

Performance of hydrogen storage of carbon nanotubes decorated with palladium^①

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Abstract: Carbon nanotubes (CNTs) decorated with palladium were synthesized and applied to hydrogen storage of gas phase. The results show that the amount of hydrogen storage of the decorated CNTs is up to 3.9% (mass fraction), of which, almost 85% H₂ can be desorbed at ambient temperature and pressure, while the non-decorated CNTs has a poor performance of hydrogen storage (only about 0.5% H₂, mass fraction). These indicate that it is feasible to enhance the performance of hydrogen storage of CNTs by further decoration with hydrogen-storing metals or alloys.

Key words: carbon nanotubes; hydrogen-storing metals; hydrogen-storing alloys; palladium; hydrogen storage

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1 INTRODUCTION

Some novel approaches were introduced to enhance the amount of hydrogen stored in CNTs, of which, pretreated technologies such as the purification, cutting procedure, defunctionalization were developed^[1, 2]; meantime, CNTs available to store hydrogen were fabricated including the alignment^[3, 4], the high defects or low graphitization^[4-6] and proper aspect ratio aspects^[7], these could enhance the porosity and the surface area of CNTs and improve diffuse channels for hydrogen, leading to an improvement of hydrogen storage performance.

Much attention was paid to hydrogen storage of hydrogen-storing alloys or metals/CNTs composite materials^[8-10]. The main roles of hydrogen-storing alloys or metals are to dissociate hydrogen molecules into atoms or protons, these produced atoms or protons have smaller diameter and lower resistance when they penetrate the sidewalls of tubes to compare with molecules. Therefore, CNTs decorated with hydrogen-storing alloys or metals can improve the performance of storing hydrogen. However, the detailed description in experiments and analyses in references were absent. In this paper, CNTs decorated with Pd were synthesized and applied to hydrogen storage of gas phase, moreover, the mechanism of hydrogen storage was discussed as well.

2 EXPERIMENTAL

2.1 Pretreatment of CNTs

CNTs were produced by catalytic pyrolytic decomposition of the propylene. As-received CNTs (75%, mass fraction) were dispersed in NaOH (2 mol/L) and (CO (NH₂)₂) respectively, and further sonicated for 1 h. Subsequently, they were refluxed in a strong mixed acid (H₂SO₄:HNO₃= 3:1, volume ratio) for 1 h to produce functional groups acted as nucleation sites or active centers to deposit Pd. After washing and drying in vacuum, the pretreated CNTs were obtained and labeled as sample A1.

2.2 Synthesis of CNTs decorated with Pd

The decorating Pd was obtained by chemical reduction reaction:



Pretreated CNTs (sample A1) of 0.5 g was refluxed and sonicated for 1 h in 200 mL PdCl₂ (1 g/L), respectively, NaBH₄ (1 mol/L) was added at a speed of 0.3 mL/min until the solution was colorless. After washing and drying, the decorated CNTs were heat-treated for 1 h at 573 K in Ar atmosphere. The results were labeled as sample B1.

2.3 Characterization of CNTs decorated with Pd

Transmission electron microscopy (TEM)

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samples were prepared by suspending the powder in acetone and dropping onto Cu grids. TEM and ED were performed using Philips CM12, operated at 120 kV. The platinum loading was determined by using of atomic absorption spectrophotometer (Varicam Spectra 30A). FT-IR spectrum and XRD pattern of pretreated CNTs were obtained by NICOLET 170SX and D/MAX-RB, respectively.

2.4 Hydrogen uptake/desorption of CNTs decorated with Pd

The hydrogen uptake/desorption of samples was investigated by pressure differential method using an instrument shown in Fig. 1. The first was to put a dried sample into the sample cell, the cell was fully vacuum-degassed and heated at 573 K for 2 h. When the cell was cooled down to room temperature, pure hydrogen (99.999 9%) was input. Hydrogen uptake curves were output automatically by a computer. When hydrogen pressure reached balance for 2–3 h, the cell was opened for hours at ambient pressure and temperature, the sample was taken out and weighed.

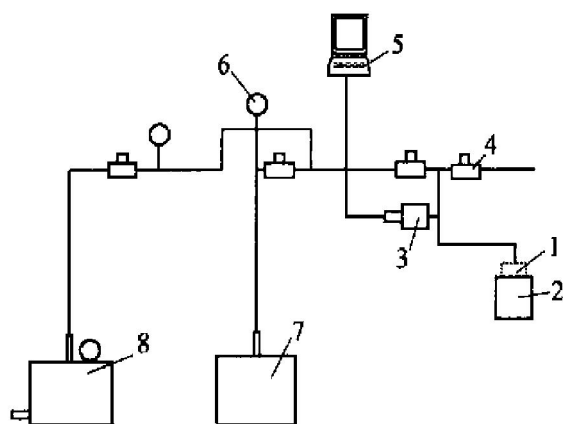


Fig. 1 Schematic of instrument for measuring amount of hydrogen uptake for CNTs

- 1—Sample cell; 2—Heating jacket; 3—High accuracy sensor;
4—Valve; 5—Computer; 6—Pressure gauge;
7—Vacuum pump; 8—Hydrogen purifying train

3 RESULTS AND DISCUSSION

Fig. 2 shows the TEM images of samples. Compared with as-received CNTs (Fig. 2(a)), the purity of pretreated CNTs (Fig. 2(b)) is greatly improved; the outer and inner diameters of tubes are relatively uniform, which are 25–50 nm and 10–20 nm respectively; and most of the caps of tubes are open. Moreover, just as Fig. 3, some groups like C=O and COO⁻ appear in the surface of CNTs during acid oxidation. Fig. 4(a) shows that about 20% of CNTs in sample B1 are enwrapped by non-uniformly distributed crystal Pd. Fig. 4(b) expresses that the coating thickness of Pd is uneven. Crystalline Pd is identified by both the ED (inset in Fig. 4(a)) and XRD pat-

terns (Fig. 5). Pd content in sample B1 is about 30% (mass fraction) determined by atomic absorption spectrophotometer.

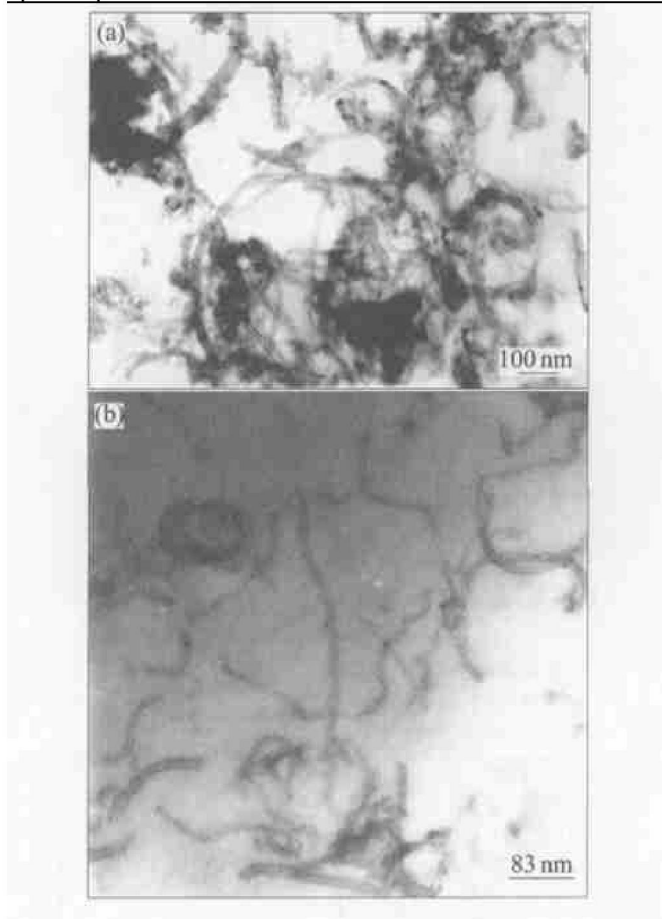


Fig. 2 TEM images of as received CNTs(a) and pretreated CNTs(sample A1) (b)

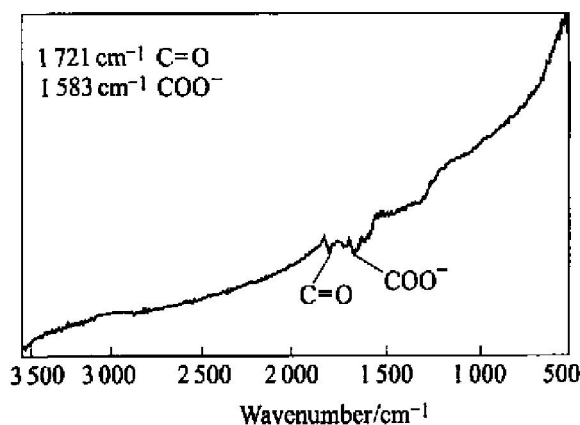


Fig. 3 IR spectrum of pretreated CNTs (sample A1)

Fig. 6 shows the hydrogen uptake curves of both sample A1 and B1. Obviously, the former, as-pretreated CNTs, has a poor amount of hydrogen storage, which maximum is only about 0.5%. Its hydrogen uptake curve has a sharp increase in first 20 min, and there is no obvious change after about 140 min. Different from sample A1, the hydrogen uptake curve of sample B1 has a sharp increase in the first 10 min, and follows a distinct hydrogen uptake plateau.

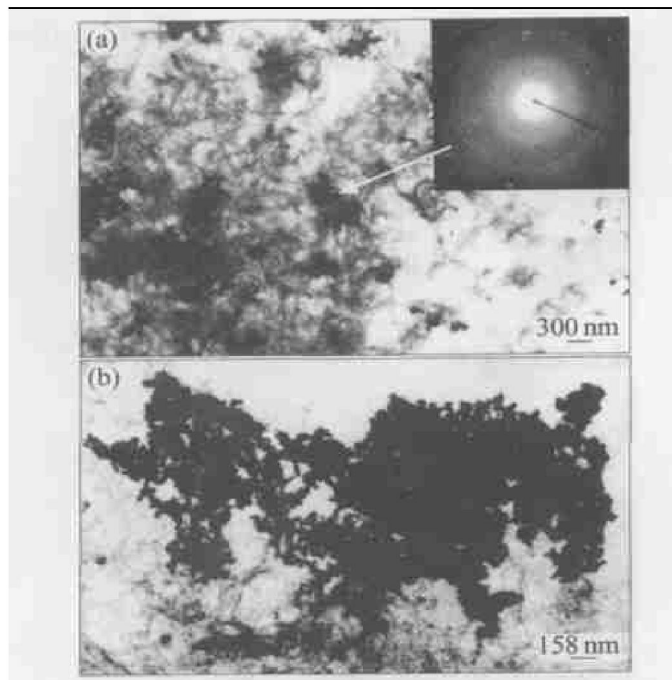


Fig. 4 TEM images of CNTs decorated with Pd (sample B1)

- (a) —Distribution of crystal Pd coatings on CNTs;
(b) —Morphology of crystal Pd coatings

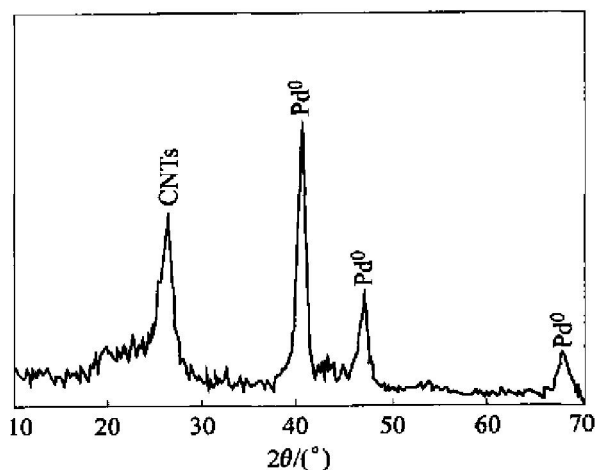


Fig. 5 XRD pattern of CNTs decorated with Pd (sample B1)

About 1 h later, the curve takes on an obvious increase and approaches to saturation after about 4 h. The amount of hydrogen storage of sample B1 is up to 3.9% (mass fraction). In fact, if the hydrogen storage effect of Pd (about 0.8% H₂, mass fraction) is deduced, the hydrogen uptake by CNTs can be as high as 5.2% (mass fraction). The desorptive tests show that almost 85% H₂ in CNTs decorated Pd can be desorbed at ambient temperature. These indicate that most of hydrogen in tubes is presented in the form of molecules.

One of major reasons that pretreated CNTs have low capacity of storing hydrogen is that hydrogen molecule can not enter the tubes effectively, because 1) the surface graphitization of CNTs is high, leading

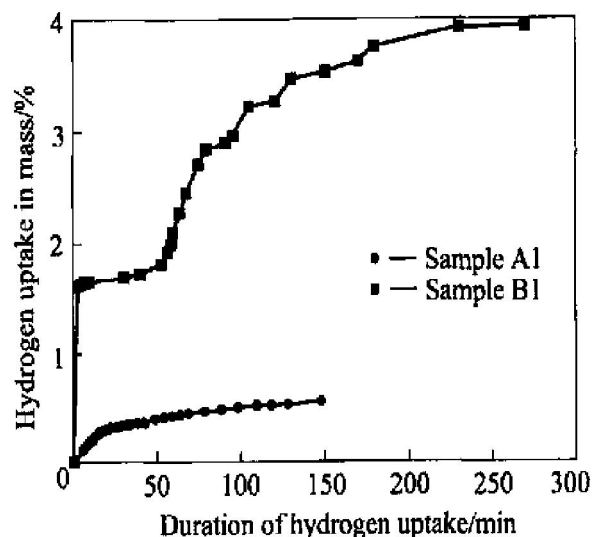


Fig. 6 Curves of amount of hydrogen uptakes of sample A1 (1 g, initial pressure 10.931 MPa) and sample B1 (0.45 g, 10.538 MPa) vs duration

to an evident resistance effects to hydrogen molecules, so hydrogen can not to be free injected to tubes; 2) furthermore, since the aspect ratio of the CNT is usually up to $10^4 - 10^{6[11]}$, it is very unlikely that hydrogen inside the CNTs accommodated exclusively by the capillarity effect through the open-ends; 3) currently, it is impossible to practically tune the optimized diameter and layer space of CNTs to achieve high H₂ storage capacities. Therefore, hydrogen adsorption of pretreated CNTs mainly occurs in the outer surface of tubes while not in the inner, leading to a low uptake amount of H₂. The rapid increase of H₂ uptake of CNTs in beginning can be attributed to a typical single layer adsorption of graphitic layers or C-atom sheets. As the single layer adsorption is completed, accompanying the descent of the interaction potential between an ad molecule and a single graphite slab^[12-14], H₂ adsorption will get saturation.

The hydrogen uptake modes of the top input, the sidewall input and the circumference input are advised to account for the adsorption mechanism of CNTs decorated with Pd (Fig. 7). For the top input mode (Fig. 7(a)), hydrogen molecules are dissociated into atoms by the catalysis of Pd whilst hydrogen atoms enter the tubes through open-ended sites driven by both capillary forces of tubes and outer pressure. For the sidewall input mode (Fig. 7(b)), hydrogen atoms enter into the tube from sidewall, the outer pressure also accelerate the process. Moreover, rare hydrogen molecules can directly enter into tubes by means of the capillary forces. For the circumference input mode (Fig. 7(c)), actually, it is a kind of composite of the above two modes. The above hydrogen uptake modes of CNTs decorated with Pd occur to some extent in samples, but mostly the Pd coatings

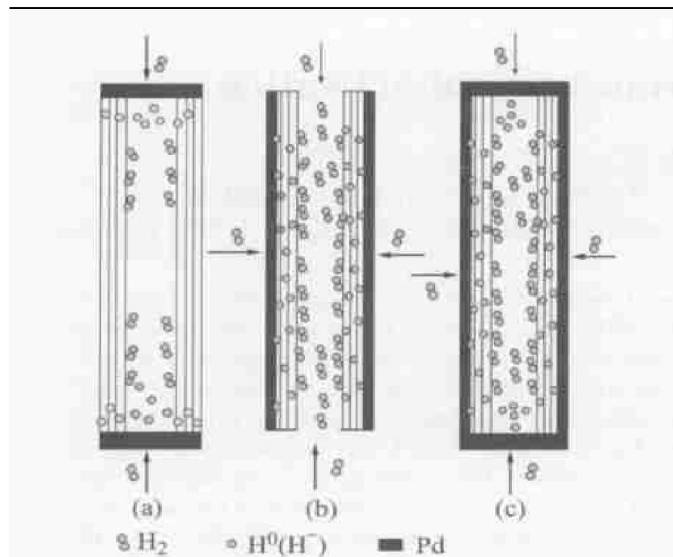
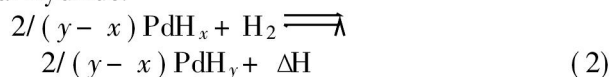


Fig. 7 Hydrogen uptake modes of CNTs decorated with Pd

(a) —Top input mode; (b) —Sidewall input mode;
(c) —Circumference input mode

are discontinuous and non-uniform. Initially, the hydrogen uptake of CNTs decorated with Pd mainly takes on the absorption of Pd and CNTs. Hydrogen molecules rapidly occupy the outer surface sites of tubes whilst the solid solution of Pd and hydrogen, PdH_x , is formed. After that hydrogen adsorption in the outer surface of tubes can get saturation quickly, while PdH_x and hydrogen further react and form the metal hydride:



where $x < 1$, $\gamma \leq 1$. The hydrogen uptake curve should take on a plateau. The duration time of the plateau may be related to the distribution of Pd, the contacting area between the Pd coating and the nanotubes, and the properties of CNTs.

After that, vast hydrogen atoms in PdH_γ will penetrate into CNTs from the top (Fig. 7(a)), the sidewall (shown in Fig. 7(b)) or/and the circumference sites (Fig. 7(c)) supported by the capillary force or/and the outer pressure to increase the amount of hydrogen uptake until the dynamic balance is reached.

4 CONCLUSIONS

The CNTs decorated with Pd are obtained by chemical reduction. The decorating Pd distributes discontinuously and non-uniformly. For the performance of hydrogen storage, the decorated CNTs with Pd have obvious difference compared with pretreated CNTs. The former has a plateau of storing hydrogen while the latter is not. Meantime, the amount of hydrogen storage of the former is about 8 times higher than that of the latter. The hydrogen storage alloys or metals can be acted as a converter to dissociate the hydrogen molecules to atoms or protons. These atoms

or protons, because of smaller diameter, can easily penetrate the sidewall than molecules to enter CNTs. Therefore it is feasible to enhance the performance of hydrogen storage of CNTs by decoration with hydrogen-storing metals or alloys.

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