Electrochemistry

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Functionalization of Carbon Nanotubes by an Ionic-Liquid Polymer: Dispersion of Pt and PtRu Nanoparticles on Carbon Nanotubes and Their Electrocatalytic Oxidation of Methanol**

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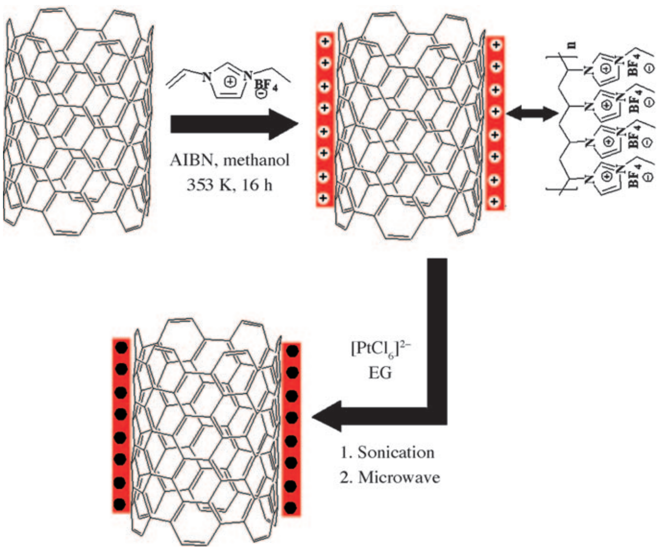
Carbon nanotubes (CNTs) possess high specific surface areas, electrical conductivities, chemical stability, and so on.[1] It has also been demonstrated that CNTs enhance the electron-transfer rate of many redox reactions.[2] These unique properties make CNTs very useful for supporting noble-metal nanoparticles, and metal-nanoparticle/CNT nanohybrids have many potential applications ranging from advanced sensors to highly efficient fuel cells.[3] Several routes have been developed to link the metal nanoparticles to the CNT surface.[4] Examples include chemical deposition with and without the aid of reducing agents,[5] electrochemical deposition,[6] and the direct assembly of metal nanoparticles.[7] It is well known that for CNTs without surface modification, there are insufficient binding sites for anchoring the precursors of metal ions or metal nanoparticles, which usually leads to poor dispersion and large metal nanoparticles, especially under high loading conditions.[3f,8] To introduce more binding sites and surface anchoring groups, surface functionalization of CNTs is generally carried out. These strategies include chemical or electrochemical oxidation at defect sites of CNTs, wrapping of CNTs with polymer,[3f,9] grafting of tethers such as dendrons,[10] and modification of CNTs with 1-aminopyrene by π stacking.[11]

Recently, imidazolium ionic liquids (ILs) were used as the solvent and stabilizer to produce metal nanoparticles.[12] Niu et al. used CNTs covalently modified with ILs to support Au nanoparticles.[13] Based on the excellent physicochemical properties of ILs, gold-nanoparticle/CNT-IL nanohybrids showed good electrocatalytic behavior toward oxygen reduction. However, this strategy includes acid-oxidation pretreatment of CNTs, which causes some structural damage to the CNTs and leads to the loss of their electrical conductivity.[3f,11,14] Also, there are insufficient binding sites to anchor the precursors of metal ions or metal nanoparticles because of the limited defect sites presented on the CNTs to immobilize ILs.

Herein, by selecting Pt and PtRu nanoparticles as the model because of wide interest in their use in fuel cells, we report an alternative strategy to disperse metal nanoparticles on CNTs. Our approach is based on the thermal-initiation-free radical polymerization of the IL monomer 3-ethyl-1-vinylimidazolium tetrafluoroborate ([VEIM]BF_4) to form an ionic-liquid polymer (PIL) on the CNT surface, which introduces a large number of surface functional groups on the CNTs with uniform distribution to anchor and grow metal nanoparticles (Scheme 1). The PIL film on the CNTs creates a distribution of ionic species with positive charge that prevents aggregation of the CNTs and induces stable nanotube suspensions in water, which serves as the medium to stabilize and anchor metal nanoparticles. On the other hand, the process of modification by PIL would lead to less structural damage of CNTs than the typical acid-oxidation treatment because of the mild polymerization of the IL monomer. It is expected that PtRu and Pt nanoparticles will be dispersed uniformly on the PIL-functionalized CNTs (CNTs-PIL) and that the obtained catalysts (PtRu/CNTs-PIL and Pt/CNTs-PIL) will show superb performance for direct electrooxidation of methanol. As a comparison, PtRu and Pt nanoparticles



Scheme 1. Schematic diagram of the modification of CNTs with PIL and the preparation of Pt/CNTs-PIL nanohybrids. EG: ethylene glycol, AIBN: 2,2′-azobisisobutyronitrile.

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were supported on the CNTs without functionalization by PIL and the electrocatalytic properties of these Pt/CNTs and PtRu/CNTs catalysts for methanol oxidation were also investigated.

CNTs surface-functionalized with PIL were characterized by thermogravimetric analysis (TGA) and Raman spectroscopy. The TGA results (see the Supporting Information, Figure S1) confirm that PIL was successfully coated onto the CNTs, and the weight ratio of the surface-bound PIL to CNTs is estimated to be 0.15:0.85. As expected, the results from Raman spectroscopy of the pristine CNTs, CNTs-PIL, and acid-oxidized CNTs (CNTs-AO; see the Supporting Information, Figure S2) indicate that the PIL modification process led to some structural damage of the CNTs, but the extent of the damage of the CNTs-PIL was much smaller than that of the CNTs-AO. This result implies that the CNTs-PIL should retain better electrical conductivity than the CNTs-AO, which is beneficial to the electrochemical properties of catalysts supported on the CNTs-PIL.

Figure 1 shows transmission electron microscopy (TEM) images of the PtRu/CNTs-PIL and Pt/CNTs-PIL nanohybrids. As a comparison, the TEM images of the PtRu/CNTs and Pt/CNTs nanohybrids are also presented. Full TEM images with different magnifications of these nanohybrids are provided in the Supporting Information (Figures S3–S6). As shown in Figure 1, TEM confirms that the CNTs-PIL are decorated successfully with many well-dispersed PtRu and Pt nanoparticles. Their size distribution was evaluated statistically through measuring the diameter of 200 PtRu (or Pt) nanoparticles in the selected TEM images. It is noted that the particle size of PtRu (or Pt) distributes mainly between 0.9 and 2.4 nm (between 0.9 and 3.0 nm for Pt) with an average diameter of about (1.3 ± 0.4) nm (ca. (1.9 ± 0.5) nm for Pt). Notably, no nanoparticle aggregation is clearly observed on the nanotube surface. However, for the CNTs without PIL modification, metal nanoparticles did not disperse uniformly on the CNT surface and had a broad distribution (2–7 nm for PtRu, 3–8 nm for Pt) with an average diameter of approximately (3.5 ± 1.0) nm for PtRu and (5.5 ± 1.5) nm for Pt. The reasons for this finding should be as follows. For the CNTs without PIL modification, the defects generated during the growth and post-synthesis treatment of the CNTs are usually not uniform. When PtRu (or Pt) nanoparticles are deposited on the CNTs, the particles tend to deposit on these localized defect sites, thus leading to poor dispersion and aggregation. However, for the CNTs with PIL modification, the PIL film on the CNTs produces a uniform distribution of the imidazole groups that serve as functional groups for the immobilization of Pt and Ru precursors on the surface of the CNTs, through electrostatic interaction and coordination.[15] Therefore, a much more uniform distribution of PtRu (or Pt) nanoparticles is observed on the surface of the CNTs-PIL. On the other hand, it is noted that the loading mass (see the Supporting Information, Table S1) of the PtRu (or Pt) nanoparticles supported on the CNTs-PIL is higher than that on the CNTs (the PIL-free samples). This further confirms that the CNTs-PIL have lots of surface functional groups to anchor and grow metal nanoparticles and are a suitable support for electrocatalysts.

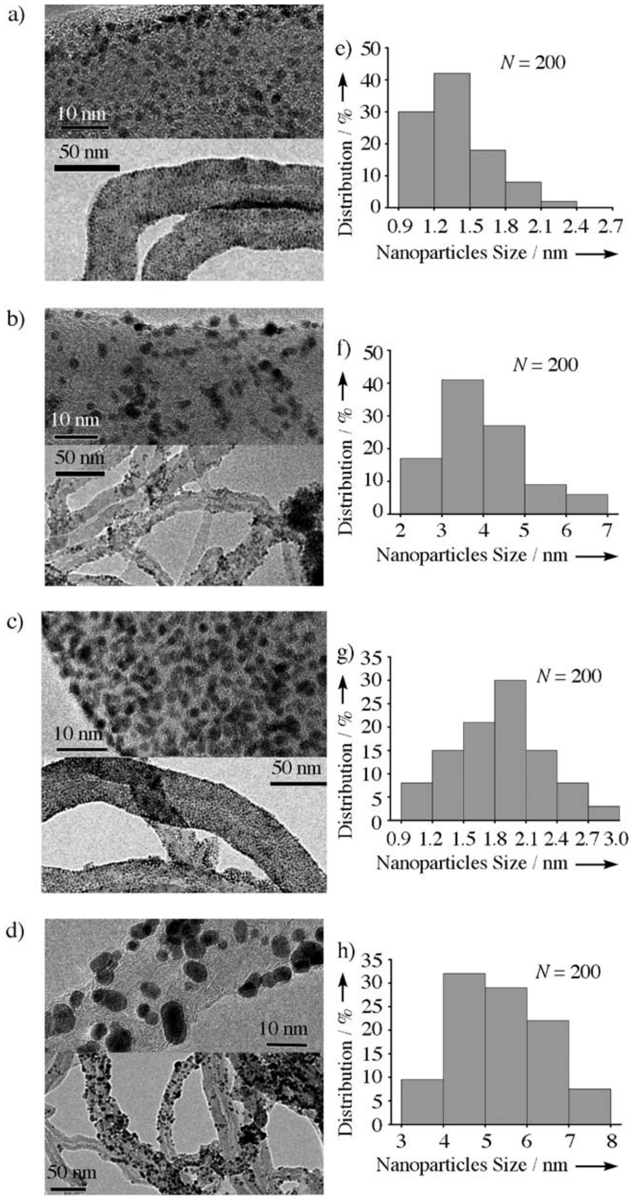

Figure 1. TEM images (left) and size distributions (right) of nanoparticles of nanohybrids. a,e) PtRu/CNTs-PIL; b,f) PtRu/CNTs; c,g) Pt/CNTs-PIL; d,h) Pt/CNTs.

By using hydrogen adsorption–desorption methods in conjunction with cyclic voltammetry, the electrochemical surface area (ESA) of PtRu (or Pt) nanoparticles supported on the CNTs-PIL or CNTs was measured[16] (see the Supporting Information, Figure S7, Table S2). The ESA value of the PtRu/CNTs-PIL (or Pt/CNTs-PIL) catalyst is 91.2 (or 71.4) $m^2 g^{-1}$ of Pt, higher than the 53.5 (or 47.1) $m^2 g^{-1}$ of Pt for the PtRu/CNTs (or Pt/CNTs) catalyst, most likely a result of the smaller size and much better dispersion of PtRu (or Pt) nanoparticles on the CNTs-PIL. This finding also demonstrates that the PtRu (or Pt) nanoparticles deposited on the CNTs-PIL are electrochemically more accessible, which is very important for the electrochemical oxidation of methanol. It is well known that the larger the ESA of a catalyst, the higher the electrocatalytic activity. It is expected that the PtRu/CNTs-PIL (or Pt/CNTs-PIL) catalyst will have a higher electrocatalytic activity than the PtRu/CNTs (or Pt/CNTs) catalyst.

The performance of the different metal-nanoparticle (PtRu or Pt)/CNTs nanohybrid materials toward the electrocatalytic oxidation of methanol was evaluated by cyclic voltammetry. Compared with the Pt/CNTs and PtRu/CNTs catalysts, a significant enhancement of the peak current and an obvious negative shift of the peak potential and the onset potential of methanol oxidation can be observed on both Pt/CNTs-PIL and PtRu/CNTs-PIL catalysts (see the Supporting Information, Figure S8, Table S3). On the other hand, the chronoamperometric technique, a useful method for the evaluation of the electrocatalysts in fuel cells,[17] was employed to further investigate the electrochemical performance of PtRu (or Pt) nanoparticles supported on the CNTs-PIL, and typical results are shown in Figure 2. We investigated several potentials and the dependence between the steady-state current and the potential is plotted in Figure 3 a. The steady-state current was recorded at 120 s from the chronoamperometry results.[18] Figure 3 a indicates that the PtRu/CNTs-PIL (or Pt/CNTs-PIL) catalyst exhibits better performance for methanol electrooxidation than the PtRu/CNTs (or Pt/CNTs) catalyst for all applied potentials. A comparison of the steady-state current obtained on the PtRu (or Pt) nanoparticles supported on the CNTs with and without PIL modification is shown in Figure 3 b. The enhancement factor *R*, which is the ratio between the steady-state current on the PtRu/CNTs-PIL and PtRu/CNTs (Pt/CNTs-PIL and Pt/CNTs) catalysts, varies between 170 and 418 % (135 and 334 %) in the potential region of 0.30–0.70 V. These results show a noticeable feature in that all PIL-modified CNT-supported catalysts exhibit higher electrocatalytic activities than the corresponding CNT samples. The reasons for the above observation could be that the metal-nanoparticle/CNTs-PIL nanohybrids have the following superior features over the metal-nanoparticle/CNTs samples: smaller sizes, better dispersion, and higher ESA of the PtRu (or Pt) nanoparticles.

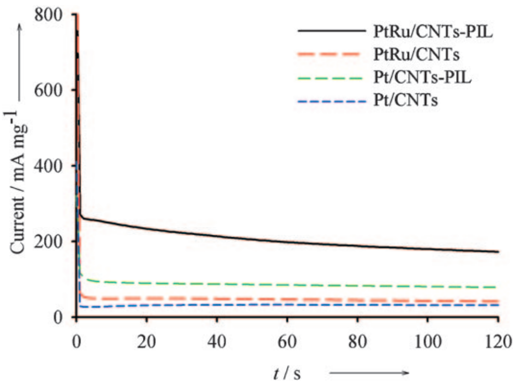

Figure 2. Transient current of PtRu/CNTs-PIL, PtRu/CNTs, Pt/CNTs-PIL, and Pt/CNTs catalysts for methanol electrooxidation at 0.50 V in nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH aqueous solution.

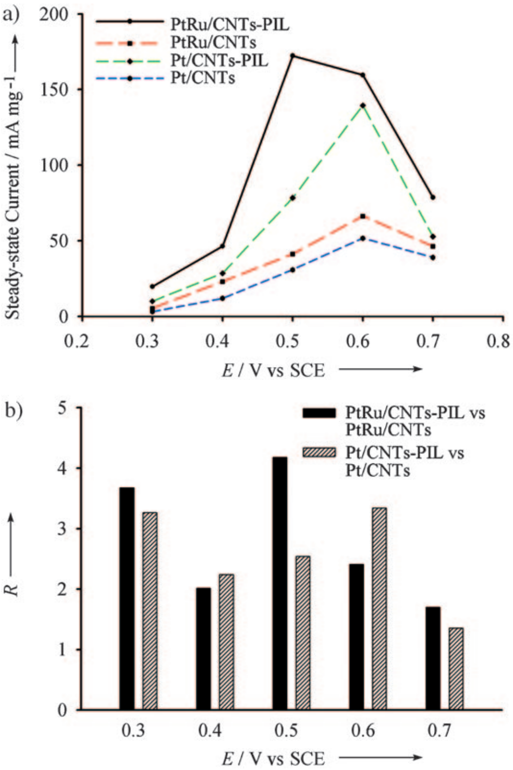

Figure 3. a) Potential-dependent steady-state current (recorded at 120 s) of methanol electrooxidation on the different catalysts. b) Dependence of the enhancement factor *R* on the potential. SCE: saturated calomel electrode.

In summary, we have developed a new strategy for the synthesis of metal-nanoparticle/CNT nanohybrids based on PIL-functionalized CNTs. As a result of the uniform distribution of the surface functional groups provided by PIL, Pt and PtRu nanoparticles supported on the CNTs-PIL have a smaller particle size, better dispersion, and higher ESA than those on CNTs without PIL modification. The PtRu/CNTs-PIL (or Pt/CNTs-PIL) electrocatalyst shows better performance in the direct electrooxidation of methanol than the PtRu/CNTs (or Pt/CNTs) electrocatalyst. The CNTs-PIL should be a suitable material for CNT-based nanohybrids and a promising catalyst support in fuel cells.

Experimental Section

Pristine multiwalled CNTs (length 5–15 μm, diameter 20–60 nm) were purchased from Shenzhen Nanotech Port Co. Ltd., China. [VEIM]BF_4 was purchased from Hangzhou Chemer Chemical Co. Ltd., China. Except where specified, all chemicals were of analytical grade and used as received.

The surface functionalization of CNTs was accomplished by the following procedure.[15a,19] CNTs (200.0 mg) were added to methanol (25.0 mL) containing [VEIM]BF_4 (210.1 mg) and 2,2′-azobisisobutyronitrile (AIBN; 6.9 mg). The mixture was ultrasonicated for 15 min and then transferred to a 50.0-mL round-bottomed flask equipped with a condenser and magnetic stirrer. The mixture was refluxed for 16 h at 353 K under vigorous stirring and N_2 protection. After that, the mixture was diluted with double-distilled water, filtered through a nylon 66 membrane, and washed with double-distilled water and acetone several times to thoroughly remove physically absorbed polymer and unreacted [VEIM]BF_4 monomer from the surface of the CNTs. The final products, referred to as CNTs-PIL, were then dried in a vacuum oven at 333 K to remove the residual solvent. The deposition of Pt and PtRu nanoparticles on CNTs with and without PIL modification was carried out as reported in reference [20] and the detailed procedure is provided in the Supporting Information. The morphology of the Pt/CNTs-PIL, PtRu/CNTs-PIL, Pt/CNTs, and PtRu/CNTs nanohybrids was characterized by TEM (JEM-3010, Joel, Japan). The corresponding loading mass of metal nanoparticles on the nanohybrids was investigated by inductively coupled plasma–atomic emission spectroscopy and is summarized in Table S1 in the Supporting Information. The ESA and the electrochemical performance of the nanohybrids were evaluated by cyclic voltammetry and chronoamperometry, and the related details are provided in the Supporting Information. The current (mA mg^{-1}) per unit of the loading mass of PtRu (or Pt) nanoparticles was used throughout. All the potentials reported herein were with respect to the SCE.

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