Solvent dispersible nanoplatinum–carbon nanotube hybrids for application in homogeneous catalysis[†]

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Solvent-dispersible carbon nanotubes/nanoplatinum hybrid structures are presented, which show excellent catalytic activity under both heterogeneous and homogeneous conditions.

Carbon nanotubes (CNTs)¹ are effective supports for nanoscale platinum (NP) particles,² and together they represent hybrid structures (NP-CNTs) that combine the unique properties of both.³ They are expected to find numerous applications ranging from electrochemistry⁴ and fuel cells⁵ to catalysts for chemical reactions.⁶ The nanotubes are chemically inert and are difficult to disperse in aqueous as well as organic solvents.^{7,8} The dispersibility of NP-CNTs has not been addressed, and the inherent incompatibility with solvents and polymers has limited their processibility as well as applicability. For example, soluble organometallic compounds containing platinum are routinely used in homogeneous catalysis.⁹ Dispersible NP-CNTs may very well represent the next generation of such catalysts. The advantage of such a system is that the CNTs can be easily separated from the solution by centrifugation or precipitation. In this paper, we report for the first time the synthesis of solvent dispersible NP-CNTs, and their application as catalysts in organic reactions.

Pre-synthesized metal nanoparticles have been deposited on CNTs via self-assembly,¹⁰ a sonochemical process¹¹ and electron-beam-induced deposition.¹² Many of these methods require elaborate instrumentation and complex procedures that limit their real-world applications. Both metals and CNTs are known to be reactive under microwave heating.^{13,14} In this study we developed for the first time a microwave induced reaction for the synthesis of dispersible NP-CNTs. A detailed description of the synthetic procedures is reported in the supplementary information.^{†15,16} Hydrophilic groups such as -COOH were generated via concentrated H₂SO₄-HNO₃ treatment under microwave irradiation to render polarity to the multi-walled carbon nanotubes (p-MWNTs) and make them dispersible in water and ethanol. The solubility depends upon the degree of functionalization and can be as high as 1 mg mL⁻¹ in the aqueous dispersion and 0.5 mg mL⁻¹ in the ethanol.¹⁵ However, the solubility of p-MWNTs in non-polar solvents was poor. Octadecylamine (ODA) was grafted onto the nanotube sidewalls to form organic dispersible derivatives

(o-MWNTs), which were highly dispersible in *o*-dichlorobenzene (ODCB), xylene and tetrahydrofuran (THF).

The NP coated unfunctionalized MWNTs, p-MWNTs and o-MWNTs are referred to as NP-MWNTs, p-NP-MWNTs and o-NP-MWNTs respectively. Solvent selection was critical in the reduction of platinum salt during the hybrid formation. Among the different solvents tested (water, ethanol, THF and DMF (dimethylformamide)), ethanol was found to be the most promising one. The controlled decomposition of platinum dichloride (PtCl₂) under microwave irradiation led to the formation of relatively uniform nanoparticles that decorated the MWNTs. The initial concentration of PtCl₂ could be varied to control the final platinum loading, which was as high as 42% by weight. This approach was also applicable to other metals, including zirconium, silver, cobalt, zinc sulfide and cadmium sulfide. In this study, we demonstrate that the whole process can be carried out rapidly under microwave induced conditions, leading to the development of a fast and scalable methodology.

The photographs in Fig. 1 clearly demonstrate the dispersibility of all the three NP hybrids. The NP-MWNTs (Fig. 1a and b) showed no evidence of dispersibility in ethanol or ODCB and sank to the bottom. The p-NP-MWNTs showed good dispersibility in ethanol due to the presence of hydrophilic groups on the nanotubes (Fig. 1c). However, its dispersibility was poor in the organic solvents. Due to the grafted ODA, the dispersion in the organic phase increased significantly for o-NP-MWNTs (Fig. 1d). Two colloidal solutions remained as homogeneous dispersions for several months without the need for shaking or other forms of assistance (Fig. 1c and d). The o-NP-MWNTs showed no aqueous dispersibility as all of the carboxylic groups were exchanged by ODA. It was evident that the NP-CNT hybrids retained their respective dispersibility.

Microscopic images of original MWNTs and the dispersible hybrids are presented to show that the nanotubes did not lose their structures. Fig. 2a is the original MWNTs and 2 b/d and c/e are p-NP-MWNTs and o-NP-MWNTs respectively. Scanning electron microscopic (SEM) images revealed that the NP were homogeneously deposited on the wall of CNTs. Based on the SEM and energy dispersive X-ray spectroscopic (EDS) maps, the distribution of nanoplatinum was quite uniform with high surface density. The deposition on o-MWNTs appeared to be more uniform than on p-MWNTs. Transmission electron microscopic (TEM) images clearly showed that the size of Pt particles ranged from 5 to 50 nm on p-NP-MWNTs and from 1 to 10 nm on o-NP-MWNTs. In order to compare the microwave-assisted platinum-salt decomposition with conventional approaches, the reaction

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Fig. 1 Photographs of NP-CNT hybrids dispersed in the different solvents: (a) non-dispersible NP-MWNTs in ethanol; (b) non-dispersible NP-MWNTs in ODCB; (c) p-NP-MWNTs in ethanol and (d) o-NP-MWNTs in ODCB (ODCB: *o*-dichlorobenzene).

was also carried out under reflux at 120 $^{\circ}$ C for over an hour. The platinum decomposition was incomplete, and there were nonuniformly distributed clusters of Pt.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface of the original MWNTs and the corresponding dispersible products. The carbon peak at 284.0 eV was used to calibrate the whole spectra. Fig. 3a–c (Fig. 3A) are the original MWNTs, p-MWNTs and o-MWNTs respectively. Fig. 3d–f (Fig. 3B) are original salt PtCl₂, p-NP-MWNTs and o-NP-MWNTs. Compared to the original MWNTs, there was no major shift for the C component at 284.0 eV. This indicated that the microwave process for the synthesis of NP-MWNTs retained the integrity of the CNT structures. The Cl component (2p3/2) at 203.3 eV was seen in the starting PtCl₂. However, this was not seen in the dispersible hybrids. This also indicated that PtCl₂ had been decomposed completely, which was in agreement with the EDS data. The spectra of the Pt component (4f) are shown



Fig. 2 SEM and TEM images of: (a) original MWNTs; (b), (d) p-NP-MWNTs and (c), (e) o-NP-MWNTs. [The scale bar is 20 nm].



Fig. 3 XPS survey scan spectra of A: (a) original MWNTs; (b) p-MWNTs; (c) o-MWNTs; and B: (d) PtCl₂; (e) p-NP-MWNTs; (f) o-NP-MWNTs.

in Fig. 3B. Platinum has three possible oxidation states, namely Pt($_0$), Pt($_I$) and Pt($_V$) corresponding to (4f) binding energies (BE) of 71.1–74.4, 72.8–76.1, and 74.3–77.6 eV respectively.⁵ The starting PtCl₂ showed a peak around 76.0 eV, characteristic of Pt($_I$). After the microwave induced reactions, the peaks of the Pt component in soluble hybrids shifted to a lower energy.

The dispersible NP-MWNTs were used in homogeneous catalytic reactions. Liquid-phase hydrogenation of nitrochlorobenzene to the corresponding chloroaniline was studied. Ethanol was used as the solvent. The o-NP-MWNTs had limited dispersibility in ethanol, while the p-NP-MWNTs were well mixed in the system. The former represented a heterogeneous catalytic environment, while the latter was a homogeneous one. In the typical reactions, 20 mL m-nitrochlorobenzene, 1 g of dispersible NP-MWNTs with 2 weight% platinum loading and 50 mL ethanol were mixed into 200 mL high-pressure autoclave. The reaction was carried out under a pressure of 1.0 MPa and 100 °C for eight hours. Both systems demonstrated catalytic activity with conversion to chloroaniline. The yield from o-NP-MWNTs was between 50-60%, but that from p-NP-MWNTs was close to 100% with negligible quantities of nitrochlorobenzene detected in the reaction product. Therefore, the homogeneous system offered higher conversion efficiency.

In summary, a fast, controlled and "green" microwaveassisted method for synthesis of solvent dispersible NP-MWNT hybrids is presented. The NP-MWNTs retained their dispersibility for long periods of time, and showed catalytic activity under both heterogeneous and homogeneous conditions. As expected, the homogeneous system showed higher yield.

Notes and references

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