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Characterization and electrocatalytic application of a fullerene/ionic-liquid composite

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Abstract

A fullerene/ionic-liquid composite was explored. Transmission Electron Microscopy (TEM) study showed that in the composite, C_{60} mainly exists as nano-clusters, Raman spectrum proved that the composite formed only by physical mix of C_{60} and 1-Butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$), the combination did not change the chemical naturation of C_{60}. The electrochemical properties of the composite modified electrode, including the electrode reaction control function and the interfacial potential effect were studied. The results showed the electrode reaction is controlled by the diffusion and the interfacial potential can be ignored on the modified electrode. At the same time, the composite was found electrocatalytic property in the electrochemical oxidation of dihydronicotinamide adenine dinucleotide (NADH).

Keywords: C_{60}; Ionic liquids; Composite materials; NADH; Electrocatalysis

1. Introduction

Room-temperature ionic liquids (RILs) [1], are from the combination of organic cations and various anions. They remain liquid state at room temperature [2–6] and have been taken as novel attractive solvents. They exhibit a serial of unique properties, including negligible vapor pressure, wide potential windows, high thermal stability, high viscosity, good conductivity and good solubility [7]. If the high ionic conductivity of RILs combined with the electrically conductive property of carbon materials together to form hybrid RILs–carbon composite materials, the result would be very interesting. The composite formed by RILs and signal-walled carbon nanotubes (SWNTs) was first reported by Aida et al. [1]. One of the gels developed by them has been used in biocatalysis study [8]. Dong et al. reported the composite formed by RILs and multi-walled carbon nanotubes or mesocarbon microbeads [9]. Because organic cations can act with π-electronic compounds through "cation-π" interation [10], the π-electrode containing materials such as SMNTs can be processed by ammonium ion based molten salts [11,12]. According to Aida's work, the mix and ground of RILs and SWNTs can cause gelation but won't change the natural quality of SWNTs. As an important member of the fullerene family, C_{60} has been found with many catalystic applications [13,14]. Similar to SWNTs, C_{60} is another carbon material that contains π-electrode, so it was expected to mix with RILs to form interesting composite. Here we characterized a $C_{60}/BMIPF_6$ composite, studied its electrocatalytic application in the oxidation of NADH. The results suggest that the composite could be used as a novel electrode modifier in the electrocatalytic study of NADH.

2. Experimental

2.1. Chemicals

C_{60} (Aldrich), $BMIPF_6$ (Solvent Innouation) and NADH (Shanghai Shenggong Co. China) are used as received without further purification. Other reagents are all at least analytical reagent grade. All water used was purified through a Millpore system.

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2.2. Preparation of the C_{60}/$BMIPF_6$ composite

The C_{60}/$BMIPF_6$ composite was prepared through the following steps: C_{60} and $BMIPF_6$ were mixed together in a ratio (optimized in control experiments to ensure there was no $BMIPF_6$ exceeding) of 2.5 mg/50 µl and ground with an agate mortar for 30 min to form a coffee-color composite. Then this composite was moved to a smooth glass slide and put in a desiccator for further use.

2.3. TEM and Raman measurements

The TEM sample was prepared via the following steps: the C_{60}/$BMIPF_6$ composite was first dispersed in water under sonication. Then 7 µl of the above solution was dropped onto the copper grid and dried in air. The samples for Raman study were prepared by placing the sample on a glass slide. TEM image was recorded on a JEOL 2000 Transmission Electron Microscopy operating at 200 kV. Raman spectra were obtained on Renishaw 2000 model confocal microscopy Raman spectrometer (Renishaw Ltd., U.K.) upon excitation at 514 nm.

2.4. Electrochemical measurement

The electrochemistry study was carried out with a CHI660B electrochemical workstation (Chenhua instrument Co. Shanghai, China). An Ag/AgCl electrode, a piece of Pt wire and a Glassy carbon electrode (diameter = 3 mm) are served as reference, counter and working electrode, respectively. Before modification, the GC electrode was first polished with 1.0, 0.3 and 0.05 µm alumina, then sonicated and washed with acetone, water and ethanol in turn, and dried in nitrogen stream. Finally, the electrode was rubbed over the composite placed on a spatula and the electrode surface was smoothed with this spatula to leave only a thin film of the composite on it. The weight of the composite mechanically attached to the electrode surface was calculated by measuring the weight of the spatula with the composite before and after the modification process.

3. Results and discussion

3.1. TEM characterization of the C_{60}/$BMIPF_6$ composite

It was found that the mix and ground of C_{60} with RILs did not cause gelation, which is identical to the previous report [1]. But the mix and ground of carbon nanotubes with RILs will cause gelation, it was because the carbon nanotubes usually exist as bundles, which are heavily entangled with one another to form 3D networks [1]. Unlike the carbon nanotubes, each C_{60} molecular has the same football-like shape and the same size, they usually exist as single molecular or congeries, TEM study (Fig. 1) showed that C_{60} exists in the composite mainly as nano-clusters, and did not form 3D networks, which may explain why they did not cause gelation when mix and ground with RILs.

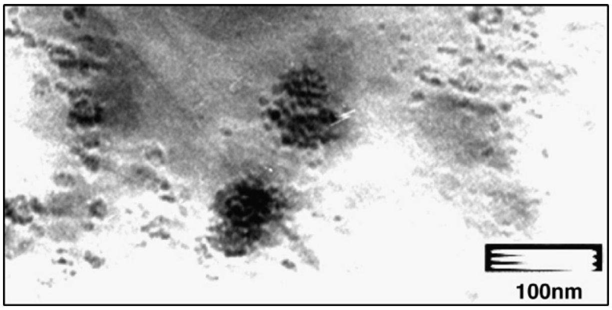

Fig. 1. TEM image of the C_{60}/$BMIPF_6$ composite.

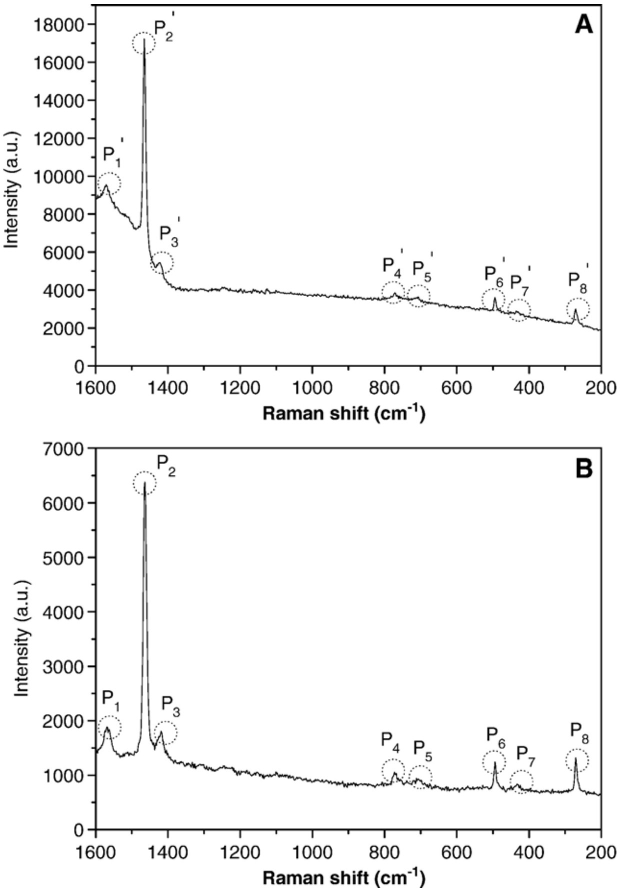

Fig. 2. Raman spectra of (A) the C_{60}/$BMIPF_6$ composite and (B) pure C_{60}.

3.2. Raman spectrum of the C_{60}/$BMIPF_6$ composite

To give the evidence whether C_{60} was chemically denaturated by combination, we compare the Raman spectrum of the C_{60}/$BMIPF_6$ composite with pure C_{60}. For pure C_{60} (Fig. 2 B), eight Raman bands (P_1–P_8) at 1570, 1467, 1423, 772, 709, 494, 433, and 270 cm^{-1} were observed. Raman bands (P_1'–P_8') of the composite (Fig. 2 A) were at 1572, 1465, 1425, 770, 711, 494, 433 and 270 cm^{-1}, which are essentially identical to those of pure C_{60}. From these spectral profiles, it can be deduced that the composite formed only by physical mix of C_{60} and $BMIPF_6$, the combination didn't change the chemical naturation of C_{60}.

3.3. Electrochemical characterization of the C_{60}/$BMIPF_6$ composite modified GC electrode

Fig. 3 was the cyclic voltammograms (CVs) of the C_{60}/$BMIPF_6$ composite modified electrode in 5 mM $K_3Fe(CN)_6$ + 1.0 M KCl solutions. The peak currents were found to increase linearly with the