Experimental

*Hydrothermal of NbO$_x$ nanoparticles and NbO$_x$@C*  In a typical synthesis, 0.27g of NbCl$_5$ was dissolved to the mixed solution of 1mL oleylamine and 34 mL distilled water, with stirring for 30 minutes. The solution was then transferred to an autoclave of 50 mL, and heated to 180 °C for 24 h. After the reaction completed, a part of the resulting product was washed with alcohol and distilled water for several times, and dried at 80 °C in vacuum overnight. Also the rest of was heated at 3°C min$^{-1}$ from room temperature to 550°C and kept at this temperature for 2 h under an argon flow to achieve NbO$_x$@C material. To study the influence of the ratio of oleylamine to distilled water, a series of controlled experiments were carried out.

*Characterization* The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu Kα source ($\lambda = 0.15406$ nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The high-resolution transmission electron microscopy (HR-TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. The specimen of HR-TEM measurement was prepared via spreading a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. Thermal gravimetric analysis (TGA) was performed to quantify the amount of carbon present in the NbO$_x$@C composite. A TG-DTA7300 instrument was used. The composite was heated at 5 °C min$^{-1}$ up to 110°C for 30 min to
remove moisture contained in the material and then heated continuously up to 800°C in air in order to oxidize the carbon from the composite.

**Electrochemical Test** The electrochemical Li intercalation performance was investigated in Li test cells. Typically, the electrode consisted of 80 wt% active material, 10 wt% conductivity agents (acetylene black), and 10 wt% binder (PVDF). After N-methyl-2-pyrrolidone was evaporated, the mixture was rolled into a sheet and cut into circular strips of 8 mm diameter. The strips were then dried at 120 °C for 10 h in air. Lithium metal was used as the counter and reference electrodes. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, in weight percent). The above three parts were assembled into test cells in an argon-filled dry glovebox, and then the cells were measured at different current densities within a voltage range of 0.01-3.0 V with a Land CT 2001 battery tester.
Fig. S1 TGA curve of NbO$_x$@C nanocomposites.
Fig. S2 TEM images of the as-synthesized NbO$_x$. 
Fig. S3 SEM image of the as-synthesized NbO$_x$@C.
Fig. S4 SEM image of the sample synthesized without oleylamine.