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Improved hydrogen storage performance of defected carbon nanotubes with Pd spillover catalysts dispersed using supercritical CO₂ fluid

Chih-Yao Chen^{a,b}, Jeng-Kuei Chang^{a,*}, Wen-Ta Tsai^b

^a Institute of Materials Science and Engineering, National Central University, Taoyuan, Taiwan

^b Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

Hydrogen storage properties of carbon nanotubes (CNTs) modified by oxidative etching and decoration of Pd spillover catalysts are investigated. A mixed H₂SO₄/H₂O₂ solution containing ferrous ions (Fe²⁺) is useful to open the caps, to shorten the length, and to generate defects on CNTs. The Pd catalysts are deposited on the CNTs with the aid of supercritical carbon dioxide (scCO₂); as a result, a highly dispersed Pd nanoparticles and an intimate connection between Pd and carbon surface can be obtained. Combination of the two approaches can optimize a hydrogen spillover reaction on CNTs, resulting in a superior hydrogen storage capacity of 1.54 wt% (at 25 °C and 6.89 MPa), which corresponds to an enhancement factor of ~4.5 as compared to that of pristine CNTs.

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1. Introduction

The world is facing energy shortage and has become increasingly dependent on the renewable courses to covert and store energy. Hydrogen is proposed as a clean and efficient energy carrier, which can be an alternative to fossil fuels [1,2]. However, to reliably store hydrogen is a bottleneck for realizing the hydrogen economics [2–6]. Among the potential hydrogen storage methods [7], including use of high-pressure cylinders, cryogenic liquidization systems, traditional metal hydrides, complex hydrides, and porous adsorbents, utilization of nanostructured carbons has attracted lots of attention due to the great hydrogen adsorption/desorption kinetics and the wonderful cyclic stability (or reversibility). However, it has become clear that the high-surface-area carbon without

modification cannot store (or physisorb) a sufficient amount of H₂ (via only a van der Waals interaction) at ambient temperature for practical applications [7,8].

Recently, a promising mechanism using a hydrogen “spillover” reaction claims to have potential for substantially improving the hydrogen storage properties of carbon adsorbents [9]. Hydrogen spillover is dissociation of H₂ molecules on catalyst particles (e.g. Pt, Pd, Ru, and V etc.) into H atoms that subsequently diffuse to and settle down on the adjacent receptor [9]. The atomic diameter of a hydrogen atom is about 0.50 Å, whereas the kinetic diameter of a hydrogen molecule is 2.89 Å [10,11]. Accordingly, the former is more likely to be adsorbed on the porous carbon. Many studies [12–14] have reported that with the spillover catalysts the hydrogen storage capacity of the adsorbents can be significantly improved,

* Corresponding author. Tel.: +886 3 4227151x34908; fax: +886 3 2805034.

E-mail address: jkchang@ncu.edu.tw (J.-K. Chang).

since the number of adsorption sites for H atoms is much larger than that for H₂ molecules. Although some encouraging results have been obtained, further understanding of the parameters that affect the spillover process and thus attempting to optimize the hydrogen storage performance are surely required.

Essentially, there are three key factors to ensure a successful hydrogen spillover reaction: (i) an effective catalyst, (ii) an intimate connection between the catalyst and the adsorbent, and (iii) a sufficient number of absorption sites on the carbon receptor. In accordance with these respects, we use supercritical carbon dioxide (scCO₂), which has a gas-like diffusivity and an extremely low viscosity [15,16], attempting to uniformly disperse nano-sized Pd particles (with superior catalytic activity) onto CNTs. Owing to the near-zero surface tension of scCO₂ and its excellent wettability toward carbon surface [17–19], a close contact between Pd and CNTs (thus a facile H migration across the hetero-substances) can be expected. For the third consideration, H₂SO₄/H₂O₂-based etching solution is adopted to create defects on CNTs, attempting to increase the hydrogen entry and storage sites. This kind of chemical has been utilized to remove organic contaminants in the semiconductor industry and to modify the material properties of CNTs [20]. However, this is for the first time used to improve the hydrogen storage properties. It should be noted that, as compared to the gas-phase etching methods [21,22], this proposed liquid-phase procedure possesses the advantages of low cost, high yield, and easy control.

Based on the above-mentioned three approaches, optimization of a hydrogen spillover reaction is attempted in this work. The hydrogen storage performance of various samples is evaluated using a high-pressure microbalance. A transmission electron microscope (TEM) and a Raman spectrometer are used to help disclose the mechanism.

2. Experimental section

2.1. Reagents and materials

All the chemicals used in this work were of the analytical grade. Commercially available multi-walled CNTs (Aldrich; purity >95%) synthesized via catalyzed vapor decomposition were used. Palladium hexafluoroacetylacetonate (Pd(hfa)₂) purchased from Aldrich was adopted as the Pd precursor. The reducing agent was dimethyl amineborane (DMAB), which was obtained from Tokyo Kasei Chemical Company.

2.2. Chemical etching of CNTs

The etching solution was a mixture of H₂SO₄ and H₂O₂ (with a volume ratio of 4:1) without and with 0.02 M FeSO₄ addition. The reagent was prepared immediately prior to use to maintain the activity and then mixed with CNTs (1 mL solution to 1 mg CNTs). Ultrasonication was used to enhance the reaction homogeneity; the etching process continued for 2 h and the temperature was maintained at 60 °C. After the treatment, the CNTs were washed multiple times until the solution approached pH neutrality. The samples were then collected by centrifugation and dried in an oven overnight.

2.3. Decoration of Pd nanoparticles on CNTs

The pristine and etched CNTs (40 mg for each batch) were subjected to Pd decoration. The deposition bath was composed of 45 mL Pd(hfa)₂-containing methanol solution and 5 mL DMAB aqueous solution (concentration: ~10 mM). The Pd(hfa)₂/CNTs weight ratio was 1/8. The mixture was loaded into a 500-mL stainless steel autoclave, which was purged and then pressurized with CO₂. A supercritical state of CO₂ was obtained when the pressure reached 20 MPa at 50 °C. The system was stirred vigorously for 2 h to allow a uniform and complete deposition reaction before the vessel was depressurized. The resulting materials were repeatedly washed with deionized water and methanol; after centrifugation, the dark products were collected. Both types of the samples were completely dried at 70 °C prior to analyses.

2.4. Materials characterization

The microstructures of various samples were examined using a high-resolution TEM (FEI Tecnai F-20 G2) operated at a gun voltage of 200 kV. For the TEM analyses, the specimens were first dispersed in anhydrous ethanol under ultrasonication and then collected using a Cu grid, which was coated with a lacey carbon film. Raman spectroscopic studies were performed to probe the bonding properties of carbon. A He–Ne laser, with a wavelength of 632.8 nm, was used as the excitation source for the analyses (Renishaw MicroRaman). The sample crystallinity was examined with an X-ray diffractometer (XRD, Rigaku MiniFlex II) with a Cu target. The X-ray detector was scanned at a rate of 0.5° per minute.

2.5. Evaluation of hydrogen storage performance

The hydrogen storage capacities were gravimetrically evaluated at 25 °C with a high-pressure microbalance (Cahn D-110 system). Before measurement, the samples were degassed at 300 °C for 2 h under vacuum. When the samples had cooled down to room temperature, high-purity hydrogen gas (99.999%) was admitted into the measuring chamber up to a pressure of 6.89 MPa. The weight changes of the samples, which corresponded to the hydrogen storage, were recorded after the microbalance reached a steady state (typically after ~1 h) while the literature [23] has indicated that the hydrogen adsorption amount can become saturated within a couple of minutes. The buoyancy effect was compensated for using the helium gas reference method; details of the calibration procedure can be found elsewhere [24]. Three parallel measurements for an identical sample were performed; the deviation was typically within 10%.

3. Results and discussion

Fig. 1(a) shows a TEM bright-field image of the pristine CNTs; the outer and inner diameters are approximately 30 and 10 nm, respectively. As illustrated, the long-range ordered carbon layers are virtually parallel to the tube axis. The tip region of a CNT is exhibited in Fig. 1(b). It was found that the catalyst (used to grow the CNT) and the amorphous carbon

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