Possibilities of atomic hydrogen storage by carbon nanotubes or graphite materials

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Abstract

Atomic hydrogen storage by carbon nanotubes (CNTs) and highly oriented pyrolytic graphite (HOPG) has been studied using a flow catalytic reactor and an ultra-high vacuum surface science apparatus including scanning tunneling microscope (STM), respectively. Defect sites on CNTs as adsorption sites of atomic hydrogen are introduced by oxidation pretreatment using La catalyst. Pd catalysts are then deposited on CNT surfaces for dissociation of $H_2$ into atomic hydrogen, which spills over to the defect sites. In the best case, 1.5 wt% of hydrogen is stored in the defective CNT with Pd particles at 1 atm and 573 K. In temperature programmed desorption (TPD) experiments, $H_2$ starts to desorb at 700–900 K depending on the annealing temperatures of CNTs prior to hydrogen storage. On the HOPG surface, hot atomic hydrogen produced by dissociation of $H_2$ using tungsten wire desorbs from graphite terraces at 400–700 K, which is much lower than that on CNTs. It is possible that one can decrease the desorption temperature by changing the method of $H_2$ dissociation.

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1. Introduction

Hydrogen storage technology is required for utilization of hydrogen as an ideal fuel with no pollutant emission during combustion. Light, environmental friendly and cheap materials are thus needed to be used for the hydrogen storage. In recent years, carbon materials such as carbon nanotubes (CNTs), carbon nanofibers and mechanically milled graphites have attracted attention owing to the availability of new carbon materials [1–14]. However, most studies concerning the hydrogen storage have been carried out at high pressures (1–16 MPa) and low temperatures (80–133 K) in order to store molecular hydrogen by physisorption. It has been often reported that hydrogen storage by physisorption remains less than 4 wt% at room temperature and even high pressures [1,2]. Although large hydrogen uptakes by CNTs have been reported [3,4], these results have not been easily reproduced. The hydrogen adsorption sites and the interaction between CNTs and hydrogen have been not yet well understood.

Our methodology here of the hydrogen storage is to adsorb atomic hydrogen at the defect sites of CNTs after dissociation of $H_2$ by Pd catalyst particles attached to the CNTs [15–17]. La catalysts have been doped to CNTs in order to introduce the defect sites [17], which catalyze oxidation of CNTs by $O_2$. We have used thick MWCNT for the atomic hydrogen storage, because the defect density on the wall of MWCNTs is expected to be much more than that on SWCNTs or thin CNTs and because MWCNTs can be obtained at low cost by catalytic decomposition of hydrocarbons as a mass production. The amount of hydrogen stored has been exactly measured by thermal programmed desorption (TPD). We report here that atomic hydrogen can be stored in CNTs by modification with catalysts for the defect-making and the dissociation of $H_2$. The amount and desorption temperature of adsorbed hydrogen depend on the procedure of defect-making.

As a surface science study, we have also examined the adsorption properties of atomic hydrogen on a highly oriented pyrolytic graphite (HOPG) surface, where the HOPG surface...
was exposed to atomic hydrogen produced by dissociation of $H_2$ by heated tungsten wire. By comparison with the hydrogen storage by CNTs, possibility of carbon materials for hydrogen storage is discussed in this paper.

2. Experimental

The CNTs (NanoTech, Co Ltd China) used in this study have been produced by catalytic decomposition of hydrocarbons. BET specific surface area of the CNTs was $98 \text{ m}^2/\text{g}$ with length of 10 $\mu$m, outer diameter of 20–50 nm, inner diameter of 3–10 nm, and wall layers of 25–60. The synthesis catalyst particles contained in the CNTs were removed by washing in concentrated HNO$_3$ (14 N) at room temperature for 1 h followed by ultrasonication in concentrated HNO$_3$. After subsequent washing with distilled water, the CNTs were dried at 373 K in air. La was doped to the purified CNTs as an oxidization catalyst by putting the CNTs into La(NO$_3$)$_3$·6H$_2$O solution dissolved in THF followed by stirring at room temperature for 1 h. The THF solution was then evaporated to deposit La ion compounds on the CNT surface as confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). In order to generate the defects and to open the ends of CNTs, the La loaded CNTs were heated in a quartz tube reactor with flowing air (10 cm$^3$/min) to 873 K. After the oxidation in air, the La catalyst particles were removed by washing in concentrated HNO$_3$ at room temperature for 30 min followed by ultrasonication in concentrated HNO$_3$ for 30 min. In order to dope the Pd catalysts, the oxidized CNTs were put into Pd(C$_5$H$_7$O$_2$)$_2$ solution dissolved in 30 ml THF. After stirring the mixture at room temperature for 1 h, the THF solution was evaporated to leave Pd-doped CNTs.

Hydrogen storage by CNTs was carried out using the flow reactor connected to a gas chromatograph (GC) (Shimadzu, GC-8A). The Pd/CNTs were heated at 573 K for 3 h in helium with 99.99% purity (1 atm) to remove impurities on CNT surfaces. The reason for the low annealing temperature is to avoid significant re-crystallization of the defective CNTs at higher temperatures above 600 K. Carboxyl groups, which are expected to be major impurities, can be removed by annealing at 373–673 K [18]. We thus chose the annealing temperature of 573 K. Then, hydrogen (99.99%) was let (30 ml/min) into the reactor at 1 atm and flowed at 573 K for 3 h. The amount of stored hydrogen and the desorption behavior were examined by temperature programmed desorption (TPD) experiments using the gas chromatograph, where $N_2$ (30 ml/min) was used as the carrier gas.

The prepared Pd/CNTs were characterized with transmission electron microscopy (TEM) (JEOL, JEM-2010F), thermalgravimetry (TG) and differential thermal analysis (DTA) (Seiko, EXSTAR6000 TG/DTA/DSC), Raman spectroscopy (Ar laser, 514.5 nm, Jasco, TRS-600), XPS (Vacuum Generator, Escalab 220i-XL) and XRD (Phillips, X’Pert MPD).

The HOPG experiments were conducted using an ultra-high vacuum-scanning tunneling microscope (UHV-STM) apparatus (1×10$^{-10}$ Torr) with facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a quadrupole mass analyzer. The HOPG sample was cleeved in atmosphere followed by annealing at 923 K in UHV for 2–3 h. The sample mounted on a silicon substrate was resistively heated by applying a current through the silicon. Defects on the HOPG surface were introduced by sputtering at room temperature and subsequent annealing at 1173 K with Ar$^+$ acceleration energy of 200 eV. Atomic hydrogen was produced by dissociation of $H_2$ by a heated tungsten wire.

3. Results and discussion

3.1. Hydrogen storage by defective CNTs

In order to generate hydrogen adsorption sites, we carried out oxidation of CNTs by air, where La or Co (or both) was doped to CNTs as a catalyst to promote the oxidation. The oxidation temperature and the effect of La and Co upon oxidation of CNTs were investigated by TG and thermal programmed oxidation (TPO). It was found that CNTs without cataly was burned out by $O_2$ at 730–800 K, while the oxidation started at lower temperatures (650–750 K) for La/CNTs.

Fig. 1 shows TEM images of La/CNTs after oxidation at 650 K. Fig. 1(a) revealed that catalysts for CNTs synthesis with the tip mechanism [19] were removed and the tube ends were opened. It is also shown that the partial oxidation of La/CNTs by air brought about opening of the tube ends and creation of the defects at the outer walls. The defects at the outer walls can be observed by the magnified TEM images shown in Fig. 1(b). It was found that the layers of a tube were partially etched and holes with 10–30 nm were formed. Based on the results, we can conclude that the La catalyst promotes oxidation of CNTs by a cycle of LaO formation and oxygen supply from the LaO [20,21]. The La compounds were not observed in TEM images, probably due to small particles. We thus consider that the holes and the defects after oxidation provide the pathway and the adsorption sites of atomic hydrogen, respectively [10]. We also confirmed deposited Pd particles on the CNTs surface as X-ray photoelectron spectroscopy (XPS) and TEM. It was found that Pd particles were deposited with 2 nm diameter and the Pd content was estimated to be 2.35 wt% by XPS.

The effect of the Pd and La catalysts upon the hydrogen storage by CNTs was examined by TPD measured with GC, where hydrogen was adsorbed at 1 atm and 573 K for 180 min. Fig. 2(a)–(c) show TPD results of $H_2$ desorption from Pd/(La)/CNTs for pretreatment temperatures of 523,
623 and 773 K, respectively. Since we could not heat the reactor over 1100 K, we once stopped heating at 1100 K during TPD experiments and kept it at 1100 K to measure the amount of stored hydrogen. The amount of hydrogen storage was estimated from the peak area to be 0.73, 0.60 and 1.00 wt% for (a), (b) and (c), respectively. As for He treatment at a lower temperature of 523 K, it is clear that hydrogen started to desorb at a lower temperature around 600 K. The annealing at 623 K resulted in the shift of the peak top to 760 K. The further annealing at 773 K caused to shift the peak top to 1000 K. These results suggest that the defects created by the oxidation are re-crystallized to graphite by annealing at high temperatures. The crystallization to graphite by heating significantly decreases the hydrogen storage [22,23]. It is thus considered that the hydrogen desorption temperature as well as the amount of hydrogen stored strongly depend on the thermal treatment.

We also found an active oxidation catalyst including both La and Co. Fig. 3 shows TPD of H₂ desorption from the Pd/(La)/(Co)/CNTs. The hydrogen desorption started from 600 K and the peak top was located at 700 K. The amount of hydrogen storage was estimated from to be 1.50 wt%. The increase of hydrogen storage by Co-doping La and Co was well reproduced. It is suggested that LaCoO₃ (mixed oxide perovskite) formed as an oxidation catalyst during oxidation of CNTs. Although it may be possible to increase the hydrogen amount by making more defects, the desorption temperature is still so high that it requires high thermal energy to release hydrogen. To decrease the desorption temperature and to look for another method for hydrogen storage, surface science study is required to examine the adsorption properties of hydrogen on CNT or graphite surface. As described in the next section, we compare the hydrogen adsorption on CNT surface with that on a graphite (HOPG) surface.

3.2. TPD of H₂ from HOPG

To study the adsorption site of atomic hydrogen, we first used STM to observe hydrogen atom on HOPG surface.
Since defected CNTs have stored atomic hydrogen as described above, we studied the adsorption of atomic hydrogen on a sputtered HOPG surface. Fig. 4(a) shows STM image of sputtered HOPG. Defects can be recognized by blight spots. A (3×3) R30° structure was observed in the vicinity of defects, suggesting modification of electronic structure around the defect. After exposure of the sputtered HOPG to atomic hydrogen, fine structures were observed in the bright spots as shown in Fig. 4(b). The corrugation decreased by 50% upon exposure to atomic hydrogen, indicating adsorption of hydrogen on the defect sites. The decrease in brightness is ascribed to disappearance of dangling bond present at the defect sites. Adsorbed CH_x (x = 1–3) species are probably formed at the defect sites. No significant difference was observed for the graphite terraces on HOPG before and after hydrogen exposure.

Fig. 5 shows TPD of H_2 from clean and sputtered HOPG. For both surfaces, two desorption peaks are observed at 520 and 600 K. The first peak has been observed by Kuppers et al. [24], who attributed the peak to adsorption of atomic hydrogen on graphite terraces without defect. The decrease in the peak area of first peak is thus due to defect formation. Although Kuppers et al. have observed a single peak at ~450 K in their experiments similar to ours, we observed the significant second peak as large as first peak. The difference in experiments is the temperature of HOPG upon adsorption hydrogen, that is, 150 K for Kuppers’s experiment and 300 K for ours. The second peak was thus ascribed to atomic hydrogen adsorbed at the inter layer sites of graphite, which should require activation energy to migrate into the site.

Although atomic hydrogen on graphite terraces was not observed by STM, TPD results clearly indicate hydrogen adsorption on the clean HOPG surface. The corrugation of the hydrogen-adsorbed graphite surface in electronic nature may be too small to be observed by STM. The desorption temperature of hydrogen from HOPG (520 K) was much lower than that from CNT (700 K). Although the desorption of hydrogen from the defect site is not clear in this study, there are possibilities to release hydrogen at the low temperature of 520 K from graphite terraces. Currently, we consider that thermal energy of atomic hydrogen as well as carbon surface is important for the adsorption of hydrogen on carbon. In the CNT’s experiments H_2 molecule is dissociated into atomic hydrogen at 500 K using Pd catalysts, while in the HOPG experiments atomic hydrogen is formed using the hot tungsten wire heated over 1000 K. It is possible that more atomic hydrogen storage on graphene layer of CNT or graphite material by introducing hot hydrogen atom.
4. Conclusion

The atomic hydrogen was stored up to 1.5 wt% at atmospheric pressure by defective CNTs prepared by oxidation using La and Co catalysts, where Pd catalysts was also doped for the dissociation of H$_2$ at 573 K. The desorption temperature of H$_2$ was so high as 700–900 K. On the other hand, desorption of H$_2$ from graphite terraces takes place at 500–600 K, where hot hydrogen atom (over 1000 K) was supplied to the graphite surface. It is thus possible that more atomic hydrogen is stored in CNT or graphite materials by supplying hot atomic hydrogen.

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