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Synthesis and electrochemical application of carbon nanotubes obtained from hexachloroethane

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Abstract Carbon nanotubes (CNTs) with the average inner (outer) diameter of 10–20 nm (20–40 nm) and length up to 100s of nanometers were synthesized via Wurtz reaction at 400 °C for 12 h, using C_2Cl_6 and Na as reactants. These CNTs, having more defects because of the sp^3 bonding raw material of C_2Cl_6, were used as electrode material to detect dopamine (DA) via cyclic voltammetry. The results show that there exists linear relation between peak currents and DA concentration in the range of 2×10^{-7}~2.8×10^{-4} mol L^{-1}.The linear regression equation is expressed as Ip (μA) = 0.089 + 0.134c (μmol L^{-1}). This CNTs-modified electrode showed high sensitivity with detection limit of 1×10^{-7} mol L^{-1}.

Introduction

Carbon nanotubes (CNTs), a kind of new nanomaterial, have attracted many researchers since the first report of their discovery [1]. Of all the preparation methods for CNTs, such as catalytic pyrolysis procedure [2], electric arc discharge techniques [3], laser ablation formations [4], solar production [5], microwave plasma chemical vapor deposition [6], and hydrothermal method [7], the catalytic routes seemed to be the most promising for large-scale production. The solvothermal method was also a catalytic route at moderate temperature, which often needed carbon sources with sp^2 bonding, such as C_6Cl_6 [8], C_6H_6 [9] and polytetrafluorethylene [10].

It is well known that CNTs' defects decrease as the number of sp^2 bonding become larger [8]. CNTs with more defects are easily modified and favor to the electron transfer in electrochemistry. So in this study, we used hexachloroethane as carbon source, a compound with sp^3 bonding, to synthesize CNTs with more defects, which were used to modify gold electrode for detecting dopamine (DA) subsequently. This CNT-modified electrode showed wide linear range of 2×10^{-7}~2.8×10^{-4} mol L^{-1} and high-sensitivity with detection limit of 1×10^{-7} mol L^{-1}.

Experimental

Apparatus and reagents

The CNTs were characterized with X-ray powder diffraction (XRD) using Shimadzu XRD-6000 X-ray diffractometer equipped with CuKα radiation (λ = 0.15406 nm), the scanning rate of 0.05°s^{-1} was applied to record the pattern in the 2θ range of 10°–70°. The transmission electron microscope (TEM) images and selected-area electron diffraction (SAED) pattern were taken with a Hitachi Model H-800 transmission electron microscopy. HRTEM image was investigated with a JEOL-2010 transmission electron microscopy. Energy-dispersive X-ray (EDX) spectrometry was carried out with spectroscope (Oxford, Link ISIS) attached to HRTEM. Raman spectrum was obtained with a Labram-HR confocal laser microRaman spectrometer; an argon-ion laser excitation at 514.5 nm was used.

Electrochemical experiments were performed with CHI 620B electrochemical analyzer with a three-electrode system.

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The modified gold electrode was used as working electrode; a saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively.

Dopamine hydrochloride was purchased from Alfa Aesar. Its purity was about 98.5%. 0.1 mol L^{-1} phosphate buffer solution (PBS) was used as solution of electrochemical experiments. All other chemicals were commercially available and used without further purification.

Preparation of CNTs and modified gold electrode

In a typical synthesis process, 0.5 g C_2Cl_6, 5 g Na, 0.01 g Fe powder and 12 mL C_6H_6 were placed into a stainless steel autoclave with a capacity of 20 mL. The autoclave was kept at 400 °C for 12 h and cooled to room temperature naturally. The black resultant was washed with ethanol, HCl (about 2 mol L^{-1}) and distilled water, then dried in vacuum at 60 °C for 2 h.

The as-prepared products were dispersed in concentrated nitric acid (68%, analytical grade), heated for 2 h at 80 °C and stood further for 4 h at room temperature. After washed with distilled water several times, the black suspended solid was dried under infrared lamp. The as-prepared products were treated by ultrasonic agitation for 10 min in dimethyl formamide to form black aqueous colloid (called acid-treated CNTs).

The gold electrode with diameter of 2 mm was polished by alumina slurry and washed in an ultrasonic bath for a few minutes. Dried gold electrode was pasted with acid-treated CNTs and dried with infrared lamp.

Results and discussion

Physical characterization of the CNTs

Figure 1 shows the XRD pattern of the products. Two peaks may be indexed as (002) and (10) of hexagonal graphite structure (JCPDS 41-1487). The (002) is strong while (101) peak is weak and wide.

The typical morphology of the products is presented in Fig. 2, which takes the shape of nanotubes with the average inner (outer) diameter of 10–20 nm (20–40 nm) and length up to 100s of nanometers. The SAED pattern presents two diffraction rings (Fig. 2, inset), which corresponds to (002) and (101) of CNTs.

The HRTEM image of a typical nanotube (Fig. 2, inset) reveals that the fabrication of the walls is made of ca. 40 layers of carbon {001} system. The lattice fringes of interspacing distance between two (002) planes could be clearly seen in the figure with inter-tube spacing of ca. 0.38 nm typical for the (002) lattice distance in hexagonal carbon. It is noticeable that there exist various defects in the wall of CNT observed from the HRTEM image, which might be resulted from raw materials with sp^3 bonding.

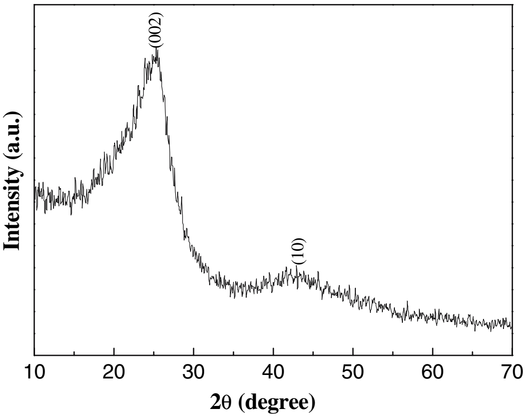

Fig. 1 XRD pattern of as-prepared products showing two diffraction peaks of (002) and (101)

There exist catalysts in the tip of nanotubes judged from the TEM picture. EDX spectrum (Fig. 2, inset) of the catalyst indicated that it is Fe. The carbon in the EDX spectrum originated from the nanotubes, Cu from the copper grid, and O from the surface adsorption of CNTs and catalyst.

Further evidence for the purity of products was obtained with Raman spectrum (Fig. 3). There exist two strong

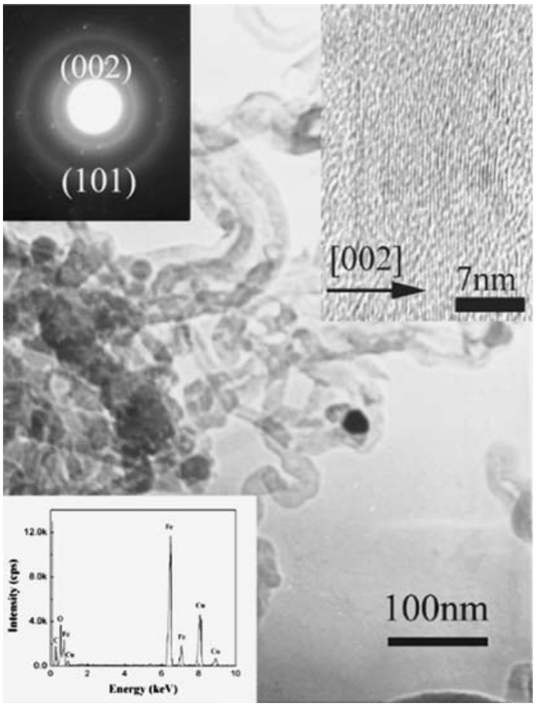

Fig. 2 TEM image, SAED pattern (inset) and HRTEM image (inset) of carbon nanotubes; and EDX spectrum of Fe catalyst (inset)

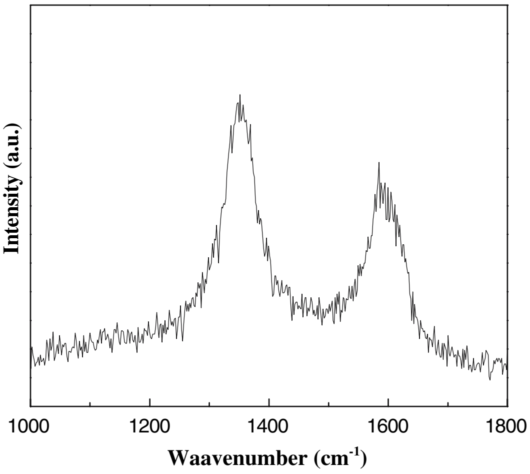

Fig. 3 Raman spectrum of as-prepared products showing two peaks around 1,590 and 1,353 cm^{-1}

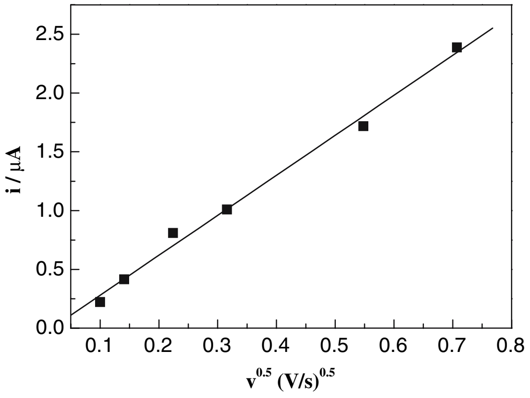

Fig. 4 The peak currents (Ipa) proportional to the square root of the scan rate

peaks at 1,590 and 1,353 cm^{-1}: the former corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer; the latter is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [11]. The latter is higher than the former, which means that the CNTs have more defects, in accordance with the results of XRD and HRTEM.

Wurtz reaction takes place as follows:

$$C_2Cl_6 + Na \rightarrow C + NaCl$$

Its free radicals mechanism has been discussed before [12].

Here, benzene solvent helps to accelerate diffusion, adsorption, reaction rate, which contribute to a lower reaction temperature.

The response of CNT-modified gold electrode to DA

The influence of the phosphate buffer pH value on the redox peak current and peak potentials was investigated using CV [13]. The redox peak currents are pH dependent in the pH range tested. The oxidation peak current (Ipa) increases from pH 9.0–5.0, while the ΔEp becomes large from pH 7.0 to 5.0. The pH 7.0 is the optimum in our detection condition considering both of the oxidation peak current (Ipa) and ΔEp.

The influence of the scan rate on the redox peak potential and peak currents was examined at pH 7.0 phosphate buffer. The redox peak potentials do not shift with altering scan rate. The peak currents increase with increasing scan rate. Ipa and Ipc were proportional to the square root of the scan rate (Fig. 4), indicating that the redox reaction of DA is controlled by the diffusion.

When CNT-modified gold electrode is placed into pH 7.0 PBS containing 2.8×10^{-4} mol L^{-1} of DA at a scan rate of 50 mV s^{-1}, a pair of reduction/reoxidation peaks are clearly observed (Fig. 5a). The cathodic and anodic peak potentials are 0.117 and 0.207 V, respectively, which has a positive direction shift for the cathodic peak potential and negative shift for anodic one comparing with the bare gold electrode (Fig. 5b). The separation between the peak potentials (ΔEp) decreases from 0.121 V to 0.090 V, indicating a more reversible system. Meanwhile, the peak currents enhance significantly. The detection limit is determined as 1×10^{-7} mol L^{-1}.

Figure 6 shows the CV curves of different DA concentrations. The peak current of reduction increases linearly as DA concentration varies from 0.6 μM to 280 μN with linear regression equation of Ip (μA) = 0.089 + 0.134c (μmol L^{-1}) and correlation coefficient of 0.9997 (Fig. 6, inset). From

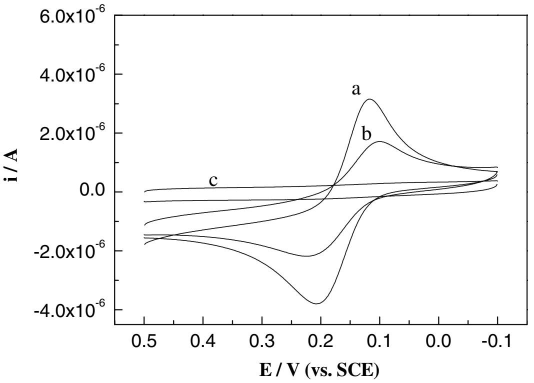

Fig. 5 CV curves obtained in 0.1 mol L^{-1} PBS with a scan rate of 50 mV s^{-1} at (**a**) CNTS-modified electrode in the presence of 2.8×10^{-4} mol L^{-1} DA; (**b**) bare gold electrode in the presence of 2.8×10^{-4} mol L$^{\circ 1}$ DA; and (**c**) CNTs-modified electrode without DA

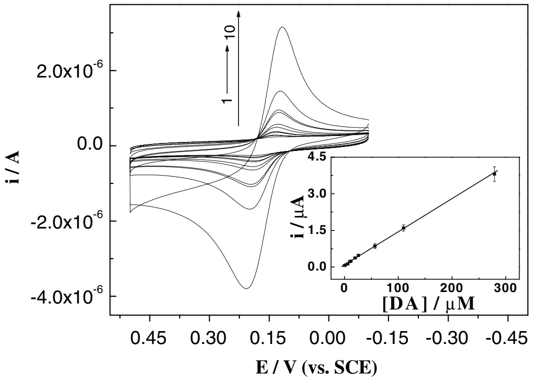

Fig. 6 CV curves of different concentrations of [DA]. [DA]: (1) 0.2 μm, (2) 2 μM, (3) 6 μM, (4) 9.9 μM, (5) 11.9 μM, (6) 19.6 μM, (7) 25.9 μM, (8) 56.7 μM, (9) 110 μM, (10) 279 μM. The peak currents increased linearly with the concentrations of DA in the range of 0.2 μM~279 μM (inset)

this equation, the sensitivity is twice more than other CNTs-modified electrode [14]. The reason is that the CNTs, synthesized from sp^3 compound hexachloroethane, have more defects. These CNTs are much easy to be treated with nitric acid and resulted in more hanging bonds, which is beneficial to the electron transfer in the CV measurement.

The experiments about ascorbic acid (AA) and other ions influence of the determination were carried out. AA (not more than 20 times DA) and large amounts of SO_4^{2-} (<0.05 M), CO_3^{2-} (<0.08 M), Cl^- (<0.85 M) and Na^+ (<0.85 M) have little interfered detection of DA.

Conclusion

We synthesized CNTs with more defects via Wurtz reaction employing sp^3 bonding compound C_2Cl_6 as carbon source. And this kind of CNTs, after treated with nitric acid, was served as a high-sensitivity material to detect DA via CV method. This work might supply a clue to the application of CNTs.

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