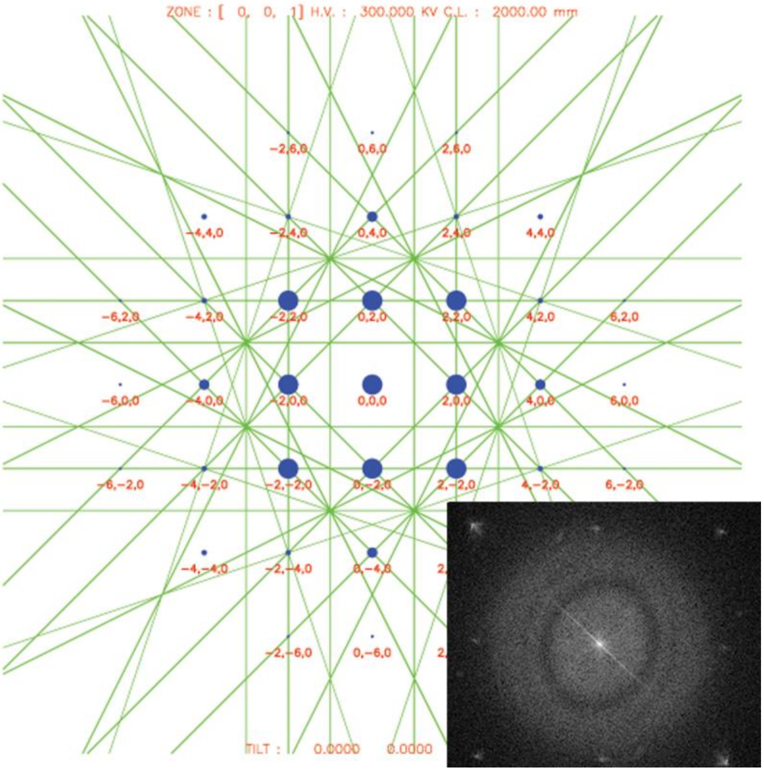


Fig. S5. A comparison of simulated Li_2O (cubic) diffraction patterns along <100> zone axis with the FFT pattern (inset) from our experiments. A good match is found. The simulation was performed using the online version of WebEMAPS software.[2]

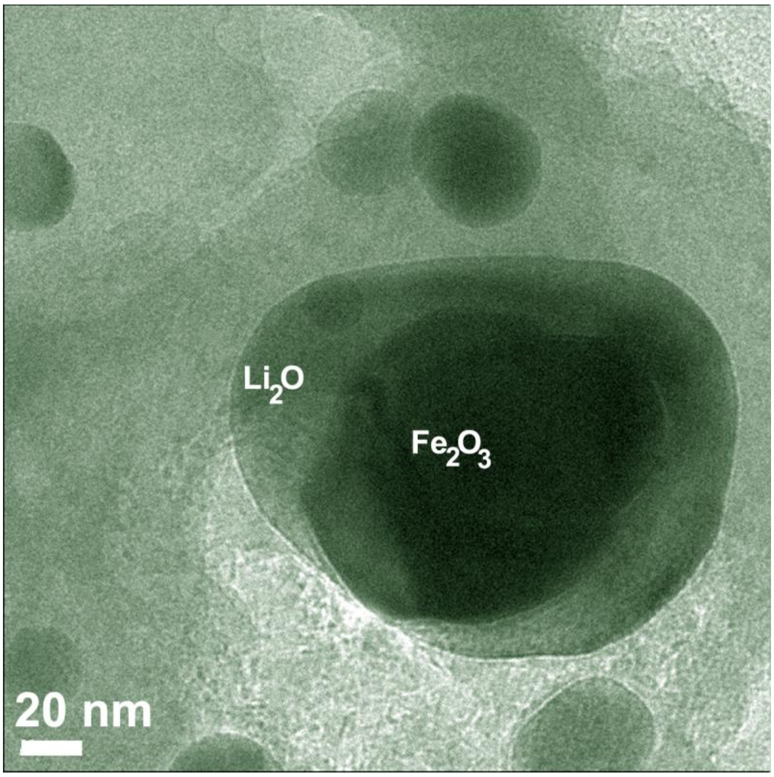


Fig. S6. A bright-field TEM image of the lithiated (α+γ)-Fe_2O_3/graphene (40 wt.%) after 30 cycles, showing a partially lithiated particle.

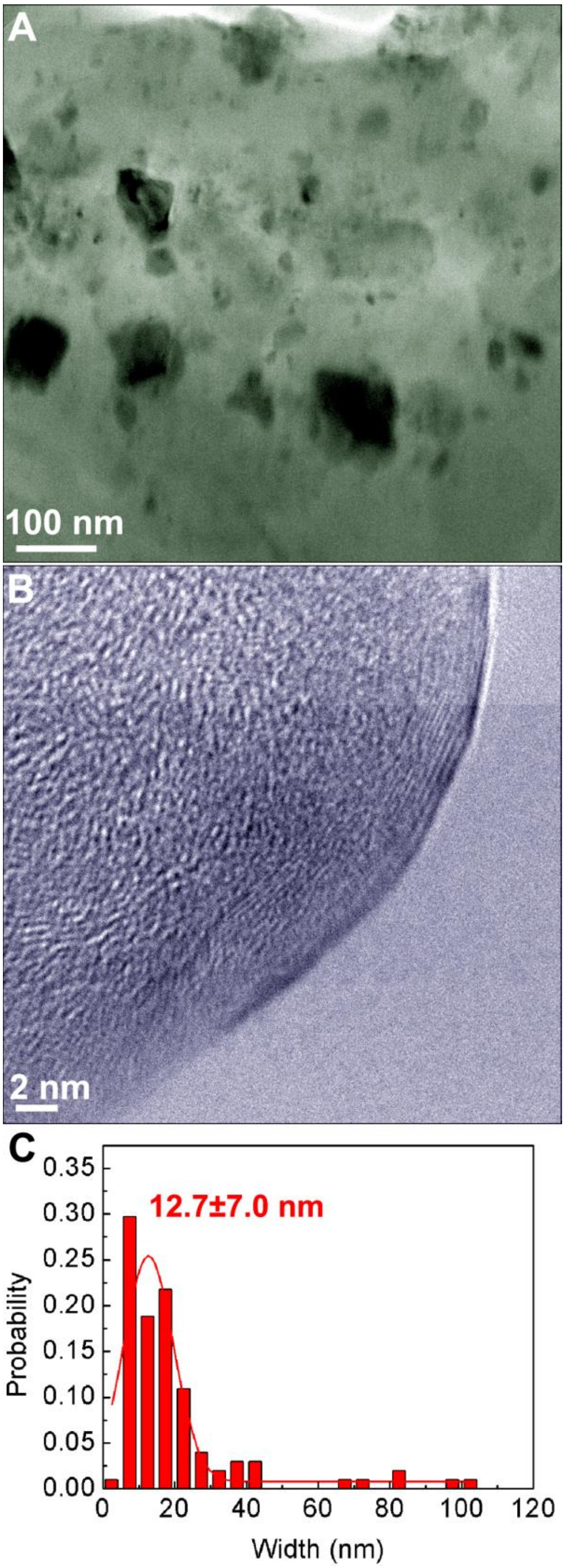


Fig. S7. Microstructure of (α+γ)-Fe_2O_3/graphene (40 wt.%) after 30 cycles. The final state of the sample is charged to 3V (i.e., delithiated). (**A**) A TEM image of Fe_2O_3/graphene, showing the faceted characteristics of particles. (**B**) A high-resolution TEM of a selected particle. (**C**) The particle size distribution from the count of 101 particles. The fitting by log-normal distribution yields an average particle size of 12.7±7.0 nm.

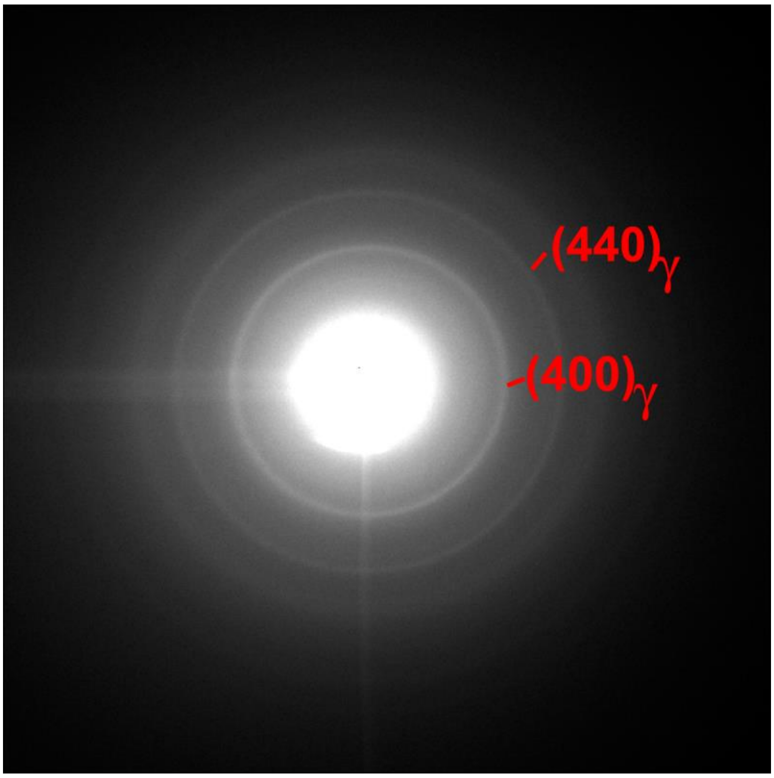


Fig. S8. Selected area diffraction (SAD) pattern taken from a (α+γ)-Fe_2O_3/graphene (40 wt.%) sample after 30 cycles and charged to the delithiated state (3.0V). The as-synthesized sample contains both α- and γ-Fe_2O_3.

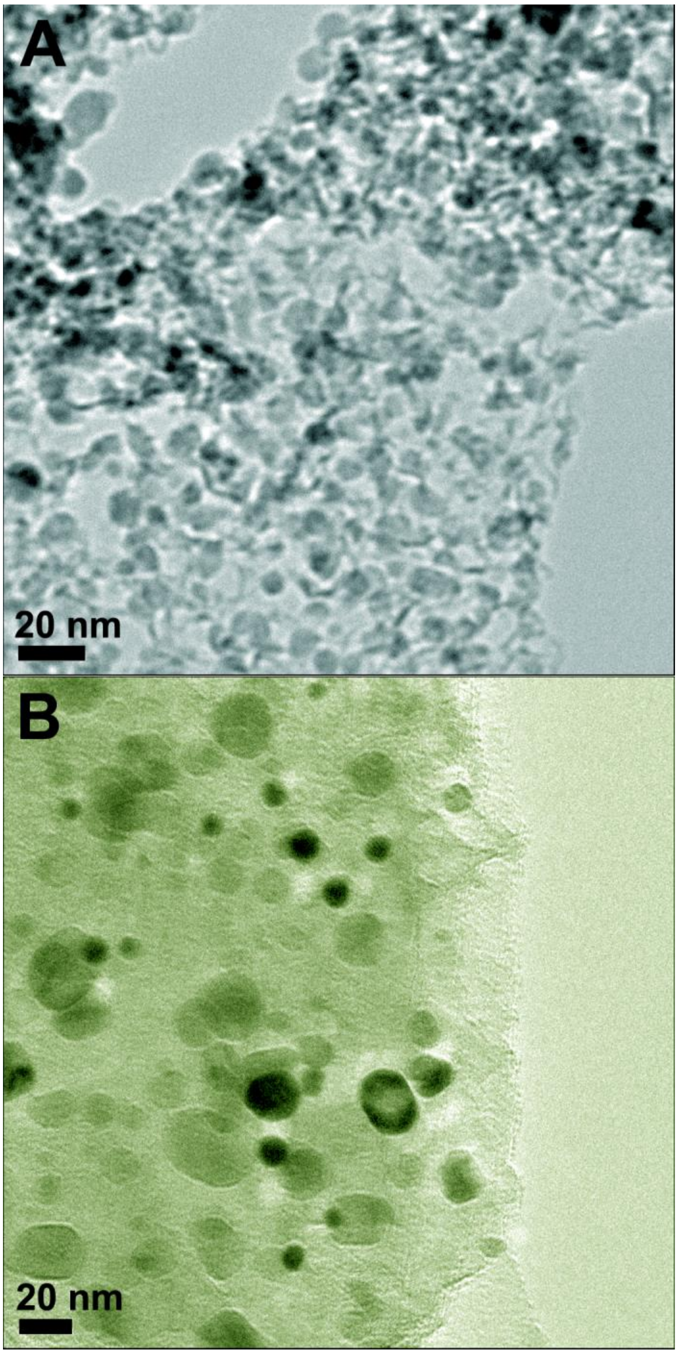


Fig. S9. Bright-field TEM images of γ-Fe_2O_3/graphene (56 wt.%) in (**A**) the as-synthesized state, and (**B**) the lithiated state after 5 cycles. The particle sizes reported in Table 2 are measured from a series of TEM images similar to the ones shown above. The average particle sizes for the as-synthesized γ-Fe_2O_3 and the lithiated state are 8.1 ± 1.2 nm (from 100 counts) and 20.6 ±7.5 nm (from 134 counts), respectively.

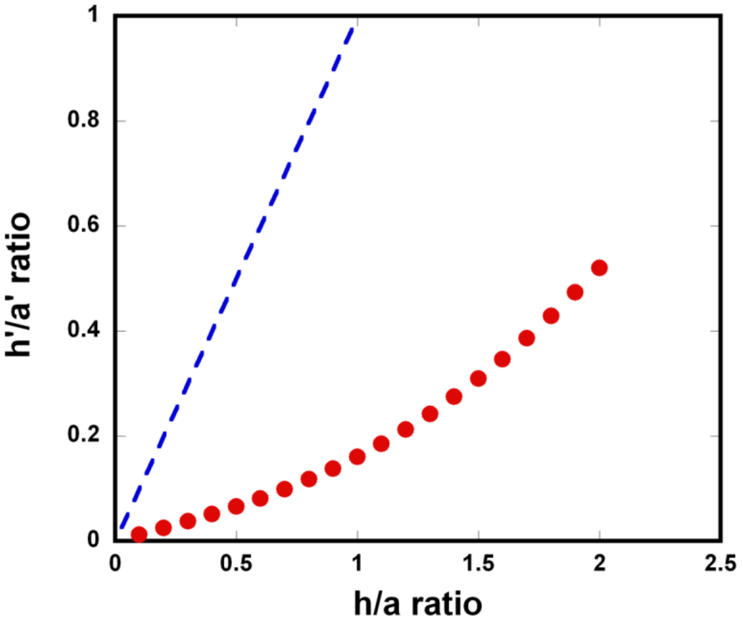


Fig. S10. The calculated ratio change (h′/a′) after the lithiation, as a function of the initial particle shape defined by h/a (see Spherical-cap model section for the details). The blue dashed line denotes $\frac{h'/a\prime}{h/a} = 1$ (i.e., uniform expansion line). Note the substantial reduction of h′/a′ after the lithiation, suggestive of "pancake" shape-change behavior. The calculation parameters are 2a=8.1 nm, and 2a′=20.6 nm, both of which are measured by TEM (see Table 2, γ-Fe_2O_3 and Fig. S10). The volume expansion is assumed as ~96%.[1]

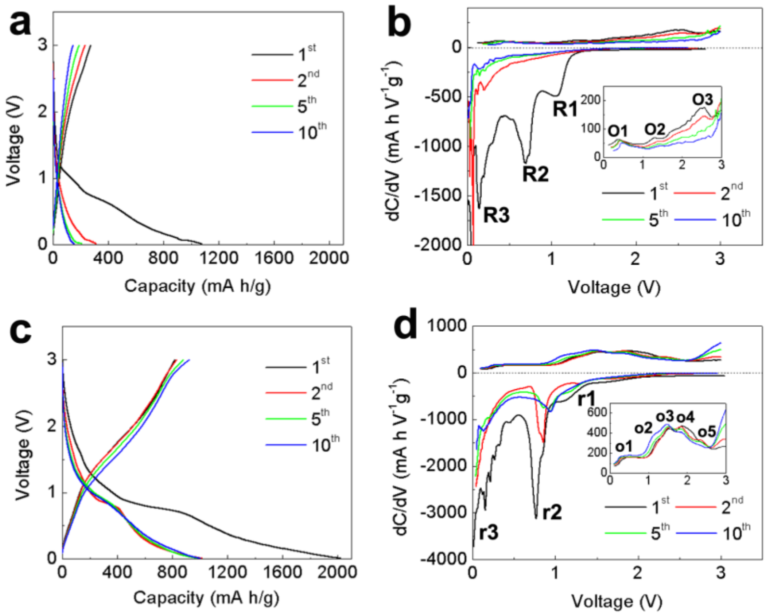


Fig. S11. (**a**)-(**d**) Selected charge/discharge cycles for (**a**) pure 3D graphene and (**c**) Fe_2O_3/graphene (40 wt.%), and their corresponding differential capacity curves, (**b**) and (**d**), respectively. Note the maintenance of multiple oxidation peaks in the nanocomposite after multiple cycles.

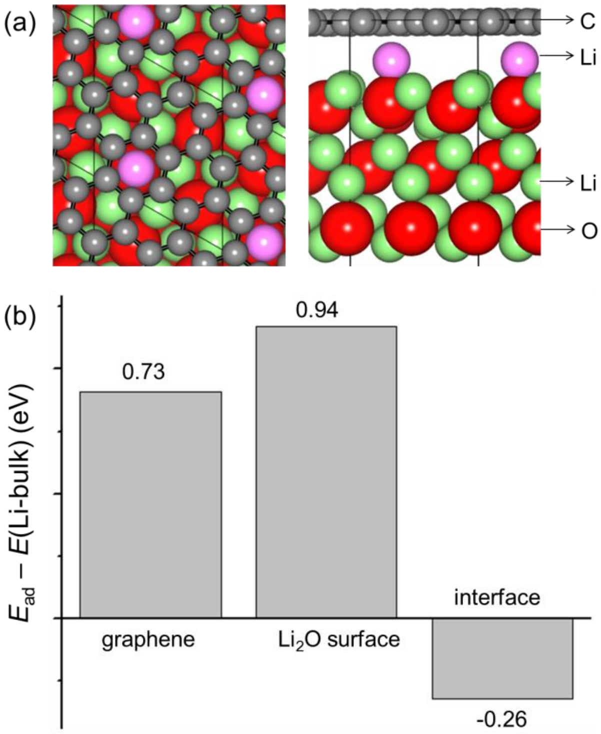


Fig. S12 (a) Structure of Li storage at the graphene-Li_2O interface. Left: top view; Right: side view. The interface Li are shown in a different color from those in Li_2O. The black lines indicate the boundary of the supercell used for calculations. (b) The adsorption energy (see Eq. 1 in the main text) with respect to the energy of bulk Li, for Li adsorbed on graphene, on Li_2O surface, and at the graphene-Li_2O interface. All three cases have the concentration of adsorbed Li.

References

1. Lin, Y. M.; Abel, P. R.; Heller, A.; Mullins, C. B., alpha-Fe2O3 Nanorods as Anode Material for Lithium Ion Batteries. *J. Phys. Chem. Lett.* **2011,** *2* (22), 2885-2891.

2. J.M. Zuo and J.C. Mabon, Web-based Electron Microscopy Application Software: Web-EMAPS, Microsc Microanal 10 (Suppl 2), 2004; URL: http://emaps.mrl.uiuc.edu/.