

# Chemical synthesis of transition metal oxide nanotubes in water using an iced lipid nanotube as a template†

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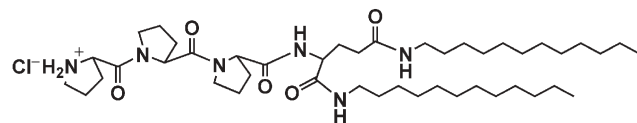
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An iced lipid nanotube has been employed as a template to perform sol-gel transcription of transition metal alkoxides in the absence of solution catalysts, giving titania, tantalum oxide and vanadium oxide nanotubes in aqueous dispersions.

The exceptional physical properties of transition metal oxides are of particular interest in developing next-generation materials in the fields of electronics and advanced catalysts.<sup>1</sup> In particular, titania nanotubes have attracted considerable attention for use in gas sensors, photocatalysts, environmental purification and high-effect solar cells.<sup>2–4</sup> Hence, many efforts have been made to fabricate and manipulate titania nanotubes using electrodeposition,<sup>3,5</sup> hydrothermal methods<sup>6</sup> and template methods.<sup>7</sup> Among these different fabrication methods, the template method, especially using organic templates, has become the most promising from the viewpoint of diverse structures and easy synthesis.<sup>8</sup> Recently, it was reported that a sol-gel transcription process using organo-gelators as templates can produce titania nanotubes or nanocoils.<sup>9</sup> However, these processes always occur in organic solvents such as dichloromethane, ethanol and butanol in the presence of only a small amount of water. Other organic templates from surfactants, lipids and biomolecules, which can self-assemble in water, only give silica structures or titania porous materials and particles.<sup>10</sup> Here we first describe the aqueous sol-gel transcription from an iced lipid nanotube template into transition metal oxide nanotubes, which proceeds in water containing no solution catalysts.



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The lipid nanotube template was obtained by the self-assembly of peptidic lipid **1**<sup>11</sup> in Milli-Q water.‡ This peptidic lipid with a secondary ammonium cation proved to act as a template in order to direct sol-gel replication to silica nanotubes.<sup>12</sup> Scanning transmission electron microscopy (STEM) for the stained assemblies from **1** indicated the formation of large amount of

tubular structures with average outer diameters of 80 nm. AFM measurement proved that these lipid nanotubes possess very thin walls consisting of only a single bilayer. Nanotubes of **1** in an aqueous solution have been directly used to undergo sol-gel transcription. Titanium isopropoxide Ti(OPr)<sub>4</sub> (10 vol%) as a precursor was dispersed into ethanol and cooled to -20 °C. To compare the present method with the general process, we carried out the sol-gel reaction using wet lipid nanotubes in aqueous solutions (case I) or vitrified nanotubes in ice (case II). In case I, an ethanol solution of Ti(OPr)<sub>4</sub> (50 μl) was added to aqueous solutions containing nanotubes of **1** (1 g l<sup>-1</sup>, 400 μl) at 0 °C. The reaction mixture was then allowed to stand at 0 °C for several days. In case II, the aqueous dispersion was firstly frozen to an iced solid state by freezing it in liquid nitrogen (30 s). The ethanol solution of Ti(OPr)<sub>4</sub> (50 μl) was then added to the iced lipid nanotubes at -20 °C and the whole reaction system was then kept at 0 °C for 2 weeks.

Interestingly, we found that the appearances of these two reaction systems after the sol-gel process differed considerably from each other. The first case gave an aqueous dispersion with a white precipitate at the bottom of the flask. The second system gradually turned out to be a gel state. The precipitate and the gel were then lyophilized under 2 Pa.

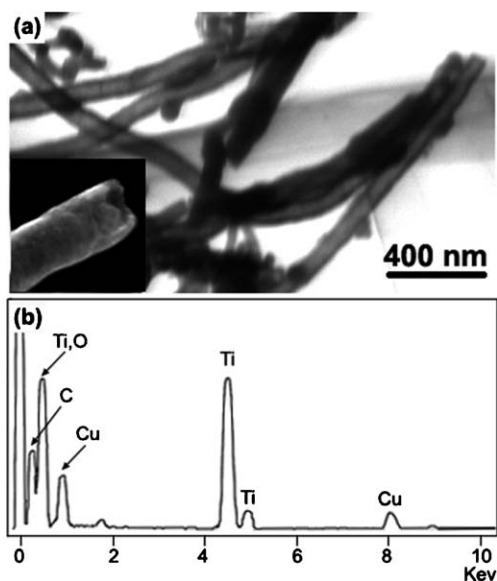
Field-emission scanning electron microscopy (FE-SEM) for the precipitate revealed that it corresponds to aggregates of small particles 20 nm wide and no tubular structures were found. On the other hand, STEM images for the gel samples indicated a large amount of tubular structures as a major product. The removal of the organic template by calcination at 500 °C under air resulted in open-ended tubular structures with outer diameters of about 80 nm, and 20–30 nm wall thickness (Fig. 1a). FE-SEM coupled with the energy dispersive X-ray (EDX) analysis for the tubular structures indicated that they are titania nanotubes (Fig. 1b).

Titanium precursors have high reactivity to water or moisture, since they are known to be more electropositive than silica precursors.<sup>13</sup> The reaction rate of the titania precursors in hydrolysis and condensation is about 5 orders of magnitude faster than that of silica precursor.<sup>14</sup> Thus, the existence of large amounts of water in case I will allow the reaction to finish in a few minutes, before the adsorption of the precursor on the template surface. The titanium precursors themselves could also affect or destroy the structures of the lipid nanotube template. We compared the amide I and II bands in the FT-IR spectra of the lipid nanotube template, the TiO<sub>2</sub>-lipid hybrid precipitate obtained in case I and the TiO<sub>2</sub>-lipid hybrid nanotubes in case II (Fig. 2). The amide I and II bands for the TiO<sub>2</sub>-lipid precipitate appeared at 1631 and 1565 cm<sup>-1</sup>, respectively, each showing slightly lower and higher wavenumber

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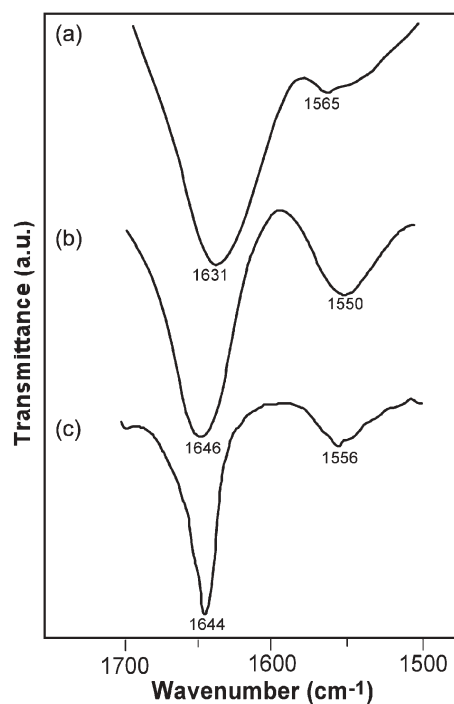
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**Fig. 1** (a) STEM image of titania tubular structures after calcination and the inset picture is a SEM image showing an open-ended titania nanotube. (b) Energy dispersive X-ray spectrum for the titania nanotubes. Copper originates from the STEM copper grid.

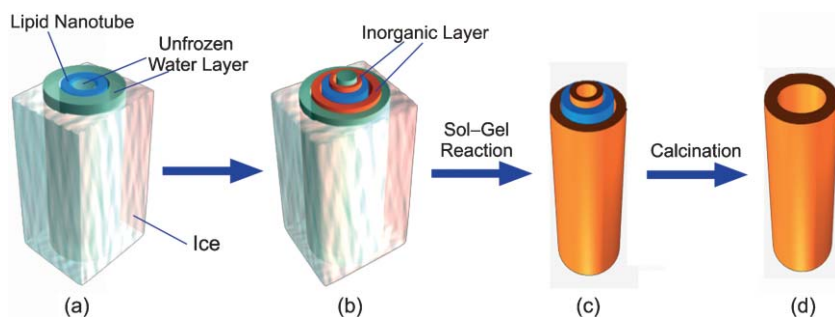
shift. The frequencies for the lipid nanotube template ( $1644$  and  $1556\text{ cm}^{-1}$ ) and the  $\text{TiO}_2$ -lipid hybrid nanotubes ( $1646$  and  $1550\text{ cm}^{-1}$ ) showed IR bands in a similar wavenumber region, indicating that the nanotube template has maintained its tubular morphology during the sol-gel transcription. These findings suggest that in case I relatively stronger hydrogen-bonding resulted in the destruction of the tubular template structures. Furthermore, we found that the self-assembled morphology of **1** was very sensitive to the amount of alcohol in the mixed alcohol-water solvent. Addition of ethanol ( $>50\text{ vol}\%$ ) resulted in no tubule formation. This factor will also be the reason for the failure of transcription in case I. However, all these unfavourable factors are suppressed in case II. The phase change from an aqueous dispersion to the iced solid state allowed the sol-gel reaction of the titanium alkoxide to proceed in gradually melted water. When the ethanol solution was added to the iced nanotubes, the antifreezing ethanol molecules would permeate into the ice and eventually melt it. We suggested that the iced lipid nanotube



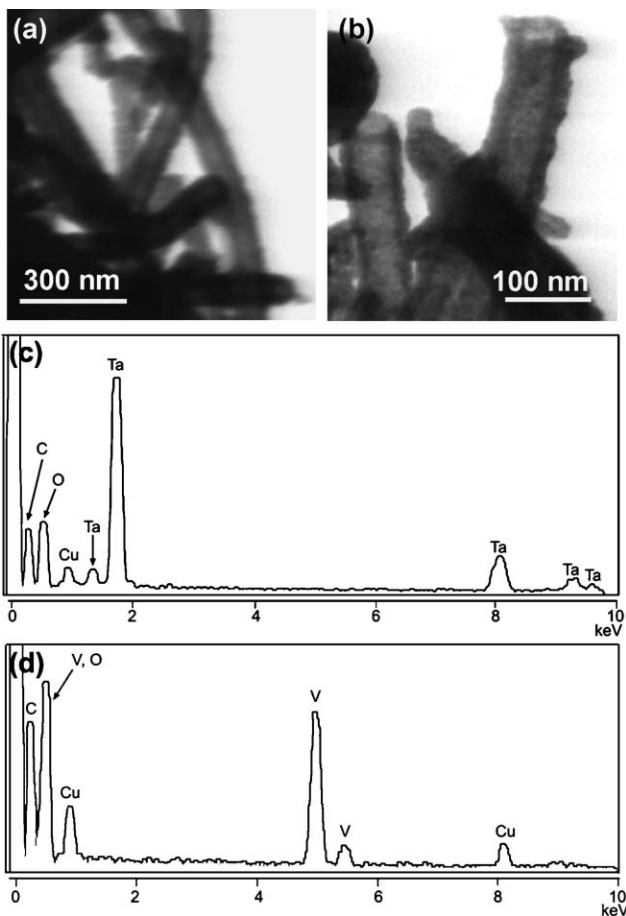
**Fig. 2** A comparison of FT-IR spectra for (a) the  $\text{TiO}_2$ -lipid hybrid precipitates in the case I, (b) the  $\text{TiO}_2$ -lipid hybrid nanotubes in the case II and (c) the dry lipid nanotube template.

obtained by short-time freezing in liquid nitrogen possessed an unfrozen water layer around the lipid nanotube surfaces. When the iced lipid nanotubes begin to melt, the ethanol solution of the precursors would permeate into this unfrozen water layer and cause initial hydrolysis (Fig. 3). Consequently, the sol-gel reaction will gradually proceed under the circumstances of iced lipid nanotubes at  $0\text{ }^\circ\text{C}$ . At this low temperature, the influence of the inorganic precursors and ethanol on the nanotube template is also negligible. Eventually titania layers form at the surfaces of the nanotube template. Thus the iced lipid nanotube has been well transcribed into titania nanotubes.

Similarly, besides titania nanotubes, we have explored the transcription of other transition metal oxides, such as tantalum oxides and vanadium oxides, by using the iced lipid nanotube as a template. Based on the STEM and SEM observation coupled with



**Fig. 3** A possible sol-gel transcription mechanism from an iced lipid nanotube to the nanotube of transition metal oxides. (a) An iced lipid nanotube vitrified in ice by freezing in liquid nitrogen. The water molecules around the lipid nanotubes are considered to be incompletely frozen due to the short time of freezing. (b) Ethanol solutions of transition metal alkoxides permeate into the ice and hydrolysis occur within the unfrozen water layer. (c) Sol-gel reaction gradually proceeds at  $0\text{ }^\circ\text{C}$ , eventually giving a transition metal oxide-lipid hybrid nanotube. (d) After calcination a transition metal oxide nanotube is obtainable.



**Fig. 4** STEM images of (a) tantalum oxide nanotubes and (b) vanadium oxide nanotubes obtained in aqueous dispersions by using the iced lipid nanotube as a template. EDX spectra of (c) the tantalum oxide nanotubes and (d) the vanadium oxide nanotubes.

EDX analysis (Fig. 4), we found that both of them produced definite tubular structures with open ends. In addition, the XRD measurement showed that these transition metal oxide nanotubes after calcination possess crystalline features.<sup>†</sup>

In conclusion, sol-gel transcription using an iced lipid nanotube as a template was successfully achieved in water to obtain well-defined nanotubes consisting of transition metal oxides. This method will have great significance in the fabrication of inorganic materials from organic templates, especially in aqueous dispersions. This bio-inspired process will certainly lead to the efficient fabrication of diverse organic-inorganic hybrid nanomaterials with well-defined morphologies.

## Notes and references

<sup>†</sup> Preparation of lipid nanotube dispersion: 1 mg lipid **1** was added into 1 ml of Milli-Q water. The aqueous dispersion was then sonicated at 50 °C until

a clear solution was obtained. Then the solution was allowed to gradually cool to room temperature.

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