

Supporting Information for

Controlled formation of core shell structures with a uniform  $\text{AlPO}_4$  nanoshell

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### Experimental section

**Materials.** The pristine  $\text{LiCoO}_2$  powders (with an average particle size of  $\sim 10 \mu\text{m}$ ) and  $\text{Co}_3\text{O}_4$  powders (with an average particle size of  $\sim 5 \mu\text{m}$ ) were purchased from Pulead Technology Industry Co., Ltd. Ag nanoparticles (55 nm) and  $\text{TiO}_2$  (Rutile) were purchased from Beijing DK nano technology Co. Ltd. Aluminum nitrate, disodium hydrogen phosphate, urea and nitric acid were of analytical pure and purchased from Sinopharm Chemical Reagent Co. Ltd.. Mili-Q water (resistance  $> 18 \text{ M}\Omega$ ) was used for all experiments.

**Preparation of  $\text{PS@AlPO}_4$ .** The sulfonated polystyrene spheres ( $d=460\text{nm}$ ) were synthesized following the literature procedures.<sup>1</sup> 0.046g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , trace amount of  $\text{HNO}_3$ , 0.044g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 0.5g  $\text{CO}(\text{NH}_2)_2$  were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, 550  $\mu\text{L}$  (100 mg/mL) the obtained PS spheres solution were added to the coating solution. Finally, the resultant solution was titrated to  $\text{pH}=2.5$  by nitric acid and then incubated at 90 °C for 3h under vigorously stirring. The obtained product was centrifuged at 8000 rpm for 1min, which was followed by washing with water and ethanol and drying at 80 °C for 10h, respectively. The obtained powder was annealed at 500 °C for 2h in air to remove the core and obtain aluminum phosphate hollow spheres. The concentration of  $\text{AlPO}_4$  solution to PS was varied to control the thickness of  $\text{AlPO}_4$  coating layer.

**Preparation of  $\text{Ag@AlPO}_4$ .** 0.2g Ag, 0.046g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , trace amount of  $\text{HNO}_3$ , 0.044g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 0.5g  $\text{CO}(\text{NH}_2)_2$  were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to  $\text{pH}=2.5$  by nitric acid and then incubated at 90 °C for 3h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 °C for 10h, respectively.

**Preparation of nano-Co<sub>3</sub>O<sub>4</sub>@AlPO<sub>4</sub>.** Nano-Co<sub>3</sub>O<sub>4</sub>, derived from micro-Co<sub>3</sub>O<sub>4</sub> with ball milling, was annealed at 900 °C for 5h in air. 0.2g the pretreatment nano-Co<sub>3</sub>O<sub>4</sub>, 0.046g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, trace amount of HNO<sub>3</sub>, 0.044g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and 0.5g CO(NH<sub>2</sub>)<sub>2</sub> were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH=2.5 by nitric acid and then incubated at 90 °C for 3h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 °C for 10h, respectively.

**Preparation of TiO<sub>2</sub>@AlPO<sub>4</sub>.** 0.26g TiO<sub>2</sub>, 0.046g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, trace amount of HNO<sub>3</sub>, 0.044g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and 0.5g CO(NH<sub>2</sub>)<sub>2</sub> were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH=2.5 by nitric acid and then incubated at 90 °C for 3h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 °C for 10h, respectively.

**Preparation of nano-LiCoO<sub>2</sub>@AlPO<sub>4</sub>.** Nano-LiCoO<sub>2</sub>, derived from micro-LiCoO<sub>2</sub> with ball milling, was annealed at 900 °C for 5h in air. 0.6g the pretreatment nano-LiCoO<sub>2</sub>, 0.046g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, trace amount of HNO<sub>3</sub>, 0.044g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and 0.5g CO(NH<sub>2</sub>)<sub>2</sub> were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH=2.5 by nitric acid and then incubated at 90 °C for 3h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol and drying at 80 °C for 10h, respectively.

**Preparation of LiCoO<sub>2</sub>@AlPO<sub>4</sub>.** 2.5g LiCoO<sub>2</sub>, 0.046g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, trace amount of HNO<sub>3</sub>, 0.044g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and 0.5g CO(NH<sub>2</sub>)<sub>2</sub> were slowly dissolved in 30 mL distilled water under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH=2.5 by nitric acid and then incubated at 80 °C for 3h under vigorously stirring. The obtained product was separated from the solution by centrifuging at 8000 rpm for 1min, washing with water and ethanol, drying at 80 °C for 10h. The samples have been annealed at 700 °C for 2 h for their electrochemical test.

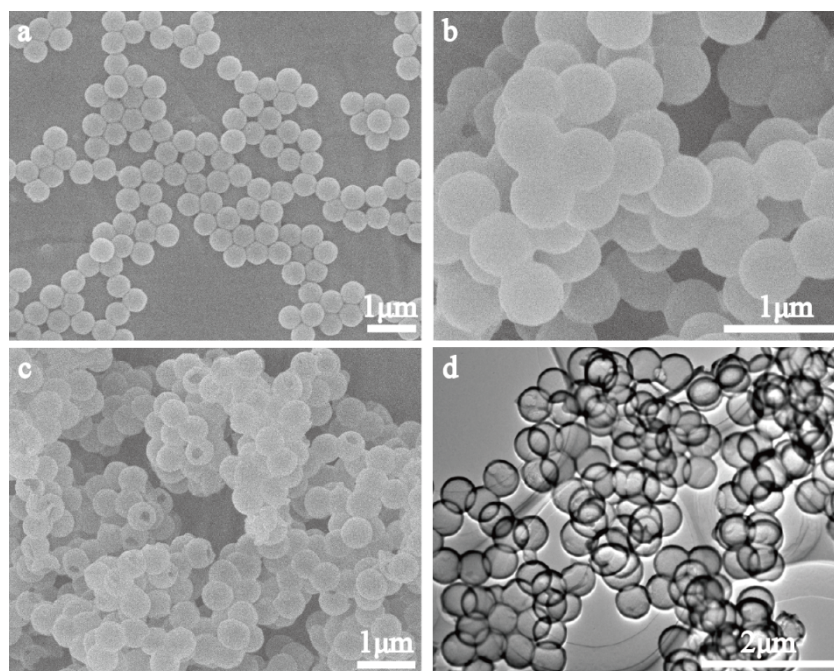
**Electrochemical measurement.** Charge-discharge tests were performed with CR2032 coin cells assembled in an argon-filled glove box, which consisted of a lithium metal as the counter and reference electrode, a cathode as the working electrode, 1M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt %) as the electrolyte, and polypropylene membrane (Celgard) as a separator. The cathode was prepared as a mixed slurry of 80 wt % active materials, 10 wt% of Super P carbon black, and 10 wt % of polyvinylidene fluoride (PVDF, Aldrich) binder in a n-methyl pyrrolidone (NMP) solvent, casting onto Al foil (99%, Goodfellow) and cutting into circular electrodes of 1.13 cm<sup>2</sup> area after drying under a vacuum at 80 °C for 10h. Galvanostatic tests of the assembled cells were performed with a Land CT2001A battery test system with a voltage window of 2.75-4.5V at room temperature.

**Characterization.** Scanning electron microscopy (SEM) was collected on Field Emission Scanning Microscopy (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-

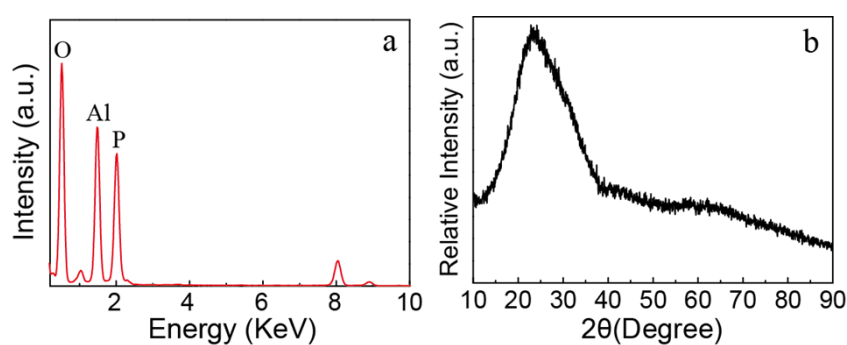
2100F and FEI Tecnai F20 operated at 200kV. X-ray diffraction (XRD) data was collected on a Rigaku D/MAX-2500 with Cu K $\alpha$  radiation at 50 kV and 250 mA. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab250Xi using 200 W monochromated Al K $\alpha$  radiation.

### References.

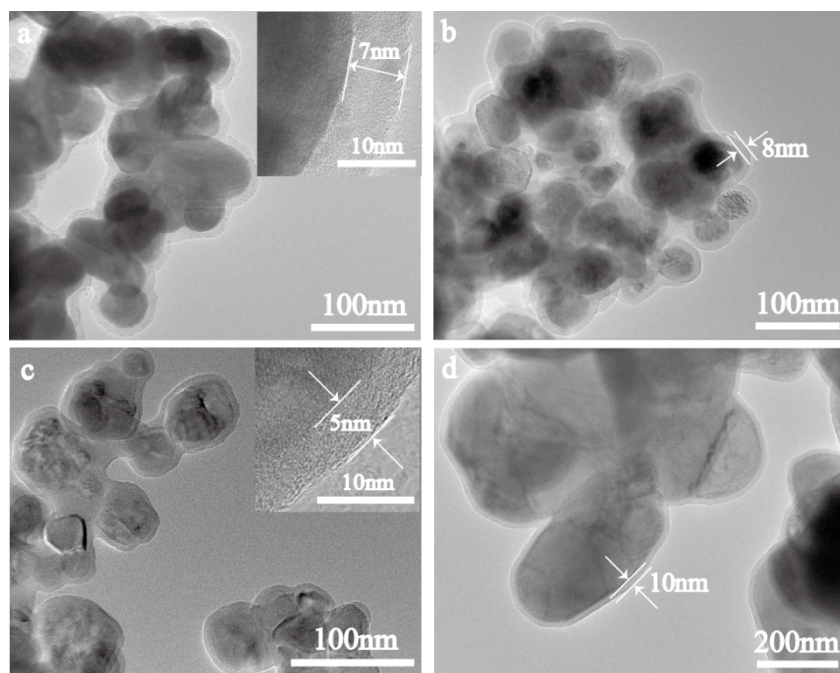
1. P. M. P, *Google Patents*, 1967.



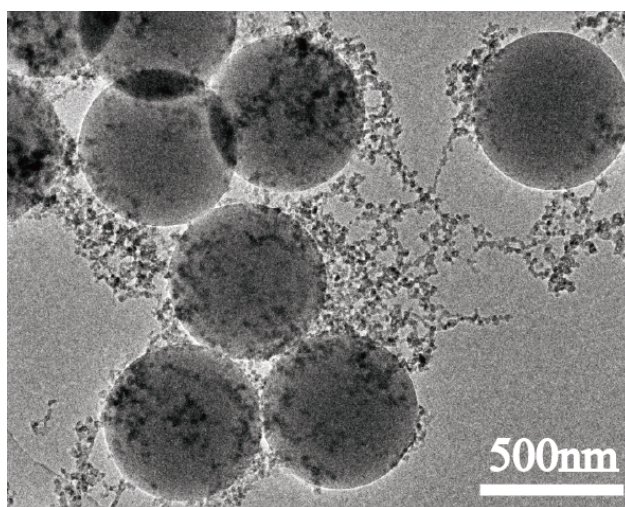
**Figure S1.** (a-c) SEM images of pristine PS (a), PS@AlPO<sub>4</sub> (b), and PS@AlPO<sub>4</sub> after annealed at 500 °C in air for 2 h (c). Low magnification TEM image of PS@AlPO<sub>4</sub> after annealed at 500 °C in air for 2 h (d). The broken sphere particles and the brighter edge clearly identified the hollow character of AlPO<sub>4</sub>spheres.



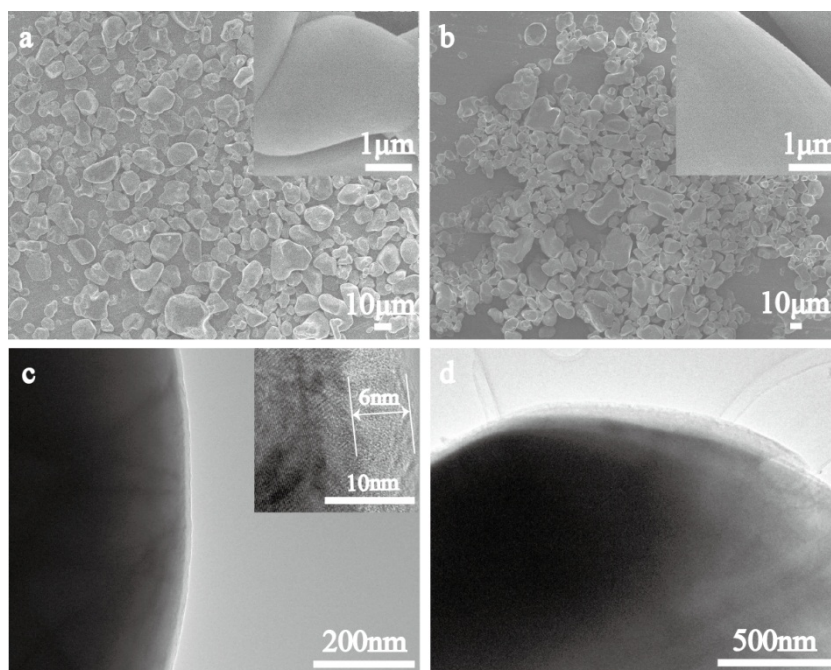
**Figure S2.** (a) The dispersive spectroscopy (EDS) pattern of the randomly picked hollow spheres. (b) XRD pattern of the PS@AlPO<sub>4</sub> after annealed at 500 °C in air for 2 h.



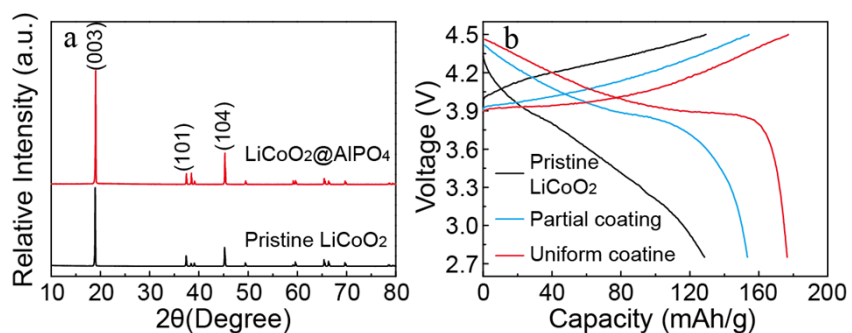
**Figure S3.** TEM images of core shell structures synthesized with different seeds: (a) Ag@AlPO<sub>4</sub>, (b) nano-Co<sub>3</sub>O<sub>4</sub>@AlPO<sub>4</sub>, (c) TiO<sub>2</sub>@AlPO<sub>4</sub>, (d) nano-LiCoO<sub>2</sub>@AlPO<sub>4</sub>.



**Figure S4.** Low magnification TEM image of PS@AlPO<sub>4</sub>, without controlling the precipitation process of AlPO<sub>4</sub>, revealed phase separation.



**Figure S5.** (a-b): SEM images of pristine LiCoO<sub>2</sub> and LiCoO<sub>2</sub>@AlPO<sub>4</sub> samples. The insets are high magnification SEM images. (c-d): TEM images of surface modified LiCoO<sub>2</sub> samples: c) uniform AlPO<sub>4</sub> coating and d) partial AlPO<sub>4</sub> coating.



**Figure S6.** (a) XRD patterns of the pristine LiCoO<sub>2</sub> and uniformly coated one. (b) Charge-discharge profiles of the 100<sup>th</sup> cycle of the pristine LiCoO<sub>2</sub>, partially coated one, uniformly coated one, which are operate at 0.1C with a voltage window between 2.75V and 4.5V at room temperature.