

TAILORING OF SINGLE WALLED CARBON NANOHORNS FOR HYDROGEN STORAGE AND CATALYST SUPPORTS

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Abstract

We report the post-processing chemical treatments of single walled carbon nanohorns (SWNHs) as a medium with tunable porosity to optimize hydrogen adsorption. Laser synthesized SWNHs are oxidized in air to achieve surface areas up to 1900 m²/g. Chemistry methods are described for the decoration of SWNHs with 1-3 nm Pt nanoparticles to probe spillover and metal-assisted hydrogen storage mechanisms. Hydrogen storage of opened SWNHs is 2.6 wt% at 77K, which is 3 times as that of as-prepared SWNHs.

Introduction

Single-walled carbon nanohorns (SWNHs) are unique single-walled, closed-shell carbon structures (Iijima, S. et al. 1999). They are irregular in shape with closed conical ends. The structure of an individual SWNH unit consists of graphene cylinders with a diameter of 2-3 nm and about 20-50 nm in length, and they are found

in ball-shaped aggregates of roughly 50-100 nm in diameter (Bandow, S. et al. 2000; Cheng, M. et al. 2007) As a novel form of nanostructured carbon with a high defect density and tunable pore sizes, SWNHs are promising candidates for hydrogen storage and metal catalyst supports (Murata, K. et al. 2002; Utsumi, S. et al. 2005).

In this paper, we report chemical treatments of SWNHs synthesized by the laser vaporization method at Oak Ridge National Laboratory (Puzetky, A. A. et al. 2000; Cheng, M. et al. 2007; Hu, H. et al.), and their effects to adjust the surface areas and hydrogen uptake of the SWNHs. As-synthesized SWNHs were used for oxidation and metal decoration without further purification in these studies.

Experimental

An industrial grade Nd:YAG laser (600 W maximum average power, $\lambda = 1.06 \mu\text{m}$) was used to vaporize graphite targets mounted in a quartz mount within a tube furnace similar to that described earlier (Puzetky, A. A. et al. 2000). The as-prepared SWNHs (AP-SWNHs)

were produced from pure carbon targets without metal catalysts under Argon (Cheng, M. et al. 2007).

AP-SWNHs were oxidized in air at 550°C to produce opened SWNHs (O-SWNHs). Thereafter, O-SWNHs were decorated with Pt nanoparticles via wet chemistry processing (Hu, H. *et al*). In the synthesis of Pt decorated SWNHs (O-SWNH/Pt), O-SWNHs were mixed with of H₂PtCl₆ in deionized H₂O and the mixture was stirred at 80°C. Sodium citrate solution was then added to the mixture and stirred at 80°C for 4 hours. After cooling to room temperature, the mixture was filtered through a 1.0 μm pore-size filter membrane, and the solid on the membrane was washed with H₂O and then dried at room temperature overnight.

Hydrogen gas isotherms were measured on a volumetric Sieverts apparatus at 77 K. All samples were degassed at 200 °C overnight and loaded into the sample cell within a He glove box.

Prompt-gamma activation analysis (PGAA) experiments were performed at the cold neutron PGAA instrument in the National Institute of Standards and Technology Center for Neutron Research (NCNR) (Paul, R.L. et al 1997; Brown, C. et al. 2007). The samples were put into aluminum foil bags and suspended in the neutron beam. The prompt gamma ray spectra of the samples were then recorded. The mass fractions of different elements in the sample were calculated by integrating the areas of characteristic peaks of the corresponding elements and comparing them to the results obtained from standard samples. The measurement of an empty aluminum bag indicated that it contributed no contamination to the characteristic peaks of Pt and C.

Results and Discussion

SEM and TEM images show AP-SWNH aggregates appear to be composed of randomly oriented individual SWNHs with conical tips which assemble into relatively uniform spherical morphologies with diameters varying from 50 nm to 100 nm (Figure 1.). AP-SWNHs have their inner volumes sealed, restricting their surface area to their external surfaces. To further

obtain higher surface areas of SWNHs for hydrogen storage, thermal annealing and chemical oxidation methods were developed to open the inner volumes (following Bekyarova, E. *et al*. 2002).

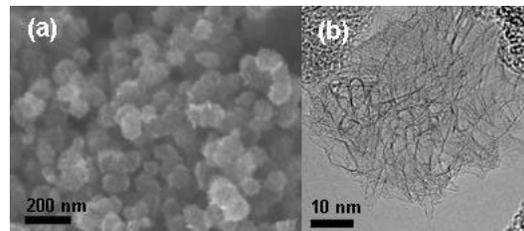


Figure 1. (a) SEM and (b) TEM images of as-prepared SWNHs.

AP-SWNHs were oxidized by heating in air at varied temperatures and times. Surface areas were measured by nitrogen BET adsorption measurements. The SWNHs heated at 550 °C for 20 min yielded the largest surface areas, up to 1900 m²/g, which is approximately 4 times larger than unopened AP-SWNHs (surface areas typically ~450 m²/g). TEM images show that O-SWNHs have more folded graphitic structures, which may have potential importance as sites for hydrogen generated by spillover (Figure 2a). The Raman spectral D/G band ratio of the O-SWNHs (1.3~1.6) showed an increase when compared with that of unopened AP-SWNHs (D/G ratio of 1.2). This is likely due to the increase of defect sites introduced by the oxidative opening treatment.

The very high surface area and unique morphology of opened SWNH aggregates makes them excellent candidates for catalyst supports and hydrogen storage. Thus, we developed a wet-chemistry *in situ* decoration method to produce Pt-nanoparticle-decorated O-SWNHs. In contrast to single walled carbon nanotubes, SWNHs exhibit a rich number of wall defects and interstitial sites to enable chemical decoration. From TEM images such as Figure 2b, Pt nanoparticles were found to uniformly decorate the SWNHs following *in situ* synthesis. The diameter of these Pt nanoparticles varied from 1 to 3 nm. TGA and PGAA results showed the loading of Pt in O-SWNH/Pt can reach at least 20 wt%.

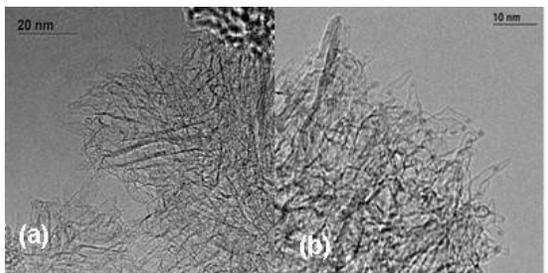


Figure 2. TEM of (a) O-SWNHs and (b) O-SWNH/Pt.

The hydrogen uptake of AP-SWNHs, O-SWNHs, and O-SWNH/Pt at 77 K is shown in Figure 3. The hydrogen uptake of O-SWNHs is 2.6 wt%, which is about 3 times of that of AP-SWNHs (0.8 wt%). However, the hydrogen uptake of O-SWNH/Pt is 2.1 wt%, which is lower than that of undecorated O-SWNHs. One possible reason for this is pore blockage on the SWNHs by the Pt nanoparticles themselves or by citrate groups. This view is supported by the decreased surface area measured for O-SWNH/Pt ($SA=998\text{m}^2/\text{g}$) compared to undecorated O-SWNHs.

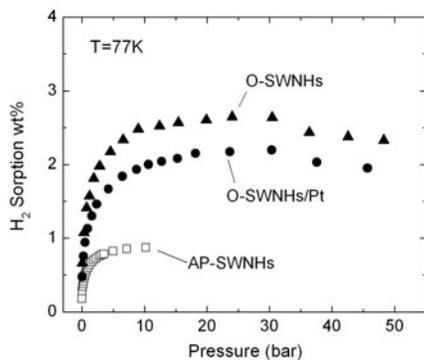


Figure 3. Hydrogen isotherm comparisons of AP-SWNHs, O-SWNHs, and O-SWNHs/Pt at 77K.

Conclusion

SWNHs synthesized by laser vaporization show potential as materials with tunable porosity and metal decoration for use as hydrogen storage media. Surface areas of $1900\text{m}^2/\text{g}$ were achieved after thermal oxidation of the SWNHs produced for this study. Chemistry methods were developed to decorate SWNHs with 1-3 nm Pt

nanoparticles of up to 20% weight loadings to probe spillover and metal-assisted hydrogen storage mechanisms. Hydrogen storage of opened SWNHs is 2.6 wt% at 77K, which is 3 times as that of as-prepared SWNHs.

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