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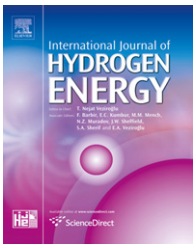

Electroless deposition of Ni nanoparticles on carbon nanotubes with the aid of supercritical CO_2 fluid and a synergistic hydrogen storage property of the composite

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ABSTRACT

A hybrid synthesis protocol that combines electroless plating and the supercritical CO_2 ($scCO_2$) technique is developed for the first time to decorate multi-walled carbon nanotubes (CNTs) with Ni nanoparticles. The $scCO_2$ fluid, which is immiscible with aqueous plating solution, renders a heterogeneous Ni deposition reaction and suppresses the lateral growth of Ni, which leads to the formation of nanoparticles. A uniform dispersion of tightly anchored particles, a few nanometers in diameter, on CNTs can be achieved. Since the electroless deposition process can be easily manipulated, large-scale production should be realizable. The constructed CNT/Ni nano-composite exhibits a synergistic property in hydrogen storage performance, which is evaluated using a high-pressure microbalance. The deposited nanoparticles enhance the hydrogen spillover reaction on CNTs, tripling the hydrogen storage amount at room temperature as compared to pristine CNTs.

1. Introduction

Nanoparticles, which exhibit properties different from those of their bulk counterparts due to the quantum size effect, have recently attracted a lot of attention both in industrial and academic communities [1]. Nanoparticles have plenty of dangling bonds and a high concentration of coordinative unsaturated sites on their surface, giving them potential applications in diverse fields, such as catalysis, chemical/biological sensing, and optoelectronics [2,3]. Carbon nanotubes (CNTs) have extraordinary characteristics, which include a large surface area, unique physical and mechanical properties, high electrical conductivity, and inherent high-aspect-ratio and hollow nano-geometry [4]. They are considered as ideal supports for heterogeneous nanoparticles [5,6]. When CNT–nanoparticle heterostructures are appropriately fabricated, the composites could have a combination of the isolated properties of their constituent components, and even show synergistic effects [7,8]. How to construct nano-architectures while preserving the intrinsic characteristics of CNTs and nanoparticles is an important topic.

CNT/Ni nano-composites have potential in many energy-related applications [9–14], such as fuel cells, rechargeable batteries, supercapacitors, hydrogen production, and hydrogen storage. Thermal evaporation [15,16], wet impregnation [9,12–14,17–19], and electrodeposition [10,20,21] processes

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have been employed to manufacture the nano-composites; each technique has advantages and limitations. The easy manipulation and low cost of electroless deposition of Ni on CNTs have made it another promising preparation protocol [22–24]. The deposition process is also simple, and thus large-scale production should be achievable. However, the relatively poor size and distribution controls of the Ni nanoparticles on CNTs in this procedure are issues that need to be resolved. Ni tends to agglomerate due to the auto-catalytic deposition reaction and it is difficult to distribute Ni inside the nanotubes because the plating aqueous solution has a high surface tension. Finding a more effective synthesis strategy is thus desirable.

Supercritical carbon dioxide ($scCO_2$), which has a gas-like diffusivity and an extremely low viscosity, has excellent mass-transfer properties and is thus ideal to disperse nanoparticles onto high-porosity supporting materials [25–27]. The near-zero surface tension of $scCO_2$ not only enables excellent penetration and wetting of pores, but also keeps the fragile pores from collapsing [27,28]. The readily accessible supercritical conditions (i.e. T_c is 31 °C and P_c is 7.38 MPa) together with abundance, low cost, non-flammability, and non-toxicity make $scCO_2$ a promising alternative fluid for green-chemistry applications [27,29]. However, the known $scCO_2$ techniques to prepare nanoparticles generally involve two steps [27]. First, ionic precursors are incorporated onto substrates using $scCO_2$; and then, the precursors are reduced to their metallic forms either by inducing high-pressure H_2 gas into the $scCO_2$ fluid or by performing a post heat treatment after depressurization. Either way is somewhat complicated and inconvenient. Combination of the $scCO_2$ dispersion and electroless deposition processes to deposit Ni nanoparticles onto CNTs, which has never been explored, is first attempted in the present study. The novelty of this idea is to directly prepare nanoparticles (i.e. a one-step process) on a pretreated surface. The proposed hybrid synthesis protocol allows deposited nano-sized particles (~10 nm) to be uniformly distributed and tightly anchored on CNTs. The combined nanoparticles and CNTs clearly exhibit a synergistic effect in the hydrogen storage (HS) performance. The hydrogen adsorption amount for the heterogeneous composite, evaluated using a high-pressure microbalance, was much larger than that expected from summing the individual constituents. The reaction mechanism is also discussed.

2. Experimental procedures

Commercially available multi-walled CNTs (from Aldrich Chemical Company), synthesized from catalyzed vapor decomposition, with a purity of higher than 95% were used. All the chemicals in this study were of the analytical grade and used as received. To impart Pd catalytic seeds on CNTs for Ni electroless deposition, a two-step pretreatment, comprising sensitization and activation procedures, was conducted at room temperature (~25 °C). Without the Pd nuclei, the electroless deposition reaction of Ni cannot be triggered. The pristine CNTs were first sensitized in a mixed solution of 0.3 M $SnCl_2$ and 2.5 M HCl for 2 min and then activated in 1.5 mM $PdCl_2$ solution (pH was adjusted to 1 by adding HCl) for another 10 min. The solution volume (mL) to CNT mass (mg) ratio was set at 2. After each step, the sample was thoroughly washed with deionized water. The treated CNTs were collected via centrifugation for the following electroless deposition.

The deposition bath was composed of nickel chloride ($NiCl_2$, 1.2 g L^{-1}), dimethylamine borane ((DMAB), $(CH_3)_2NHBH_3$, 0.35 g L^{-1}), sodium acetate (CH_3COONa, 0.66 g L^{-1}) and sodium dodecylbenzenesulfonate ($C_{12}H_{25}C_6H_4SO_3Na$, 0.5 mg L^{-1}). The pH was adjusted to 5.5 using dilute HCl. DMAB is a reducing agent, CH_3COONa is a complexing agent, and $C_{12}H_{25}C_6H_4SO_3Na$ is a surfactant. The details about the bath composition and the plating chemistry can be found in the literature [30]. For the $scCO_2$-assisted electroless deposition, 80 mg of the activated CNTs with 160 mL of the plating solution was loaded into a 500 mL stainless autoclave. The autoclave was then purged and pressurized with CO_2 up to 10 MPa at 35 °C, at which point a supercritical state of CO_2 was formed. Fig. 1 schematically shows the configuration of the $scCO_2$ deposition system. The $scCO_2$-containing plating bath was stirred vigorously for 30 min to allow a uniform electroless deposition. After the reaction vessel was depressurized (and CO_2 was released from the plating bath), the resulting CNTs were repeatedly washed with deionized water and ethanol. For comparison, conventional electroless deposition of Ni on CNTs (without $scCO_2$) was also conducted. The operation parameters were identical to those described above (except the CO_2). Both batches of the obtained Ni-plated CNTs were dried overnight in an oven at 70 °C before further analyses.

The microstructures of various CNT samples were characterized using a high-resolution transmission electron microscope (TEM, JEM-2000FX or JEM-2100F) operated at a gun voltage of 200 kV. For TEM analyses, the samples were first dispersed in anhydrous ethanol solution under ultra-sonication and then collected using a Cu grid, which was coated with a lacey carbon film. The chemical compositions of the samples were inspected with X-ray energy dispersive spectrometers (EDS) attached to the TEM and a scanning electron microscope (SEM, Hitachi SU-1500). In addition, the crystal structures were examined using an X-ray diffractometer (XRD, Rigaku MiniFlex II) with a Cu target. The X-ray detector was scanned in a 2θ range from 40° to 80° at a speed of 0.5° per minute.

The HS capacities of pristine CNTs and the two types of Ni-plated CNTs were gravimetrically evaluated at 25 °C with a high-pressure microbalance (Cahn D-110). A schematic of the experimental apparatus is shown in Fig. 2. Before measurement, the samples were degassed at 300 °C for 2 h under vacuum. When the samples were cooled down to room

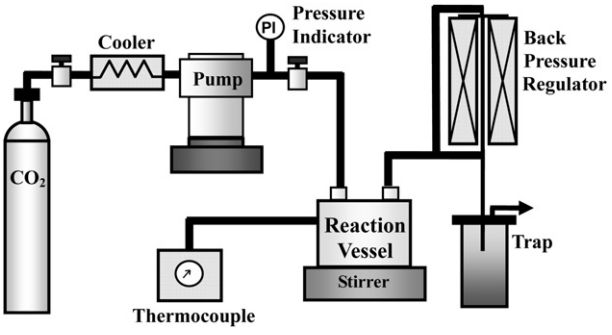

Fig. 1 – Schematic of the $scCO_2$ deposition system.