

Derivated titanate nanotubes and their hydrogen storage properties

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Titanate nanotubes and their derivates, Pd-loaded and Co²⁺, Zn²⁺, Cu²⁺, and Ag⁺ ion-exchanged titanate nanotubes, were respectively prepared and characterized by XRD, HR-TEM, and EDS. Their hydrogen storage properties were investigated, and the results revealed that the derivated titanate nanotubes had better hydrogen storage characters. Pd-loaded titanate nanotubes exhibited the highest hydrogen storage capacity of 1.03 wt%, which is three times higher than that of raw titanate nanotubes. The ion-exchanged titanate nanotubes also showed enhanced capacity. Especially, Co-TiNT reached a storage capacity of 0.80 wt%. The reason why hydrogen storage capacity was enhanced in titanate nanotubes was a pilot study. These results indicated that oxide nanotubes provided some new opportunities for hydrogen energy applications.

Keywords titanate nanotube, Pd-loaded, ion-exchanged, hydrogen storage capacity

1 Introduction

As a kind of nanoporous materials with crystalline structure, nanotubes in varied compositions and sizes have attracted intensive study interests [1–4]. Their utilities in many fields, such as catalysis and sorbents, have also been extensively investigated in the last ten years [5–7]. One-dimensional nanostructured compounds are a kind of promising materials for hydrogen storage owing to their unique chemical, physical, thermodynamic, and transport properties [8,9]. However, in the field of hydrogen storage, only the nanotubes of carbon were carefully studied [10–12]. The applications of other inorganic counterparts, especially oxide nanotubes were rarely reported [13–15]. Recently, titanate nanotubes attracted

more and more attention [16] because of their potential applications in various fields, such as catalysts [17], gas sensors [18], Li-ion batteries [19], solar batteries [20], and absorption materials for radioactive ions [21]. However, the investigation of titanate nanotubes as hydrogen storage materials, especially those with addition of small amounts of noble or transition metals, was seldom reported [22]. Herein, we presented our approach to Pd-loaded and transition metals ion-exchanged titanate nanotubes. The investigations of their hydrogen storage properties revealed the possibility of practicing them for hydrogen energy applications in the future.

2 Experimental

Titanate nanotubes (TiNT) were synthesized based on established method [23,24]. Loading of Pd nanoparticles on titanate nanotubes was performed using a reflux method with alcohol as reductive [25]. All reagents were in A.R. grade. In a typical procedure, 0.5 g titanate nanotubes were dispersed in the mixture of 30 mL water and 20 mL alcohol, aided by ultrasonication for 10 min. 0.03 g PdCl₂ was dissolved in 2 mL diluted aqueous HCl solution (pH = 3) and then added dropwise to the above suspension with simultaneous ultrasonication for another 10 min. The resulting mixture was stirred and refluxed for 1 h before cooling to room temperature. The product was obtained after filtration, rinsed with water and alcohol for 3 circles, and dried at 80°C for 4 h.

Transition metals ion-exchange reactions were carried out at ambient temperature and pressure [24]. In a typical process, 25 mmol transition metal salts (CoCl₂, NiCl₂, ZnCl₂, or AgNO₃) were dissolved in 50 mL water to form clear aqueous solutions. Concentrated aqueous ammonia solution was added dropwise under ultrasonication until the initially formed precipitations were dissolved to form clear ammine solutions. Then, 0.5 g titanate nanotubes with intercalated Na⁺ ions were dispersed and ion-exchanged in the above solutions under ultrasonication for 0.5 h. After filtration, the wet samples were dispersed again in newly prepared transition metal ammine solutions to further eliminate the residual sodium ions in the nanotubes. Such process was repeated three times until sodium ions were not detectable by energy dispersive X-ray analysis (EDS). The samples were filtered, washed, and dried at 80°C for 4 h.

Products were characterized using transmission electron microscopy (TEM, Hitachi 800, and JEM JEOL2010F, both operated at 200 kV) and X-ray diffraction (XRD, Bruker D8 advanced, Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). Hydrogen storage experiments were performed at room temperature in a computer-controlled “gas reaction controller” apparatus,

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which was manufactured by the Advanced Materials Corporation [14]. The raw Pd-loaded or transition metals ion-exchanged titanate nanotubes with a mass of about 0.5 g were used each time for characterization. The pressure of high purity hydrogen gas (99.999%) was controlled to be ranging from 0.01 to 40 atm. The hydrogen adsorption content was defined as the ratio of the mass gain to the mass of raw titanates nanotubes plus mass gain. LaNi₅ alloy was used as standard sample to check the accuracy of the apparatus before and after hydrogen storage experiments.

3 Results and discussion

The raw (TiNT) and Pd-loaded (Pd-TiNT) titanate nanotubes were characterized by XRD and TEM, as shown in Figure 1 and Figure 2, respectively. The XRD pattern of Pd-loaded titanate nanotubes displayed the typical diffraction lines of crystalline TiNT. The position and intensity of diffraction line

series were almost the same as the precursor. The essentially same XRD patterns suggested an identical crystal structure of the two samples, indicating that the crystalline nanotubes had satisfactory chemical stability even after the reflux reaction. The TEM micrograph of Pd-loaded titanate nanotubes, as illustrated in Figure 2 (a), showed that crystalline Pd-TiNT had the similar morphology to the precursor. However, some tiny nanoparticles were observed on the surface of the material. They showed higher contrast due to higher density of Pd electron cloud. This observation confirmed that all the nanotubes retained their tube-like structure after reflux. The Pd nanoparticles loaded on the nanotubes were generally less than 5 nm and were fairly monodispersed in size. Moreover, the atomic ratio of Pd to Ti was about 1/30 according to the EDS data on the Pd-loaded sample, as shown in Figure 2 (b). Because the Pd nanoparticles were small crystallites and little in amount, they were silent in XRD characterization.

The raw and Pd-loaded titanate nanotubes were used for hydrogen storage characterization. Their pressure-composition-temperature (PCT) curves (Figure 3) presented a similar trend: hydrogen adsorption content increased monotonously and thereafter reached a plateau as monitored by the variation in hydrogen pressure. However, the hydrogen content of Pd-loaded titanate nanotubes was clearly higher (~3 times) than that of the unloaded sample under present conditions. It was shown that hydrogen storage capacity of Pd-TiNT was about 1.03 wt% at about 30 MPa, while the amount for TiNT was only 0.33 wt%. Increasing the pressure up to 40 MPa could not further enhance the adsorption amount, implying the saturation of the two samples. Before reaching saturation, Pd-TiNT showed a higher slope than TiNT, suggesting the enhanced storage capacity at low hydrogen pressures. This result was in accordance with that observed on silicate nanotubes [15], in which case the Pd-loaded samples also showed enhanced hydrogen storage capacity before and after

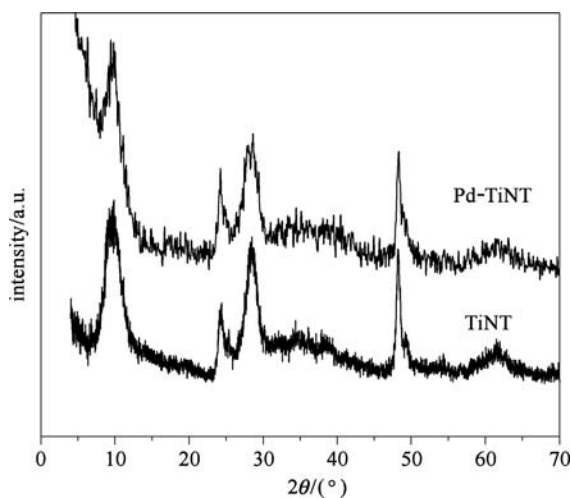


Figure 1 XRD patterns of TiNT and Pd-TiNT.

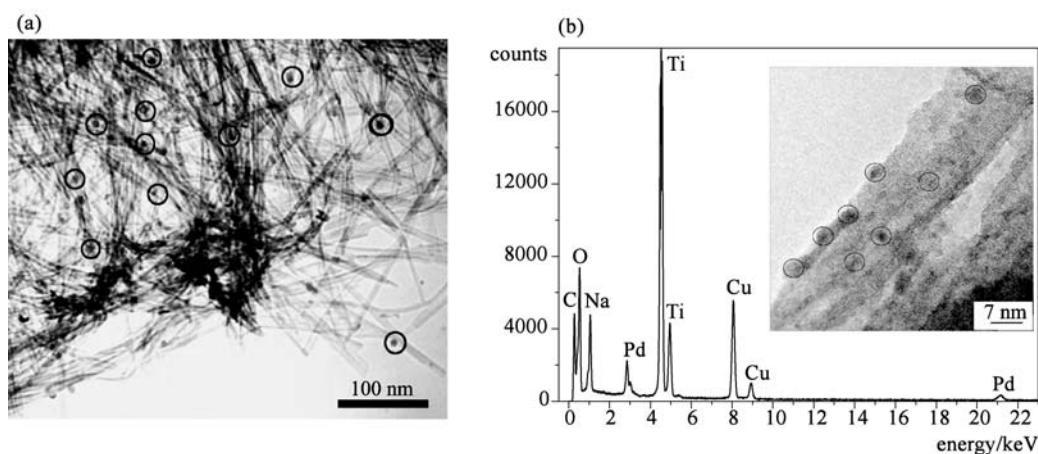


Figure 2 (a) The TEM image of Pd-TiNT; (b) The HRTEM image and the corresponding EDS result.

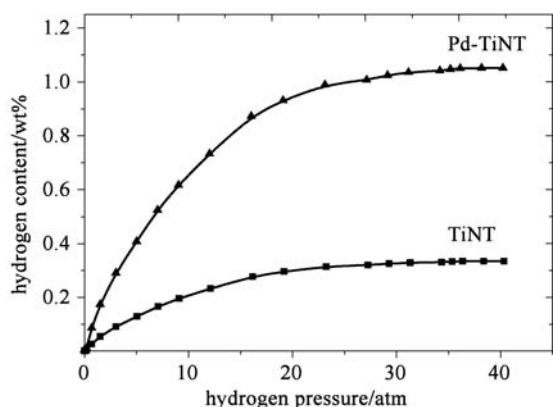


Figure 3 PCT curves for H₂ adsorption of TiNT and Pd-TiNT.

saturation. Actually, the former work had also indicated that Pd-coating on Ni/Mg alloy or Pd-containing in microporous NaY zeolite could increase the amount of stored H₂ [26,27]. The strong enhancement was attributed to the catalytic effect of Pd nanoparticles, which might act as a “hydrogen pump” [26,28]. In this case, the Pd-loaded amount was as low as only 3.3 % in Pd/Ti atomic ratio according to EDS characterization, so that such a large enhancement could not be merely attributed to hydrogen absorption on the Pd nanoparticles.

Another method was explored to enhance hydrogen storage capacity of the nanotubes. Previous work had indicated that transition metal ions in the porous structures might enhance the capacity [29,30] so that we tried to use the transition metals ion-exchanged titanate nanotubes (Co-TiNT, Zn-TiNT, Cu-TiNT, and Ag-TiNT) for hydrogen storage.

TEM images of the ion-exchanged titanate nanotubes confirmed that all the samples retained their tubular structure after ion-exchange reactions. According to the EDS results, the amounts of transition metal ions were even more than the interlayer sodium ions in raw materials, implying that some interlayer protons in the nanotubes were simultaneously

exchanged with the additive ions [24]. For example, Figure 4 displayed the high resolution TEM (HRTEM) micrograph of Co²⁺ ion-exchanged titanate nanotubes and the corresponding EDS spectrum obtained on an individual nanotube. HRTEM image showed that the layered morphology of crystalline Co-TiNT looked like raw TiNT and EDS were employed on more than 10 individual nanotubes to acquire an average Co/Ti atomic ratio of about 1/4. Furthermore, for Ni²⁺ or Zn²⁺ ion-exchanged sample, the atomic ratio of transition metal to Ti was essentially the same as that of Co-TiNT, while Ag⁺ ion-exchanged sample had a different atomic ratio of nearly 1/3. The different ion-exchange capacity for transition metal ions might be related to the various valences of ions: Ag ions were monovalent while the other three were divalent. However, the relative value was not 1/2 because monovalent ions had relatively weak static electronic interactions with negatively charged titanate framework.

The PCT curves of varied transition metals ion-exchanged titanate nanotubes (Figure 5) showed different hydrogen storage properties. The hydrogen storage capacity of Co- and Zn-TiNT after saturation reached 0.80 wt% and 0.54 wt%, respectively. The capacity was better than that of raw TiNT of 0.33 wt%, while the amount of Cu- and Ag-TiNT only reached 0.34 wt% and 0.28 wt%, respectively. It appeared that some transition metal ions could enhance the hydrogen storage capacity of nanotubes but others could not. In fact, the real hydrogen storage capacity of the ion-exchanged titanate nanotubes was enhanced in different degree concerned by the actual content of nanotubes in the samples. The reason is that the hydrogen adsorption content was defined as the ratio of the mass gain to the mass of raw nanotubes plus mass gain, and the quantity of the samples put into the hydrogen storage experiments was fixed at about 0.5 g. However, the ion-exchange reactions essentially led to a mass increase comparing to raw TiNT (~10% for Co-, Zn-, Cu-TiNT, and ~31% for Ag-TiNT). As estimated, the real capacities of Co-

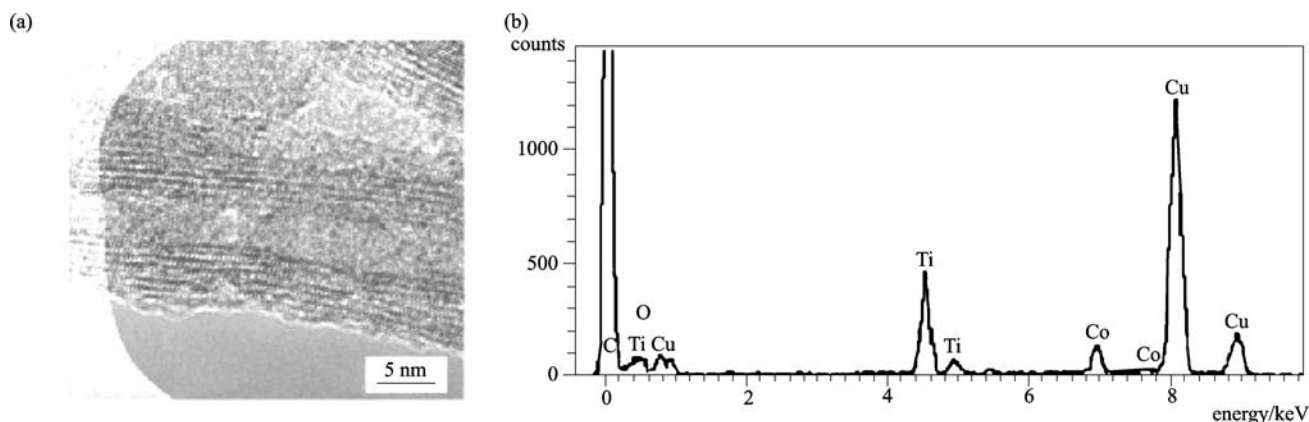


Figure 4 (a) The HRTEM image of Co-TiNT; (b) the corresponding EDS result.

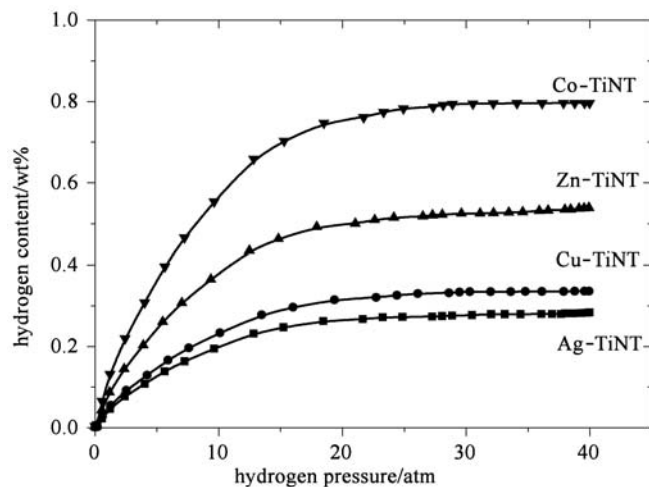


Figure 5 PCT curves for H₂ adsorption of Co²⁺, Zn²⁺, Cu²⁺, and Ag⁺ ion-exchanged TiNTs.

Zn-, Cu-, and Ag-TiNT are ~265%, ~180%, ~115%, and ~110% of raw TiNT, respectively.

The mechanism on how hydrogen is stored in titanate nanotubes and also how transition metal ions and Pd nanoparticles enhance hydrogen storage capacity is still unclear. However, since many reports had revealed that open-ended layer-structured silicate, i.e., TiS₂, MoS₂, and carbon nanotubes, shared good hydrogen storage properties, it was believed that high specific surface areas and layered structures were favorable for hydrogen storage. According to the study on gas-sensing property, hydrogen atoms might have specific interactions with titanium oxides especially in the case of presence of noble metals [31], which also might affect the hydrogen storage process. Further study is required to elucidate the mechanism in detail.

4 Conclusions

The raw titanate nanotubes, i.e., Pd-loaded and Co²⁺, Zn²⁺, Cu²⁺, and Ag⁺ ion-exchanged titanate nanotubes, were prepared and characterized for hydrogen storage property. The Pd-loaded titanate nanotubes exhibited significantly enhanced hydrogen storage capacity comparing to the raw titanate nanotubes. The ion-exchanged ones also obviously enhanced hydrogen storage properties considering the actual content of nanotubes in the samples. The increased hydrogen storage properties might be related to the structure of titanium oxides besides the effect of dispersed noble metal particles. These results indicated that oxide nanotubes were potential hydrogen storage materials and thus provided some new opportunities for hydrogen storage as well as catalytic hydrogenation.

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