Supplementary information

Visualizing the roles of graphene for excellent lithium storage

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Figure S1 A nano-cell setup in a TEM chamber. (a) Diagram of a nano-cell constructed for *in situ* TEM observations. (b) TEM image of a nano-cell using NiO@graphene as an example.



Figure S2 Calculation of Li^+ diffusion rate in NiO@graphene. (a) Pristine NiO@graphene. (b) Spot 1 begins to expand. The yellow dashed arrow marks a shortcut for Li^+ diffusion from the lithium base to the spot. The Li^+ diffusion rate is obtained by the following formula: the length of the shortcut / the time it takes from applying the bias to the spot 1 starting to expand. Due to the actual Li^+ diffusion path will longer than the shortcut, the result by calculation will be lower than the actual one. The Li^+ diffusion rates in NiO/graphene and NiO NSs are calculated by the same method.



Figure S3 Relationships between Z_{re} and $f^{1/2}$ in the low frequency region from the EIS measurements. The data was reproduced from our previous paper¹.



Figure S4 Electron energy loss spectroscopy (EELS) elemental mapping in NiO@graphene. (a) The zero loss image along with the distributions of (b) carbon, (c) oxygen and (d) nickel.



Figure S5 Scanning transmission electron microscope (STEM) elemental mapping of graphene. (**a**, **e**) STEM images of the graphene plane in NiO@graphene and NiO/graphene. (**b**) STEM image of the graphene plane in NiO@graphene with (**c**) C- and (**d**) O-elemental mapping images. (**f**) STEM image of the graphene plane in NiO/graphene with (**g**) C- and (**h**) O-elemental mapping images.



Figure S6 *In situ* interfacial binding test between NiO and graphene in (a, b) NiO/graphene and (c, d) NiO@graphene. The pristine NiO is outlined in yellow (a, c).



Figure S7 TEM images and electron diffraction patterns of pristine NiO and lithiated NiO in NiO@graphene. (a) The pristine NiO and (d) after lithiation. (b, e) The corresponding HRTEM images. The dashed circles in (e) indicate Ni nanoparticles. (c, f) ED patterns of (c) the pristine NiO and (f) after lithiation, display a transition from polycrystal NiO to Ni and a Li₂O matrix.



Figure S8 TEM images and electron diffraction patterns of pristine NiO and lithiated NiO in Pure NiO NSs. (a) The pristine NiO and (d) after lithiation. (b, e) The corresponding HRTEM images. The dashed circles in (e) indicate Ni nanoparticles. (c, f)

ED patterns of (c) the pristine NiO and (f) after lithiation, display a transition from polycrystal NiO to Ni and a Li₂O matrix.



Figure S9 The time cost for Li^+ reaction with NiO along the Li^+ diffusion direction in (a) NiO/graphene; (b) NiO@graphene and (c) NiO NSs. In NiO/graphene, In NiO/graphene, due to a various extent of the interfacial contact between NiO and graphene, the Li^+ reaction is varied (a). In NiO NSs (c), the time cost for lithiation increased along the Li^+ diffusion direction, from 15s to 165s. However, the time required to produce full lithiation of a NiO NS is uninfluenced by the Li^+ diffusion distance in both NiO/graphene and NiO@graphene, which is contrary to that in pure NiO NSs (c).



Figure S10 TEM images of the size change of a NiO nanosheet in NiO/graphene during the electrochemical process. (a) The pristine NiO/graphene. (b) The NiO/graphene after lithiation. (c) Delithiation of lithiated NiO/graphene. NiO underwent an expansion during lithiation from 135.9 nm to 154.9 nm. After applying a 3.0 V bias, the expansion decreased to 139.6 nm after delithiation.

Table S1 Statistical data for complete conversion in individual NiO NSs in NiO@graphene. The average reaction time is 5 s, and the average expansion ratio (the ratio of the NiO diameter after and before lithiation) is 0.08 for NiO NSs in NiO@graphene.

NiO@graphene	Diameter (nm)	Reaction time (s)	Distance from lithium (nm)	Expansion ratio
1	286	5	330	0.09
2	315	5	512	0.05
3	227	4	256	0.09
4	232	6	655	0.1
5	86	4	159	0.09

Table S2 Statistical data for complete conversion in individual NiO NSs in NiO/graphene. The average reaction time is 21 s, and the average expansion ratio (the ratio of the NiO diameter after and before lithiation) is 0.14 for NiO NSs in NiO/graphene.

NiO/graphene	Diameter (nm)	Reaction time (s)	Distance from lithium (nm)	Expansion ratio
1	156	19	413	0.12
2	75	16	189	0.15
3	89	14	672	0.16
4	143	27	657	0.13
5	139	19	10	0.18
6	129	28	456	0.11

Supplementary Movies

Movie S1.

 Li^+ reaction kinetics with NiO in NiO@graphene. The graphene served as a high Li^+ diffusion path to fulfill the lithiation of NiO.

Movie S2.

 Li^+ reaction kinetics with NiO in NiO NSs. The playback is at 10× speed.

Movie S3.

 Li^+ reaction kinetics with NiO in NiO/graphene.

Movie S4.

Interfacial restricting effect of graphene during lithiation. The playback is at $10 \times$ speed.

Supplementary method:

First-principles calculations: A large 2D (5×5) supercell consisting of 50 C atoms with 20 Å vacuum space in the z direction was constructed to represent graphene as shown in Fig. 2a. The hollow site in the center of a hexagon of carbon atoms in the graphene is the most energetically favorable adsorption site for an isolated Li adatom with the largest adsorption energy (E_{ad}) , 1.23 eV per Li atom. In order to model amorphous Li₂O, a crystalline 2×2×2 supercell consisting of 64 Li and 32 O atoms was first constructed, melted at 4000 K and then cooled to 1 K at a rate of 20 K ps⁻¹ to obtain an amorphous structure (Fig. 2b). The radial distribution function (RDF) g(r) from this simulation is displayed in Fig. 2c, showing a typical RDF form of an amorphous structure. Here, we only show the first RDF peak of Li-Li distance ranges from 1.7 to 3.0 Å. Therefore, the center Li site and its eight neighboring Li sites located within a distance of 3.0 Å from the center Li atom were selected as the starting point and final positions, respectively, for Li^+ diffusion within this amorphous Li₂O cell. In the case of Li^+ diffusion on the NiO (111) surface, we used a $p(2\times 2)$ octopolar reconstruction of the NiO (111) surfaces (consisting of 6 layers of Ni atoms and 6 layers of O atoms with the most central layers of O and Ni atoms fixed to their bulk positions, see Fig. 2d). This model was proposed by Wolf², which is proven to be thermodynamically stable by recent theoretical calculations^{3,4} and confirmed by previous experimental observations^{5,6}. Spin polarization was included to account for the antiferromagnetic ground state structure of the $p(2\times 2)$ octopolar reconstruction of the NiO (111) surface. We found that the Li adatom most energetically prefers to take the fcc hollow site and bond with three neighboring surface O atoms on the O-terminated side of the slab.

Reference

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