

A novel synthetic route to TiO₂-pillared layered titanate with enhanced photocatalytic activity†

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A novel pillaring procedure has been developed to prepare TiO₂-pillared layered titanate with large surface area, high thermal stability, and enhanced photocatalytic activity.

Recently, intense research efforts have been devoted to the pillaring of sol particles into layered inorganic solids, since this can provide a useful method not only of creating novel porous materials but also for improving the catalytic activity of pillaring agents. Actually, it has been reported that the pillaring of semiconducting materials such as CdS–ZnS, Fe₂O₃ and TiO₂ gives rise to a remarkable enhancement of their photocatalytic activity compared with unsupported catalysts.^{1–3} Such photocatalytic activity of semiconductor pillars is also known to be dependent on the type of host layer. For example, a CdS–ZnS pillar stabilized in the interlayer space of a layered semiconductor shows much higher photoactivity than that pillared in the insulating host lattice.^{1,3} This can be understood from the fact that recombination between electrons and holes is effectively suppressed due to electron transfer between guest and host.⁴ In spite of this advantage of the semiconductor–semiconductor pillar system, it is not easy to construct a semiconducting pillar such as TiO₂ in layered titanate or titanoniobate since these types of host materials do not possess swelling ability. In order to overcome this shortcoming of layered semiconducting materials, a templating technique has been suggested in which the interlayer spacing of layered transition metal oxide was pre-expanded with long alkylamine chains and then metal oxide sol particles were subsequently introduced.⁵ However, the TiO₂-pillared layered titanate prepared by the templating method also exhibits some limitations, such as poor thermal stability, low surface area, and poor crystallinity.⁶ This limitation of the templating method could be explained as resulting from the high layer charge of the host lattice which prevents an effective intercalation of TiO₂ sol particles, since the interlayer space of the host layer does not undergo sufficient swelling to permit large guest species to be intercalated. In this regard, a new synthetic route is much needed in order to synthesize a semiconductor–semiconductor pillar system with suitable porosity. More recently, exfoliation of various layered host materials has been extensively studied since it allows the fabrication of thin/thick films or nanoparticles through lattice engineering.^{7–9} Among various semiconducting compounds, a caesium titanate with a lepidocrocite-like structure is known to be exfoliated into single sheets by intercalating a bulky tertiary

ammonium salt.¹⁰ In light of this, we have developed a novel exfoliation–restacking route to generate a well ordered TiO₂-pillared layered titanate with enhanced photocatalytic activity. This TiO₂-pillared titanate shows larger interlayer spacing with higher surface area than the other pillared systems produced *via* conventional methods.^{4–6}

The host caesium titanate, Cs_{0.67}Ti_{1.83}□_{0.17}O₄, was prepared by heating a stoichiometric mixture of Cs₂CO₃ and TiO₂ at 800 °C for 20 h.¹¹ The corresponding protonic form, H_{0.67}Ti_{1.83}□_{0.17}O₄·H₂O, was obtained by reacting the caesium titanate powder with 1 M HCl aqueous solution at room temperature for 3 days. During the proton exchange reaction, the HCl solution was replaced with a fresh one every day.¹² The layered protonic titanate was exfoliated into single titanate sheets by intercalating the TBA (tetrabutylamine) molecule, as reported previously.¹⁰ On the other hand, a mono-dispersed and non-aggregated TiO₂ nano-sol was prepared by adding dropwise titanium isopropoxide (30 ml) with acetylacetone (20.38 ml) to 0.015 M HNO₃ aqueous solution (180 ml) with vigorous stirring, and then by peptizing at 60 °C for 8 h.¹³ A TiO₂-pillared layered titanate was prepared by hybridizing the exfoliated layered titanate particles with the TiO₂ nano-sol at 60 °C for 24 h. The resulting powder was collected by centrifuging (12 000 rpm, 10 min), washed with a mixed solution of distilled water and ethanol (1:1, v/v) to remove excess TiO₂ sol, and then dried in ambient atmosphere. Finally, the obtained material was heated at 300 °C for 2 h in order to complete the pillaring process.

Both the XRD patterns of the pristine layered caesium titanate and its protonated derivative are found to be well indexed on the basis of the lepidocrocite structure with orthorhombic symmetry (ESI†). Upon acid treatment, the (020) reflection is shifted toward a higher angle indicating a lattice expansion due to the intercalation of water molecules into the interlayer space of layered titanate. Fig. 1 represents the XRD patterns of the selected samples under the pillaring process. From the (020) reflection at $2\theta = 9.6^\circ$ [Fig. 1(a)], a basal spacing of 0.92 nm for the layered protonic titanate can be determined. Before the ion-exchange reaction with the TiO₂ nano-sol, the layered protonic titanate was exfoliated by intercalating tetrabutylammonium hydroxide. The exfoliated titanate does not show any basal reflections, indicating that the titanate single sheets are dispersed in an aqueous medium. Upon reaction of the exfoliated titanate with anatase TiO₂ nano-sol, the (020) reflection of the protonic form is displaced to the (010) reflection of the restacked titanate at a lower angle ($2\theta = 2.1^\circ$, $d = 4.36$ nm), suggesting that the mono-dispersed TiO₂ nano-sol is stabilized in the interlayer space of titanate. The well developed (000) peaks at $2\theta = 2.1$, 4.2 and 6.3° indicate that the resulting TiO₂-pillared titanate is fairly well ordered along the *b*-axis [Fig. 1(b)]. After calcinating at 300 °C for 2 h, its basal spacing decreases to 2.56 nm [Fig. 1(c)], which is

†Electronic supplementary information (ESI) available: XRD patterns and crystallographic data for pristine layered caesium titanate and its proton exchanged form, and XRD pattern of the anatase TiO₂ nano-sol used as pillaring agent. See <http://www.rsc.org/suppdata/jm/b1/b104551m/>

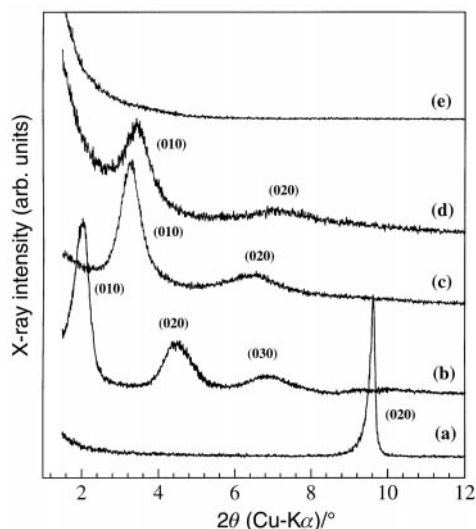


Fig. 1 Powder XRD patterns of the layered protonic titanate (a), TiO₂ nano-sol intercalated titanate (b), TiO₂ nano-sol pillared titanate with the heat treatment at 300 °C (c), 350 °C (d) and 400 °C (e) for 2 h, respectively.

mainly attributed to the dehydroxylation of the pillared TiO₂ nano-sol particle and to the pyrolysis of acetylacetonate molecules coordinated to the surface of the TiO₂ nano-sol. Such a pillared structure is maintained even after calcining at 350 °C for 2 h [Fig. 1(d)], whereas it becomes collapsed to an amorphous phase above 400 °C [Fig. 1(e)]. It is worthwhile to mention here that the thermal stability of the layered titanate is significantly enhanced by pillaring TiO₂ sol particles, which is attributed to the formation of strong bonds between TiO₂ nanoparticles and the layered titanate lattice in the interlayer space.

According to the nitrogen adsorption–desorption isotherms, the present TiO₂-pillared layered titanate could be of type I and/or IV in the BDDT classification,¹⁴ which is characteristic of microporous adsorbents (Fig. 2). In addition, the hysteresis loop resembles H4 in the IUPAC classification,¹⁴ indicating the presence of open slit-shaped pores with fairly wide bodies and narrow, short necks. The surface area of the TiO₂-pillared titanate is determined to be *ca.* 460 m² g⁻¹ with a pore volume of 0.17 ml liquid nitrogen per gram of material, which is significantly larger than that of the pristine layered caesium titanate (*ca.* 1 m² g⁻¹), and is the largest surface area among semiconducting nano-sol particle-pillared layered transition

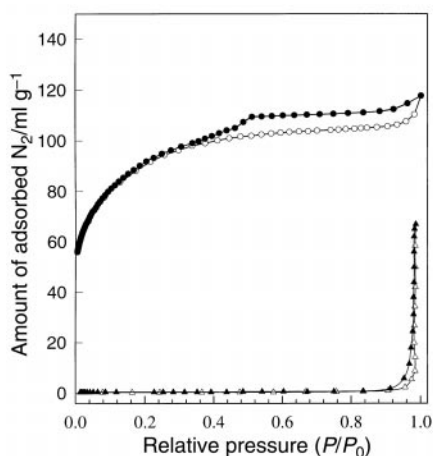


Fig. 2 Nitrogen adsorption–desorption isotherms of the layered caesium titanate (triangles) and the TiO₂-pillared layered titanate (circles) calcined at 300 °C for 2 h. The filled and open symbols represent adsorption and desorption data, respectively.

metal oxides so far reported. The pore size distribution curve has been calculated by using the micropore analysis (MP) method, which reveals that the pores in TiO₂-pillared titanate consist mainly of micropores with a size of *ca.* 0.95 nm.¹⁵

It is worthwhile to note here that the present TiO₂-pillared titanate shows not only the largest specific surface area but also the highest thermal stability up to 350 °C. It could only be realized by combining two notable steps, namely the exfoliation of the host titanate layer and its restacking in the presence of the well developed anatase TiO₂ nano-sol. Such a pillaring between exfoliated titanate and anatase TiO₂ nano-sol at the molecular level is found to be advantageous for the preparation of porous structured material, since it provides a way of accessing guest species freely in the interlayer space of the host lattice without any steric hindrance. A driving force for the hybridization reaction might be a kind of van der Waals interaction between tetrabutylamine molecules on the surface of the exfoliated titanate sheet and acetylacetonate molecules on the TiO₂ nano-sol. In this regard, the most important step for hybridization is thought to be the step involving the preparation of the mono-dispersed and non-aggregated TiO₂ nano-sol particles. This can be accomplished by using a strong complexing ligand such as acetylacetonate since it also plays a role as a blocking agent preventing the particle growth. The obtained TiO₂ nano-sol particle is also found to be anatase from the XRD measurements.

The photocatalytic activity of the pillared material was evaluated by measuring the total volume of hydrogen gas evolved during the irradiation of catalyst suspensions in water (Fig. 3). Compared with the pristine layered caesium titanate (2.00 μM h⁻¹), the TiO₂-pillared titanate shows higher catalytic activity (8.68 μM h⁻¹), which is not only due to the presence of the anatase TiO₂ nano-sol particles stabilized in the interlayer space of layered titanate but also to the suppression of electron–hole recombination. It is worthwhile to note here that the photocatalytic activity result for the present samples was obtained in a Pyrex reactor with a very small capacity of 30 cm³.¹⁶ Since the photocatalytic activity is dependent on the number of photoinduced electrons, which are proportional to the surface area of catalyst interacting with photons, a further study is therefore needed in order to enhance the photocatalytic activity by enlarging the reactor size (>1000 cm³) and its design.

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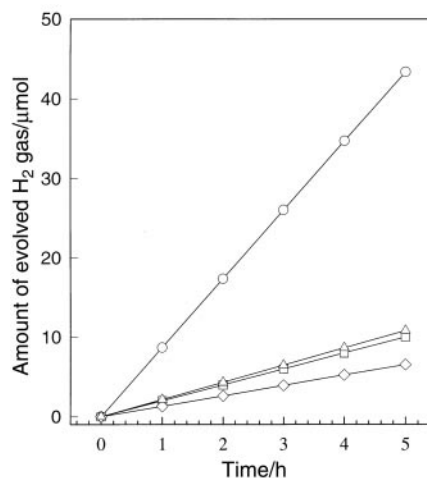


Fig. 3 Cumulative amount of hydrogen gas evolved from 30 cm³ solution of 0.1 M triethanolamine containing 10 mg of dispersed layered caesium titanate (squares), layered protonic titanate (diamonds), anatase TiO₂ nano-sol particles (triangles), and TiO₂-pillared layered titanate (circles), respectively.

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- 16 Photocatalytic reactions have been carried out in a Pyrex reactor with a capacity of 36 cm³, which is attached to an inner radiation-type 600 W Xe lamp. The inner cell had thermostated water flowing through a jacket between the Xe lamp and the reaction chamber, and was constructed with quartz glass. The catalyst (10 mg) was dispersed in 30 cm³ of 0.1 M triethanolamine solution by magnetic stirring and was irradiated by a Xe lamp for 20 h. The photocatalytic activity of the catalyst was determined by measuring the total gas volume of hydrogen evolved during the irradiation of the catalyst suspension in water with a gas burette after confirming the production of hydrogen by gas chromatography (HP5890) using a molecular sieve 13X column.