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Metal nanoparticles inside multi-walled carbon nanotubes: A simple method of preparation and of microscopic image analysis

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ABSTRACT

A simple and efficient method was developed for the introduction of metal nanoparticles inside multi-walled carbon nanotubes (MWCNTs). The method is based on the incipient wetness impregnation using the aqueous solution of a metal salt precursor, followed by the reduction in hydrogen. A hydrophobic MWCNT outer surface is created, which minimizes the wetting of the impregnation solution on MWCNT outer surface, leading to the highly selective deposition of metal particles inside MWCNTs. The selectivity toward nanoparticles inside MWCNTs is about 80% based on a particle number average. Also, a new method was developed for the analysis of microscopic images from transmission electron microscope (TEM) so that the fraction of particles inside MWCNTs can be accurately characterized without 3D TEM. This method is based on the measurement of r/R , the ratio of the inside to outside diameters of the MWCNTs.

1. Introduction

Carbon nanotubes (CNTs), including both multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs), have been widely used in different research fields such as electronics [1,2], composites [3], bioengineering [4,5], environmental engineering [6], and catalysis [7,8], due to their exceptional physical and chemical properties [9–13]. CNTs also provide a nano-confined environment, in which many materials have been found to show very interesting property changes compared with the same material in non-confined environments: the melting point increases when an ionic liquid is confined inside MWCNTs [14], the reaction between alkene and atomic hydrogen shows lower reaction activity when confined inside SWCNTs [15], the electron binding energy is different for Pt nanoparticles inside and outside MWCNTs [16], and the redox properties of metal and oxide nanoparticles can also be tuned when confined inside MWCNTs, for example, the autoreduction of iron oxide nanoparticle is enhanced inside MWCNTs, while the oxidation of iron is retarded [17,18].

MWCNTs were used as catalyst supports shortly after their discovery [19], due to their excellent electronic, mechanical, thermal and sorptive properties [7]. The pore structure of open-ended MWCNTs consists mainly of mesopores with a small or negligible portion of micropores, which prevents any possible transport limitation from micropores [7]. It has been discovered that metal nanoparticles inside the nanochannels of MWCNTs show unique catalytic behavior. For example, the selectivity in hydrogenation of unsaturated aldehydes is highly selective toward the hydrogenation of the $C{=}O$ bond when the catalytic particles are inside MWCNTs, and the total catalytic activity is also increased, compared with the catalyst with particles outside MWCNTs [20]. It has also been reported that metal nanoparticles inside MWCNTs can facilitate catalytic activities as well as tune the selectivities for Fischer–Tropsch reaction [21], ethanol synthesis [22], etc.

Different methods have been reported for depositing nanoparticles inside MWCNTs. The early work of Green et al. refluxed MWCNTs with a mixed solution of nitric acid and a metal nitrate [23]. The inner space of MWCNTs is opened by reaction with nitric acid, and the metal nitrate enters the inner channel of MWCNTs. The sample was then centrifuged and calcined to obtain metal oxide particles inside MWCNTs, which were then reduced in hydrogen to form metal particles. The authors also compared this method with the impregnation with excess precursor solution, and showed that the latter is less selective for particles inside MWCNTs. Later works showed that intensive sonication or a long period of stirring of open-ended MWCNTs in a metal salt solution, followed by filtration, drying and reduction, can also be used to prepare nanoparticles inside MWCNTs [24,25]. The problem with these methods, however, is that the metal loading is not controllable. There are other methods to introduce nanoparticles inside

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MWCNTs, such as sublimation of the precursor [26], a microfluidic method [27], direct synthesis by combined arc discharge of metal and carbon [28], etc., however, the control of metal loading remains an issue.

The impregnation method provides good control of metal loading, but the location of particles is difficult to control in this case. Although, in principle, the capillary force would drive the precursor solution to the inner nanochannel of MWCNTs, the wetting of the solution at the outer surface of MWCNTs retains a reasonable portion of the precursor solution [29], thus forming particles outside the MWCNTs. Tessonnier et al. showed that incipient wetness impregnation could preferentially deposit Pd nanoparticles inside MWCNTs, but still resulted in nanoparticles outside the MWCNTs [30]. Recently several methods have been developed for selective deposition of metal nanoparticles inside MWCNTs. Bao et al. introduced Ru nanoparticles inside MWCNTs by impregnation using an excess of $RuCl_3$ acetone solution with extensive ultrasonication and slow evaporation, followed by hydrogen reduction at 450 °C, resulting in more than 80% of particles inside MWCNTs [31]. Su et al. introduced an impregnation-washing method to selectively wash off the precursors outside the MWCNTs, so that only precursors inside MWCNTs remained, which were converted into nanoparticles after hydrogen reduction, and the selectivity toward particles inside the MWCNTs was 75% [32,33]. Both methods require use of organic solvents, and the experimental procedures are not easy to control. Serp et al., however, obtained 80% selectivity toward particles inside the MWCNTs by a simple impregnation of nanoparticles dispersed in THF [20]. The authors functionalized the outer surface of MWCNTs with long alkyl chains so that the impregnation solution tends not to wet the outer surface.

Determining the selectivity toward particles inside MWCNTs is not an easy task. Normal 2D TEM is not applicable for a quantitative determination of inside/outside selectivity, as illustrated in Fig. 1. Fig. 1a shows a sketch of a normal 2D TEM image of an MWCNT. The image can be divided into two regions, region A and region B. If a particle is found in region A, the particle is unambiguously located on the outside walls of the MWCNT. But if a particle is observed in region B of Fig. 1a, one cannot determine whether the particle is inside or outside of the MWCNT. The accurate identification of a particle's relative location inside or outside the MWCNT usually requires 3D TEM (TEM tomography) [20,32,34,35]; while sometimes a 2D TEM with tilting and rotational sample stages may also provide an estimate of the distribution between inside-particles and outside-particles [22]. Since most researchers have limited access to a 3D TEM, a simple analysis method is desired to extract selectivity information from normal 2D TEM images.

In this paper, a simple thermal annealing method is introduced to make the outer surface of the MWCNTs hydrophobic. Incipient wetness impregnation, followed by drying and hydrogen reduction, is used to prepare metal nanoparticles selectively located inside the MWCNTs. The hydrophobic outer surface of the MWCNTs minimizes the wetting of the impregnation solution on the outer surface, leading to high selectivity toward inside-particles. Also, a simple analysis method is developed to estimate the particle location selectivity (inside/outside the MWCNTs) from normal 2D TEM images.

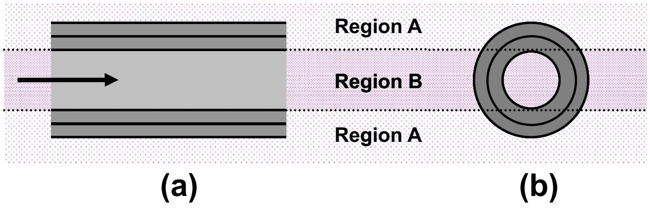

Fig. 1. (a) Illustrative scheme of a normal 2D TEM image of an MWCNT and (b) the axial view of the same MWCNT.

2. Materials

MWCNT samples were purchased from Cheaptubes Inc. (catalog number sku-030103). The MWCNTs were refluxed with nitric acid for 4 h to open the tube ends, as well as to introduce some oxygen containing groups (OCGs) on the surface. After nitric acid treatment, the sample was filtered, washed with water and ethanol, and dried at 60 °C overnight, and then annealed at 1000 °C in an inert atmosphere for 1 h. The MWCNT samples as received, after nitric acid treatment, and after high temperature annealing at 1000 °C are denoted as MWCNT-r, MWCNT-n and MWCNT-ht, respectively. Nitrogen physisorption was carried out on a Quantachrome Autosorb-3B sorptometer to study the porosity of the different MWCNTs.

The Pt nanoparticles on MWCNTs were prepared by incipient wetness impregnation. Tetra-ammine platinum (II) nitrate (from Sigma Aldrich) was dissolved in DI water, and the aqueous solution was added to the MWCNT powders dropwise until incipient wetness. The samples were then dried at 60 °C overnight. The concentration of the solution was controlled so that the Pt loadings in all Pt/MWCNT samples were at 8 wt.%.

The dried samples were then placed in a fixed bed reactor for hydrogen reduction. The reactor was first purged with hydrogen for 20 min, and then the temperature was ramped to 400 °C at 20 °C/min and held at 400 °C for 30 min. *In situ* X-ray absorption near edge structure (XANES) measurements verified that the Pt in the samples has been fully reduced to Pt (0).

For TEM sampling, 1 mg of each sample was sonicated with 10 ml ethanol for 1 h, and then dropped onto a TEM copper grid coated with a holey carbon film. TEM images were taken with a Phillips Tecnai F12 electron microscope operated at 120 kV. TEM image analysis was carried out using ImageJ software.

MWCNT samples have been characterized by nitrogen physisorption and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The Pt/MWCNT samples have been characterized by extended X-ray absorption structure (EXAFS) spectroscopy, XANES, TEM, hydrogen and CO chemisorption, and tested for catalytic performances in aqueous phase reforming, hydrocarbon reforming and oxygenates gas phase reforming. These results are reported elsewhere [16], and the oxygen content and particle size results are summarized in Table 1.

3. Analysis method

As stated above, in Fig. 1a, when a particle is observed in region B in a 2D TEM image, it is not easy to determine whether it is located inside or outside of the MWCNT nanochannel. But if we look along the axial direction of the tube (the direction of the arrow in Fig. 1a), the scheme becomes Fig. 1b, in which the location of a particle can be clearly identified. Unfortunately, this view rarely can be seen under TEM. However, the selectivity toward inside-particles can be calculated from normal 2D TEM images using the idea of the axial view, as described in detail below.

Assuming there are x particles in region A, all of which are outside the MWCNTs, and y particles in region B, in which z particles are outside the MWCNTs and $(y-z)$ particles are inside the MWCNTs, then the selectivity toward particles inside or outside the MWCNTs would be:

$$inside\% = \frac{y-z}{y+x} \qquad (1)$$