Decorating catalytic palladium nanoparticles on carbon nanotubes in supercritical carbon dioxide

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Hydrogen reduction of a Pd(II)-β-diketone precursor in supercritical carbon dioxide produces palladium nanoparticles on multi-walled carbon nanotubes that exhibit promising catalytic properties for hydrogenation of olefins in carbon dioxide as well as electro-reduction of oxygen in fuel cell applications.

In recent years, carbon nanotubes (CNTs) have been considered as new supports for metal catalysts due to their small size, high chemical stability and large surface area to volume ratio.[1,2] Several methods have been developed to decorate CNTs with catalytic metal nanoparticles.[3–10] However most of them usually involve tedious and time-consuming treatment and the known wet decoration processes also generate aqueous wastes.

Supercritical carbon dioxide (scCO$_2$) has been extensively studied as a green medium for chemical reactions and separations.[11] ScCO$_2$ can dissolve solutes like a liquid and yet possesses low viscosity, high diffusivity and zero surface tension like a gas. These unique properties make scCO$_2$ an attractive medium for delivering solutes to small areas with complicated surfaces and poorly wettable substrates to attain a high uniformity and homogeneity of the materials deposited. Unreacted materials and byproducts from the scCO$_2$ processes can be easily removed from the system by flushing the system with the fluid. A number of metal films have been deposited on planar surfaces and mesoporous substrates by various chemical processes in supercritical fluid solutions.[12] Most of these supercritical fluid metal film deposition processes are performed at modest temperature and pressure with considerable flexibility of experimental conditions.

The aim of this communication is to report a rapid, direct and green procedure to decorate multi-walled CNTs (MWCNTs) with catalytic palladium nanoparticles by a simple hydrogen reduction of a Pd(II)-β-diketone precursor using scCO$_2$ as the medium. The produced Pd nanoparticle–MWCNT composite is an effective catalyst for selective hydrogenation of olefins in CO$_2$ and for electrochemical reduction of O$_2$. To the best of our knowledge, we are not aware of any other report on a rapid and direct synthesis of catalytic Pd–MWCNT nanocomposite in supercritical CO$_2$.

MWCNT decoration was carried out using the experimental setup illustrated in Fig. 1. The MWCNTs, produced by a CVD method[13] and with open terminals, were obtained from NanoLab (Brighton, MA) with a purity of ~95%. Most of the MWCNTs have a diameter about 20–30 nm and length about 3 μm. A hydrated palladium precursor, Pd(hfa)$_2$·xH$_2$O (hfa = hexafluoroacetylacetonate) was purchased from Aldrich Chemical Company and used as received. In a typical trial, 10 mg of the MWCNTs were loaded in a 3.47 ml high pressure stainless steel reactor along with 10–50 mg of Pd(hfa)$_2$·xH$_2$O. After loading the precursor, valve V1 was closed while valves V2, V3 and V4 were opened and hydrogen at 3 atm was allowed to flow through the reactor for 5 min to expel the air inside. After hydrogen loading, valves V2, V3 and V4 were closed and V1 was opened to charge the H$_2$–CO$_2$ mixing vessel with 80 atm of CO$_2$. After mixing of H$_2$ and CO$_2$, valve V3 was opened forcing

the mixture into the reactor. Valves V1 and V3 were then closed for the dissolution of the precursor in the CO$_2$ solution. To ensure complete dissolution, the reactor was left undisturbed for 30 min. After that, the reactor was heated to 80 °C and kept at this constant temperature for 5–10 min. After the reaction, the reactor was cooled and vented, and neat CO$_2$ was used to flush the reactor twice. The remaining MWCNT powder was removed from the system and weighed. The weight gain of the MWCNTs due to metal loading was about 10–30%. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analyses of the decorated MWCNTs were carried out using a Jeol JEM 2010 microscope equipped with an Oxford ISIS system.

TEM image of the MWCNTs after scCO$_2$ deposition using 10 mg of Pd(hfa)$_2$ is shown in Fig. 2a. Well-dispersed, spherical particles were anchored onto the external walls of MWCNTs, and the size range of these particles was about 5–10 nm. EDS examination confirmed the presence of Pd in the MWCNT samples. A commercial Pd on activated carbon catalyst sample was also examined for comparison. The commercial Pd/C sample showed numerous very large Pd particles irregularly distributed on carbon surfaces. The MWCNT appears to provide a template for decoration of nanometer-sized Pd metal particles on the carbon surfaces. By increasing the amount of Pd(hfa)$_2$ precursor, the loading density of Pd nanoparticles on the outer walls of CNTs can be increased (Fig. 2b to 2c). Fig. 2(d) shows that MWCNTs were densely covered by Pd nanoparticles when 50 mg of the Pd(hfa)$_2$ precursor was used for deposition.

The reduction of the precursor Pd(hfa)$_2$ in the supercritical CO$_2$ system proceeds according to the reaction H$_2$ + Pd(hfa)$_2$ → Pd + 2 Hhfa.[12] Probably due to the high curvature of the MWCNT, only certain sizes of the Pd nanoparticles can be attached to the outer walls of the substrate. In commercial Pd/C catalyst, activated carbon provides a support to stabilize small Pd particles that are highly reactive. The MWCNTs apparently are capable of stabilizing nanometer-sized Pd particles on the external surfaces.

Chemistry in ecologically benign solvents such as liquid or supercritical CO$_2$ is of increasing interest in recent years. We have recently reported that Pd nanoparticles dispersed by a
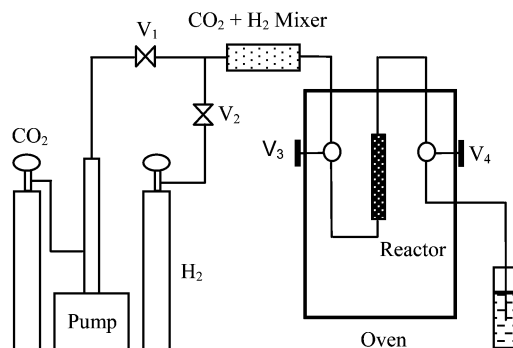

Fig. 1 Experimental set-up for MWCNT decoration using scCO$_2$.

water-in-CO_2 microemulsion are very effective catalysts for hydrogenation of a number of olefins.[14] However, separation of products from the surfactants and reuse of the catalyst are potential technical difficulties associated with the micro-emulsion technique. Developing effective heterogeneous catalysts that can be reused for chemical synthesis in liquid or supercritical CO_2 is currently of great interest to the chemical industry. The Pd nanoparticle–MWCNT composite may provide an effective catalyst for chemical synthesis in a green solvent that allows easy separation of products and minimization of waste solvent generation.

The catalytic capability of the Pd–MWCNT composite was tested for hydrogenation of a CO_2-soluble olefin *trans*-stilbene in liquid CO_2. In this test, stilbene was dissolved in a mixture of 5 atm H_2 and 100 atm of CO_2 to make a 0.033 mol L^{-1} solution. The solution was pumped into a 6.94 ml stainless steel vessel loaded with 5 mg of the Pd–MWCNT composite (reported in Fig. 2b) at room temperature (23 °C). Ultrasonication was applied to the vessel for 10 s to disperse the catalyst. The product was collected in $CDCl_3$ at different times and analyzed by proton NMR (Bruker, AMX 300). According to our NMR results, conversion of stilbene to 1,2-diphenylethane was about 80% and 96% after 5 and 10 min of reaction, respectively.

A number of noble metal–carbon fiber or metal porphyrin–graphite composites have been demonstrated to catalyze electrochemical reactions significantly.[5,15] Our Pd–MWCNT composite was also tested for its electrocatalytic activity in oxygen reduction that is important in fuel cell applications. For comparison, graphite powder, MWCNTs and Pd–MWCNT 2b were mixed individually with mineral oil to make three different carbon paste working electrodes. Cyclic voltammetry measurements were conducted at room temperature in a three-compartment electrochemical cell. The electrolyte was 1.0 M H_2SO_4 saturated with oxygen. The potential was cycled between +0.60 and −0.10 V at 40 mV s^{-1}. As shown in Fig. 3,
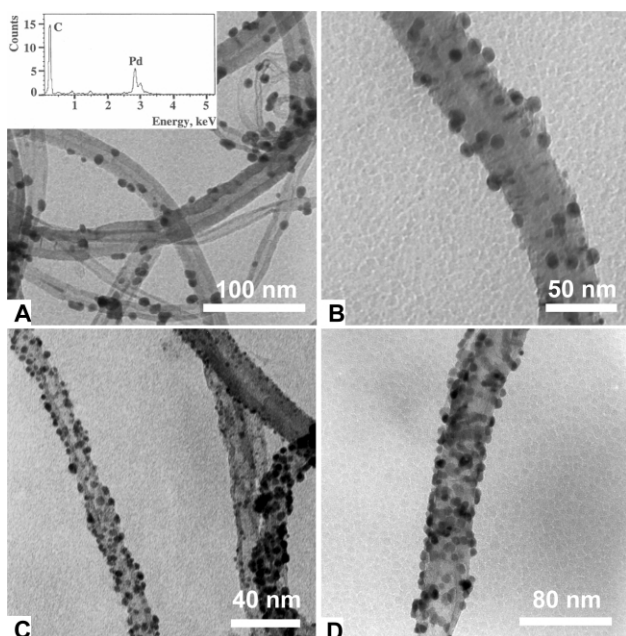

Fig. 2 TEM images of MWCNTs decorated with Pd nanoparticles after hydrogen reduction of (a) 10 mg, (b) 20 mg, (c) 30 mg and (4) 50 mg $Pd(hfa)_2$.
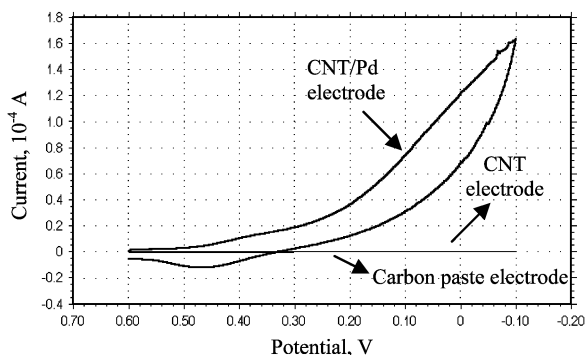

Fig. 3 Cyclic voltammograms of oxygen reduction in 1.0 M H_2SO_4.

essentially no O_2 reduction was observed over the potential window for the carbon paste electrodes of bare MWCNT and graphite powder. In contrast, for the Pd–MWCNT electrode, a very large O_2 reduction wave was observed at potentials characteristic for Pd electrocatalysis. The enhancement of the cathodic current indicates a high electrocatalytic activity of the Pd–MWCNT electrode for the reduction of oxygen.

In summary, this study has demonstrated that palladium nanoparticles (5–10 nm in diameter) can be successfully deposited on MWCNTs by hydrogen reduction of $Pd(hfa)_2$ using supercritical CO_2 as a reaction medium. Preliminary tests indicated that the Pd–MWCNT composite exhibits a high catalytic activity for hydrogenation of olefins in CO_2 as well as a high electrocatalytic activity for oxygen reduction in potential fuel cell applications. This simple and green nanoparticle deposition technique is not limited to Pd; it may be used to prepare a variety of metal nanoparticles on MWCNT surfaces for catalysis applications.

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