

Charge Transfer in Carbon Nanotubes-Supported Nanoparticles

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Due to their outstanding mechanical and electrical properties, carbon nanotubes (CNTs) are being considered as promising materials in various fields such as electronic, material engineering, sensor design and catalysis. A potential application of carbon nanotubes consists of using them as support of nanoparticles for heterogeneous catalysis.^[1] Aiming this, we chose mixed-metal clusters as precursors of bimetallic catalysts from which a synergic effect between constituting metals is expected. Moreover, the size and composition of the activated metallic nanoparticles can be easily controlled by selecting the appropriate starting cluster. More specifically, we synthesized the $[\text{Ru}_5\text{PtC}(\text{CO})_{14}\text{COD}]$ cluster compound as nanoparticle precursor.^[2]

As previously reported, interactions between support and precursors are of critical importance in the preparation of heterogeneous catalysts.^[3] A chemical modification of the nanotubes allows to introduce anchoring groups on their surfaces. Among the carbon nanotubes covalent functionalization pathways, diazonium salts are widely used as radical reagents. This type of compounds is used for the covalent grafting of phenyl derivatives on the carbon nanotubes surface. Subsequent modification of those grafted moieties allows the bimetallic cluster compound to be anchored securely. In this work, we developed a four-step functionalization pathway of single-walled carbon nanotubes (SWNTs): (i) covalent functionalization of carbon nanotubes by diazonium salt; (ii) derivatization of the functionalized nanotubes in order to anchor a ligand for cluster coordination; (iii) cluster coordination; and eventually (iv) thermal activation (Figure 1). At the end of this process, we obtained 'naked' Ru-Pt nanoparticles of 1-2 nm size supported on carbon nanotubes (Figure 2), which are expected to exhibit catalytic activity.^[4]

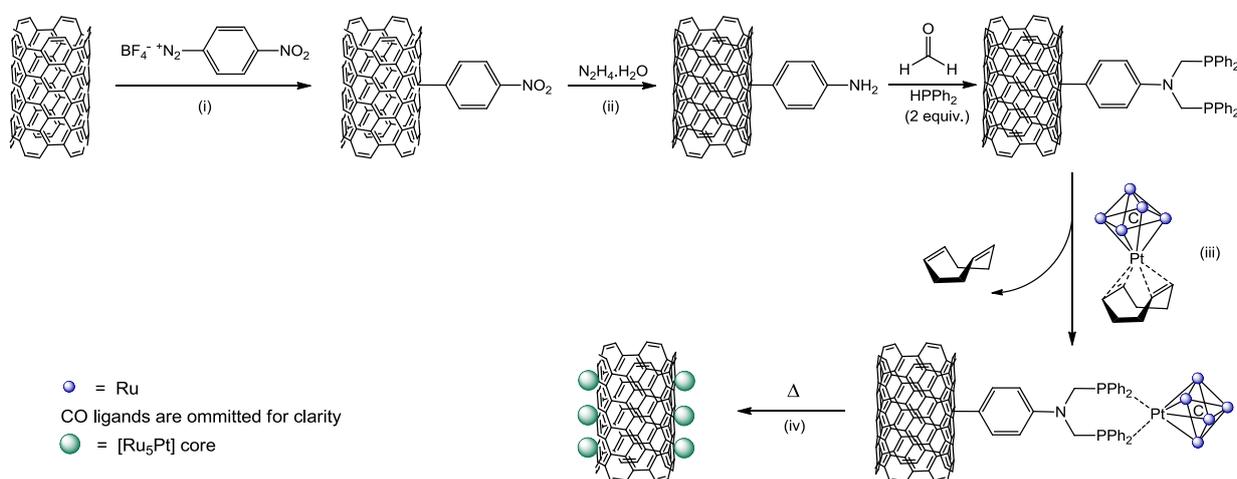


Figure 1. Reaction scheme of the functionalization pathway developed for the formation of $[\text{Ru}_5\text{Pt}]$ nanoparticles on carbon nanotubes.

Those nanoparticles-decorated carbon nanotubes can be used to study the charge transfer between nanotubes and nanoparticles. In order to do this, individual single-walled carbon nanotubes field-effect transistors (SWNT-FETs, Figure 3a) were prepared by dispersion and deposition of SWNTs on n-doped SiO_2/Si , followed by conventional optical lithography and lift-off techniques.^[5] These devices were used to measure the electrical response of nanotubes-supported nanoparticles. Drain-source current (I_{ds}) was measured while varying gate voltage (V_g) for pristine-, functionalized- and nanoparticles decorated-carbon nanotubes.

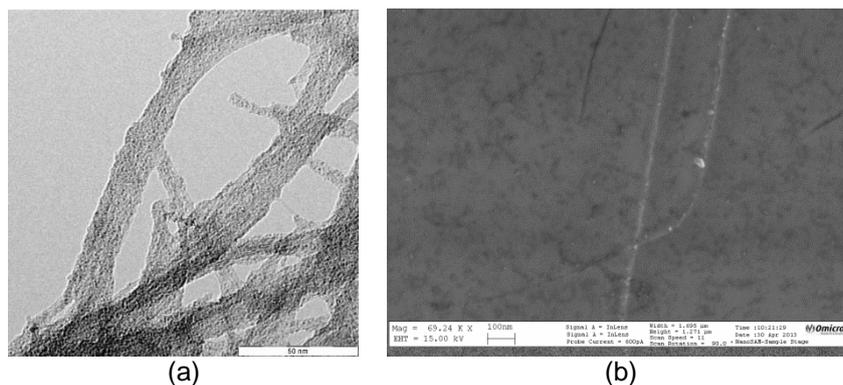


Figure 2. (a) TEM image of SWNTs supported nanoparticles; (b) HR-SEM image of Si-supported nanoparticles-decorated SWNTs.

Measurement of functionalized-carbon nanotubes revealed a high loss of conductance (70 to 80 %) compared with pristine-CNTs. This result is due to the covalent nature of the functionalization step, which alters the aromaticity of the nanotube.^[6] Modification of the grafted moieties does not change the electrical characteristics, since the tube is not further altered by these steps. During thermal annealing, activated nanoparticles are deposited on the carbon nanotube surface. After this activation step, carbon nanotubes recover about 60 % of their initial conductance. Moreover, these measurements show evidence of a charge transfer from the nanotube to the nanoparticle, as revealed by the p-doping of the carbon nanotubes (Figure 3b). This charge transfer is of significant relevance for catalytic applications, since the nanoparticle can be viewed as an electron sink.

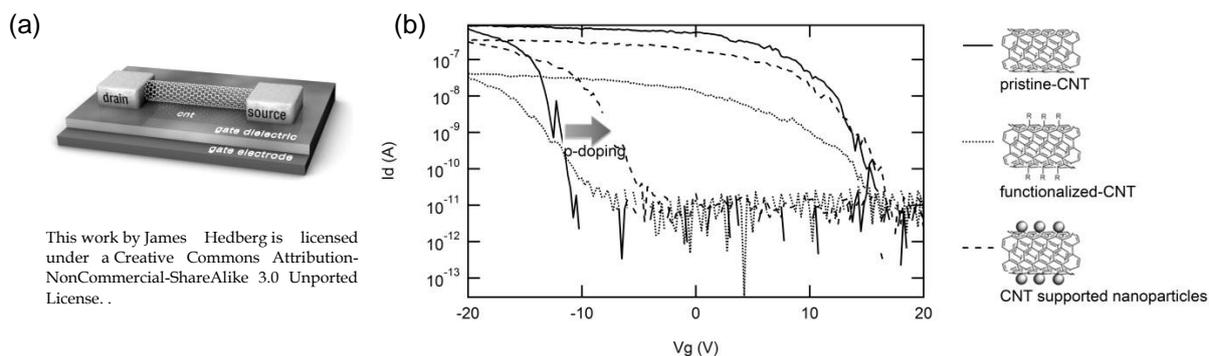


Figure 3. (a) Schematic representation of a CNT-FET; (b) Charge transfer in carbon nanotubes supported nanoparticles.

In summary, we have covalently grafted Ru_5Pt clusters on single-walled carbon nanotubes. After thermal activation, we obtained bimetallic nanoparticles-decorated carbon nanotubes. Electrical characterization of those nanohybrids revealed a charge transfer between nanoparticles and carbon nanotubes as evidenced by p-doping of CNTs. Those materials are expected to exhibit catalytic activity.

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