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COMMUNICATION

Controlled formation of core shell structures with a uniform AlPO₄ nanoshell

Fen-Li Yang,[a] Wei Zhang,[a] Zi-Xiang Chi,[a] Fu-Quan Cheng,[b] Ji-Tao Chen,[b] An-Min Cao[*a] and Li-Jun Wan[*a]

Uniform AlPO₄ nanoshells are successfully achieved on different core materials by controlling its formation kinetics in solution. The application of this coating protocol on LiCoO₂ shows an obvious improvement in its battery performance.

Core shell structure has drawn great attention from the scientific community due to their unique physicochemical properties.[1] It's widely acknowledged that the introduction of a surface coating layer can not only act as an effective protecting layer on the surface, but also endow the core material new properties in various applications covering catalysis, biomedicine, energy conversion, and energy storage.[2] For example, the shell-isolated metal nanoparticles have been confirmed to show an amplified Raman signal, which promise a much higher detection sensitivity as a powerful spectroscopy technique.[3] Meanwhile, it is reported that a surface protection layer is crucial to improve the thermal stability of the core materials.[4]

Generally, a successful construction of core-shell structure relied on the capability of a good control on the shell formation. Recent progresses in wet chemistry have witnessed the rapid development of different approaches for the deposition of uniform nanoshells. Typically, surface coatings made of metals or metal oxides have been achieved by means of solution-based synthetic routes.[2b, 5] On the contrary, despite of those important achievements, it is still an open challenge to form a uniform shell of metal phosphates. The precipitation of metal phosphate in solution is usually very fast due to their low solubility-product constants, resulting in a self-nucleation process to form independent particles instead of core-shell structures. Recently, the technique of atomic layer deposition (ALD) showed promising potential in forming thin nanoshells.[6] Unfortunately, it is a high-cost procedure characterized by a tedious operation with very limited processing capability. For the construction of core-shell structured materials in a large quantity, it is of great importance to develop new synthetic protocol so that metal phosphate nanoshell can form in a simple and easy way.

We have special interest in the formation of a uniform nanoshell of AlPO₄, which is an important metal phosphate with wide applications in catalysis, ceramics and high temperature oxidation resistance.[6b, 7] Typically, the coating of cathode materials by AlPO₄ has been widely applied in the practice of lithium ion batteries

(LIBs). For different kinds of cathode materials, typically LiCoO₂, it is proved that an obviously-improved battery performance can be achieved by treating their surface with AlPO₄.[8] The existence of AlPO₄ turned out to be very helpful to alleviate the side reactions on the interface during the highly unstable charge-discharge process, probable due to the strong P=O bond in PO₄³⁻.[9] For an optimal protection of the cathode materials, it is reasonable to expect that a nanoshell with full AlPO₄ coverage on the cathode material should provide better protection. However, the fast formation of AlPO₄ in solution makes the coating process extremely hard to achieve.[5b] The so-called coating procedure for LiCoO₂ usually exists as an adsorption process to introduce the preexisting AlPO₄ nanoparticles onto LiCoO₂.[8c] It is highly demanded that new synthetic protocol be developed so that uniform AlPO₄ nanoshells can be easily achieve for better cathode materials in LIBs.

In this contribution, we reported our progress on the controlled formation of AlPO₄ nanoshells on various substrate materials. For the first time, we demonstrated that a uniform AlPO₄ coating layer can be achieved in solution by means of the kinetics control during the precipitation of AlPO₄. The application of this coating protocol to LiCoO₂ produced a core-shell structure of LiCoO₂@AlPO₄, which showed much improved battery performance as far as the cyclability of the cathode material is concerned.

Taking polystyrene (PS) as an example, we firstly prepared PS nanospheres with a diameter around 460 nm (figure 1a), and then they were used as seeds for further surface treatment (See supporting information for experimental details). To prevent the direct precipitation of PO₄³⁻ and Al³⁺, we started from an acidic environment with a relatively-low pH value around 2.5, which gradually increase due to the slow decomposition of urea added in the solution, resulting a well-controlled formation of AlPO₄. Figure 1b showed the transmission electronic microscopy (TEM) image of the PS sample after the surface treatment. A thin shell could be seen around each PS particles and a higher magnification TEM (HMTEM) in the inset in 1b clearly revealed the existence of a nanoshell, forming a typical core shell structure. A thorough examination on the scanning electron microscopy (SEM) images before and after coating (figure S1a-b) revealed that no phase separation happened and

nanospheres existed as the only morphology, indicating that all the formed $AlPO_4$ existed as the shell on the surface.
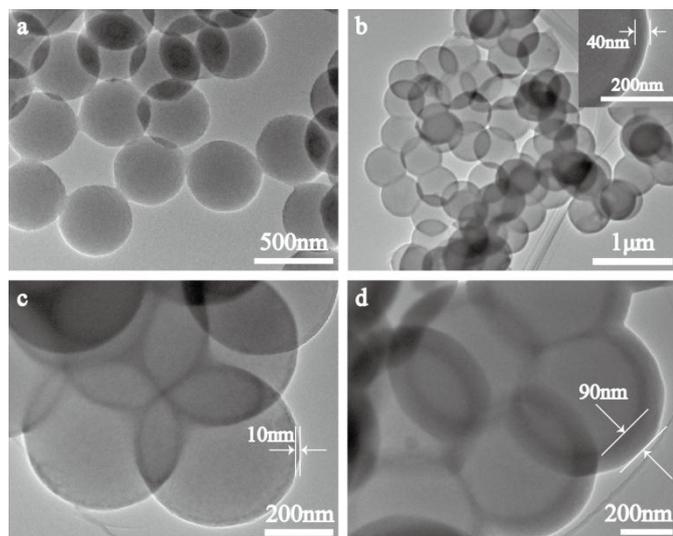
Fig. 1 TEM images of the pristine PS (a) and surface coated samples (b-d). The $AlPO_4$ thicknesses were controlled by using different amounts of PS seeds: b) 40 nm (55 mg), the inset is a HMTEM image, c) 10 nm (130 mg), d) 90 nm (23 mg).

We found that it was easy to control the thicknesses of the nanoshells by simply changing the amount of PS seeds while the concentrations of the other reactants remain unchanged. A thinner layer would be achieved when more PS seeds (130 mg compared to 55 mg in figure 1b) were used. Figure 1c showed that the surface layer turned 10 nm in thickness while the shell was still continuous and uniform on the surface. On the contrary, thicker layers of 90 nm were prepared when only 23 mg PS seeds were used as shown in figure 1d. Meanwhile, we were also able to control the shell thicknesses by changing the concentrations of $Al(NO_3)_3$ when a fixed amount of PS was used.
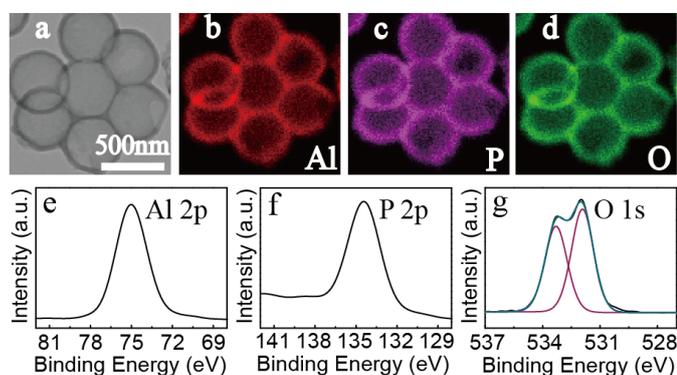

Fig. 2 (a-d) STEM images and (e-g) XPS characterizations of the hollow nanospheres prepared by removing the PS cores of the PS@$AlPO_4$ samples: (a) TEM morphology; (b-d) elemental mappings: b) Al, c) P, d) O; (e-g) XPS spectra: e) Al 2p, f) P 2p, g) O 1s.

To have a better understanding on the surface shell, the sample in figure 1b was subject to a high temperature treatment in air so that the PS core could be totally removed. The SEM and TEM characterizations (figure S1c-d) further confirmed

that all these particles were hollow nanospheres with an evenly-distributed shell. Several particles were randomly picked for detailed elemental analysis with their morphology shown in figure 2a. Their elemental mappings were recorded under the scanning TEM (STEM) mode, which showed a homogeneous distribution of Al, P, O (figure 2b-d, figure S2a), confirming the formation of an $AlPO_4$ shell. Moreover, the characterization by X-ray photoelectron spectroscopy (XPS) also confirmed the existence of Al, P, and O (figure 2e-g). It could be concluded that an $AlPO_4$ shell had formed through our synthesis control. The X-ray diffraction (XRD) characterization on these hollow nanospheres showed that the $AlPO_4$ was amorphous (figure S2b).

In addition to the organic core of PS, we found that our synthetic protocol could be well expanded to coat a large variety of core materials, typically metals and metal oxides. Figure S3 showed representative TEM images for different samples we tested including Ag (figure S3a), Co_3O_4 (figure S3b), TiO_2 (figure S3c), and $LiCoO_2$ (figure S3d). It was noteworthy that all these core materials were commercially purchased with no further surface modification. Despite of their aggregation in solution due to the high surface area of nanoparticles, we could still achieve a uniform coating for all the exposed surfaces as revealed in figure S3.

Further synthesis efforts revealed that the formation of nanoshells could be mainly ascribed to a control on the growth kinetics of $AlPO_4$, which was achieved by using urea as a special release agent to mediate the precipitation. Scheme 1 showed two simplified chemical reaction equations related to our synthesis. First, a fast $AlPO_4$ precipitation should be prevented, otherwise the $AlPO_4$ would nucleate itself into separate particles. As shown figure S4, a mixture of PS and $AlPO_4$ spheres formed from the un-controlled reaction between Al^{3+} and PO_4^{3-}. To slow down this reaction, we started the reaction in an acidic environment with the pH value controlled at around 2.5, which was able to drive the reaction 1 to go leftwards and no $AlPO_4$ formed at the beginning. Second, the gradual increase of the temperature would lead to a gradual decomposition of urea.[10] The pH value would accordingly increase as a result of the slow releasing of hydroxide ions. The reaction 1 then gradually shifted rightwards and $AlPO_4$ forms without a fast precipitation process, resulting in a uniform coating layer instead of separate $AlPO_4$ particles.

$$Al^{3+} + HPO_4^{2-} \rightleftharpoons AlPO_4 + H^+ \qquad (1)$$

$$CO(NH_2)_2 + 3H_2O \longrightarrow 2NH_4^+ + CO_2 + 2OH^- \qquad (2)$$
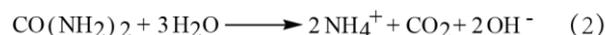
Scheme 1 Two chemical reaction equations related to the formation of $AlPO_4$ nanoshells. We started the reaction at a pH of 2.5, and the final pH value turned around 7 due to the gradual decomposition of urea.

Considering the importance of surface $AlPO_4$ to different cathode materials,[11] we expected that a uniform $AlPO_4$ nanoshell could be more favourable due to a much better protection on the electrode surface, which was of special importance when high working voltage was enforced, typically 4.5 V for $LiCoO_2$ due to the increasing demand on a high energy density. Our preliminary experiments on the cyclability of $LiCoO_2$ did show a much improved battery performance could be achieved from our synthesis trials on a core-shell structure of $LiCoO_2$@$AlPO_4$. Figure S5b-c showed the $LiCoO_2$ samples after coating procedure. The existence of a surface

shell could be identified due to our synthesis control as introduced before. The XRD patterns of $LiCoO_2$ before and after coating showed no discernible changes (figure S6a), indicating the coating process does not change the structure of the pristine $LiCoO_2$. For comparison, a sample with partially-covered surface was also prepared (figure S5d). Figure 3 showed the battery performance of different samples we tested at 0.1C rate between 2.75 and 4.5 V. The surface treatment did show small changes (figure 3a) on the charge/discharge profiles, probably due to the polarization caused by the surface layer. Interestingly, an obviously improved cycling stability could be observed. After 100 cycles, the capacity retention for the pristine $LiCoO_2$, partially coated one, and uniformly coated one were 128.5mAh/g, 153.4mAh/g, and 176.5mAh/g respectively (figure 3b, figure S6b), highlighting the importance of a controlled surface treatment in our synthesis. The detailed mechanism for such an improvement in cyclability is under way for a better understanding on the charge/discharge process.
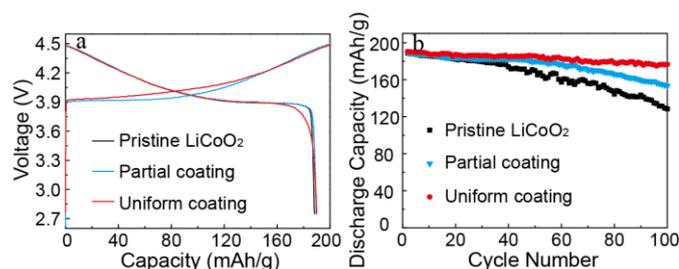
Fig. 3 (a-b) Electrochemical performances of the pristine $LiCoO_2$, partially-coated one, and the uniformly-coated one, respectively: a) charge-discharge profiles, b) cycle-life performance profiles, which are operated at 0.1 C with a voltage window between 2.75 and 4.5V at room temperature.

In summary, a simple and effective synthetic protocol has been developed for the formation of a uniform $AlPO_4$ nanoshell. By controlling the initial pH value and using urea as a special releasing agent in the solution, the growth kinetics of $AlPO_4$ could be successfully mediated so as to avoid its fast precipitation, leading to the formation of core shell structured materials. We also demonstrate that such a synthesis route can be expanded to a large variety of core materials including metal, metal oxides and organics. Our preliminary results on the surface modification of $LiCoO_2$ by $AlPO_4$ reveal that such a uniform coating could be highly favourable as long as a stable cathode material of LIBs was concerned.

Notes and references

a Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China. E-mail: anmin_cao@iccas.ac.cn; wanlijun@iccas.ac.cn.

b College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China.

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