Alkali metal cation intercalation properties of titanate nanotubes

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Hydrothermally synthesized titanate nanotubes show high alkali metal cation intercalation reactivity evidenced by high resolution microscopic examination, elemental mapping and profiling techniques as well as wet chemical analysis.

Recently, a simple method pioneered by Kasuga *et al.* based on hydrothermal re-crystallization of TiO_2 in concentrated aqueous NaOH solution routinely producing high purity nanotubes has generated great interest.[1–4] Crystallographic descriptions of these nanotubes were proposed based on tetragonal anatase TiO_2,[1,3] layered protonic titanates such as monoclinic trititanate $H_2Ti_3O_7$[2] or orthorhombic lepidocrocite-type $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$ ($\square$: vacancy).[4] Currently it is reasonably accepted that the nanotubes are of layered titanate nature with an interlayer distance ~0.9 nm. Successful layer-by-layer assembly of the titanate nanotubes into ultrathin films and incorporation of monodispersed noble metal nanoparticles (Ag, Au) into the tube cavity have been demonstrated.[5,6] Due to their structural origin, derived from TiO_2, the nanotubes invite potential in photocatalysis, solar energy conversion, electrochromic and self-cleaning devices.[7,8]

The interlayer chemistry of bulk layered titanates has been studied extensively.[9–11] Layered titanates are usually composed of stepped or corrugated host layers of edge-shared TiO_6 octahedra and interlayer alkali metal cations (H^+/H_3O^+ in protonic form). The interlayer cations are exchangeable with a variety of inorganic and organic cations. On the other hand, the titanate nanotube is constructed from rolling-up a titanate sheet with a spiral cross section.[4] Inspired by the excellent ion-exchange/intercalation ability of the parent titanates, it is of particular interest to look into the interlayer chemistry of the peculiar nanotubular framework *via* some soft chemical methods. However, there is still no work specifically dealing with this important topic. Herein we report for the first time the interlayer chemistry of the nanotubes investigated by the means of intercalation with alkali metal cations. The high resolution microscopic examination and advanced elemental profiling clearly indicate the intercalation of alkali metal cations into the tubular layers. The high intercalation reactivity features make us anticipate potential applications of titanate nanotubes in ion-exchange and separation processes, solidification/immobilization of radioactive nuclides, and lithium batteries.

The method employed for nanotube synthesis basically follows our previous report.[4] The obtained nanotubes are likely to be of protonic titanate nature ($H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$) without detectable residual Na. Nanotubes (0.1 g) were soaked with 10 cm^3 of aqueous solutions containing alkali metal (Li, Na, K, Rb, Cs) hydroxides (concentration of 0.1 mol dm^{-3}) at room temperature for 3 days. The soaked sample was centrifuged, washed repeatedly with copious amounts of deionized water and air-dried.

The solid phases separated from the above procedures were examined by means of X-ray powder diffraction (XRD), wet chemical analysis and microscopic characterization. XRD patterns were collected on a Rigaku Rint-2000 diffractometer with a monochromatic Cu-Kα irradiation (λ = 0.15405 nm). High resolution transmission electron microscopy (HRTEM) characterizations were performed on a field emission JEM-3000F (JEOL) electron microscope operated at 300 kV equipped with a Gatan-666 electron energy loss spectrometer (EELS) and energy dispersive X-ray spectroscopy (EDS). A newly developed high-resolution energy filtering transmission microscope (JEOL, 3100F Omega filter) was also employed to perform elemental mapping and profiling.

During the soaking of the nanotubes in alkali metal hydroxide solution, the interlayer protons (in the form of H_3O^+) are anticipated to be exchanged for the alkali metal ions. The ~0.9 nm layered distance of the nanotubes after the exchange processes, verified by XRD measurements (not shown), remains almost unchanged. The uptake amount, x mol per formula weight in $A_xH_{0.7-x}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$ (where A denotes alkali metal cations), for Li^+, Na^+, K^+, Rb^+, Cs^+ is determined by chemical analysis to be 0.51, 0.53, 0.46, 0.49, 0.44, respectively. The ~0.5 mol uptake capacity per formula weight is very close to that of bulk lepidocrocite titanate.[10] The uptake capacity corresponds to ~70% consumption of exchangeable protons and a monolayer arrangement of the cations and H_2O molecules in the galleries. In bulk lepidocrocite titanate, an overloading of Li ions expanding the gallery spacing to ~1.1 nm was observed. This is not the case for the current nanotubes. The interlayer spacing of nanotubes may be more difficult to expand than bulk titanate as a result of the peculiar morphology.

Microscopic observations on the cation-exchanged nanotubes reveal that they become more "robust" than the original ones. In fact, the layered structure of as-prepared protonic titanate nanotubes are very fragile with interlayer H^+/H_3O^+ and are easily damaged by the electron beam irradiation during observations. However, the cation-exchanged nanotubes are generally more stable under the electron beam, probably due to the intercalated alkali cations playing a role in pinning adjacent layers. Here we chose nanotubes exchanged by the heaviest Cs cations to show this effect. A typical TEM image of the Cs^+-exchanged nanotubes is shown in Fig. 1. The robust layered structure is not sensitive to the electron beam, allowing detailed high resolution microscopic examinations.

Fig. 2a displays a HRTEM image of a Cs^+-exchanged nanotube. The dark contrast parallel fringes may be regarded as the tubular layers of TiO_6 octahedra, as labeled by white lines. The

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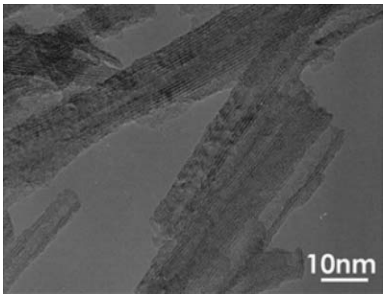

Fig. 1 Typical TEM image of Cs^+-exchanged nanotubes.

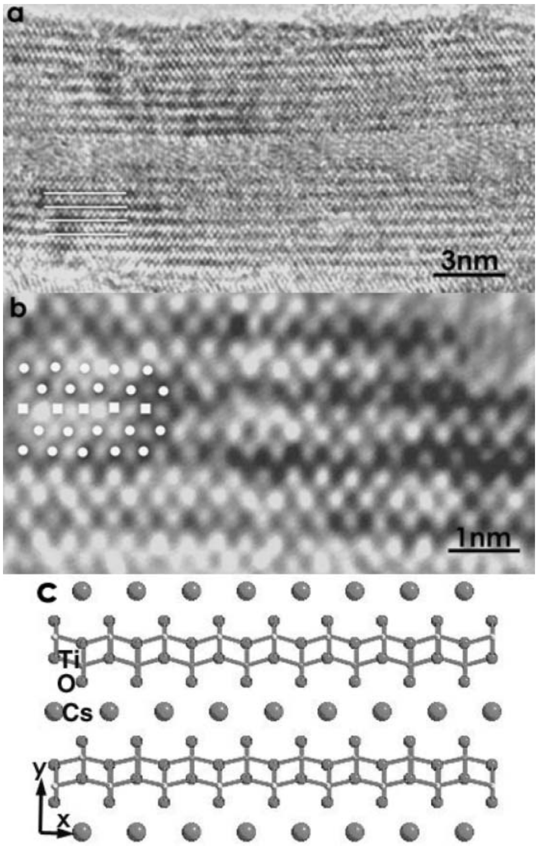

Fig. 2 (a) HRTEM image (white lines indicate the titanate layers). (b) Enlarged image with atomic positions of TiO_6 octahedra (circles) and Cs cations (squares) illustrated. (c) Atomic model of lepidocrocite $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ viewed along [001].

lattice fringes are further enlarged in Fig. 2b. The dark contrast dots in the image are likely to correspond to TiO_6 octahedra and Cs cations. The possible atomic positions of the octahedra (circles) are thus illustrated. The zigzag octahedra at two different levels along the layer normal reflect corrugated host layers. The exact position of the interlayer Cs cations (squares) can also be determined. The image agrees well with the schematic atomic model of $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ viewed along [001] (Fig. 2c). The excellent consistency provides evidence for the intercalated nature of Cs cations into tubular titanate host layers.

Fig. 3 shows the elemental profiling results of the Cs^+-exchanged nanotubes using Ti-K, O-K and Cs-L edges. In Fig. 3b–d, the elemental maps represent the distribution of atomic concentrations of Ti, O and Cs in the nanotubes. The signal : noise ratio of Cs-L mapping is somewhat poorer than that of Ti-K and O-K. Nevertheless, it still distinguishes the spatial correlation of Cs concentration within the nanotubes. To further identify the distribution of Cs in an individual nanotube, an elemental profile was obtained by scanning a finely focused electron probe across a nanotube (arrowed in Fig. 3a) and recording the EDS spectra (so-called line-scan profiling).[12] Again, the K-edge weights were normalized for Ti and O while the L-edge was used for Cs. As shown in Fig. 3e, all the profiles of Ti, O and Cs show two peaks with a central valley, featuring tubular geometry due to the projection of cylindrical distribution.[12] As the Cs-L profile changes accordingly with that of Ti-K and O-K, it strongly indicates that the Cs cations are indeed intercalated into the nanotube layers, not adsorbed on the outer/inner surface.

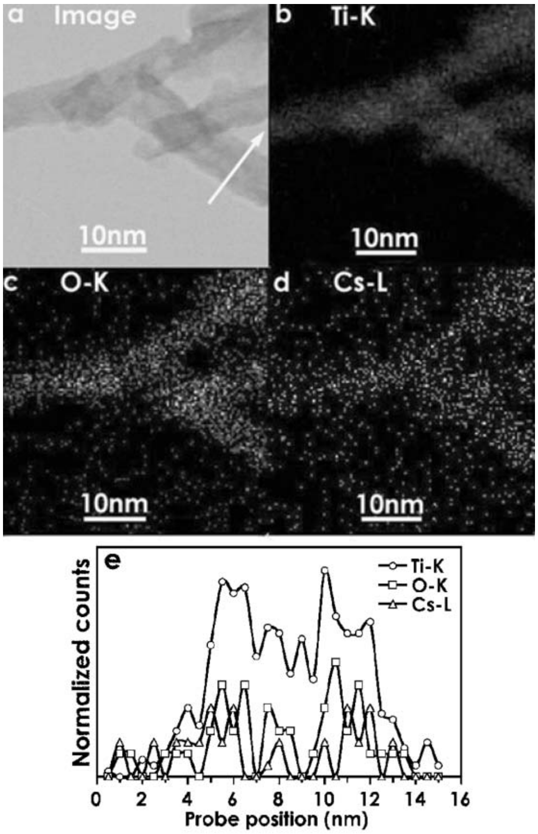

Fig. 3 Elemental mapping (a–d) and line-scan profiling (e) of Cs^+-exchanged nanotubes with Ti-K, O-K and Cs-L edges.

In summary, titanate nanotubes show high ion-exchange reactivity with alkali metal cations. The cations, intercalating into the tubular layers and pinning adjacent ones, enable better crystallinity of the nanotubes. This work may provide a new clue for chemical modification of the nanotubes. Besides inorganic cations, it should be also of interest to study the intercalation properties of the nanotubes with organic ammonium ions. This is in progress and may be reported elsewhere.

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