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Electropolymerization and catalysis of well-dispersed polyaniline/carbon nanotube/gold composite

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Abstract

Polyaniline/multi-walled carbon nanotube/gold (PANI/MWNT/Au) composite film was synthesized via a two-step electrochemical process. First the mixture of aniline and MWNT was heated at refluxing and was electropolymerized. Then, the Au nanoparticles were dispersed into the film of PANI/MWNT by electrochemical reduction of HAuCl₄. The morphology of sample was analyzed by scanning electron microscopy (SEM). Raman measurement indicates a well electrochemical deposition of PANI on MWNT, and XPS result confirms the formation of Au⁰ nanoparticles. Further, cyclic voltammograms show that the film exhibits a good electrochemical activity and electrocatalysis towards ascorbic acid. Based on these investigations, a formation mechanism of the PANI/MWNT composite film was proposed.

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1. Introduction

Carbon nanotubes (CNTs), discovered by Iijima [1], have attracted tremendous interests in view of a variety of their applications in fabricating a new class of advanced materials due to their unique structure, and mechanical, electronic, and thermal properties. Apart from potential uses in molecular electronic devices, micromechanics, electron field emission, nano-conductive wires, etc., they are also considered for some electrochemical applications, such as membrane support of catalyst for the electrocatalytic reduction of oxygen and the oxidation of methanol [2], the storage of hydrogen and lithium [3,4], and super-capacitors [5]. With highly promising potential for the applica-

tions, they become attractive building blocks for the development of future nanotechnology, resulting in novel materials and devices of great practical interests [6]. For example, CNTs are considered as the potential supports for making heterogeneous catalysts [7–9]. Electrocatalysts with Pt nanoparticles loaded onto carbon tubule membranes [2] have been proven to be effective towards oxidation/reduction reactions. However, there are difficulties in dispersing metal nanoparticles with uniform dispersion and regular sizes on the CNTs surfaces. So, in order to obtain a good mono-dispersity of metal nanoparticles, the surface of CNTs must be modified via a proper functionalization.

Conducting polymers have been proven to be suitable host matrices for dispersing metallic particles. The composites of conducting polymers with metal nanoparticles permit a facile flow of electronic charges across the polymer matrix during electrochemical processes. Conducting polymer plays an additional role in the electrochemical

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processes. In addition, metallic nanoparticles can also be dispersed well into the matrix of these polymers [10]. As all we know, gold nanoparticles have unique optoelectronic, magnetic and mechanical properties, and potential applications in microscopic research and nanodevices [11]. So, through a suitable combination of conducting polymers and gold nanoparticles, newly modified surfaces could be generated with higher surface area and enhanced catalytical/electrocatalytical activities.

Herein, we reported a preparation and application of PANI/MWNT/Au composite film. MWNT was used to form pendant chains of polyaniline (PANI) through electrochemical polymerization. Au nanoparticles were electrochemically dispersed into the matrix of PANI/MWNT. Electrochemical technique, field emission scanning electron microscopy (FESEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were applied to investigate the morphology and properties of the composite film. Based on our observation, the mechanism of the formation of PANI/MWNT/Au composite film was proposed.

2. Experimental

2.1. Chemical and reagents

Multi-walled carbon nanotubes (sponsored by Northeast Normal University) and HAuCl_4 (Shanghai Chemical Reagent Company) were used as received except aniline (Beijing Chemicals Company) which was distilled under a nitrogen atmosphere at reduced pressure and kept below 0°C . Other chemicals were analytical pure. All aqueous solutions were prepared with ultrapure water obtained from Millipore System ($>18\text{ M}\Omega\text{cm}$). And all experiments were carried out at room temperature (25°C).

2.2. Apparatus

Electropolymerization and electrochemical characterizations were carried out with a CHI660 (CH Instruments, USA) Electrochemical Workstation.

The morphology of the resulting precipitates was characterized with a XL 30 ESEM FEG scanning electron microscopy at an accelerating voltage of 20 kV and a JEOL 2000 transmission electron microscopy (TEM) operating at 200 kV. Raman spectrum was recorded with a Renishaw 2000 system using an Argon ion laser operating at 514.5 nm with a CCD detector. XPS measurements were conducted with an ESCLAB MK II spectrometer (VG Co.) with Mg K_{α} radiation as the X-ray source. The UV-visible absorbance spectra were acquired with a Cary 500 UV-Visible-NIR spectrometer (Varian).

2.3. Preparation of MWNT–aniline solutions

Multi-walled carbon nanotubes were treated using a 3:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ prior to the experiments. The obtained MWNT were then added into 5 ml of

aniline. The mixture was heated at refluxing in the dark. After a while, the refluxing solution of the colorless aniline first became brownish and then turned dark, indicating that MWNTs have been dissolved well into aniline. After refluxing for 3 h, the solution was cooled to room temperature, a MWNTs solution was obtained by filtration through a $0.1\ \mu\text{m}$ diameter Supor Membrane Disc Filter (Gelman).

2.4. Preparation of PANI/MWNT/Au composite film

PANI/MWNT composite film was deposited in a solution of 1 M H_2SO_4 containing appropriate aniline dissolved MWNTs (as-produced by refluxing) in a three compartment cell. The cleaned silicon wafer sputtered with Pt, a KCl-saturated silver–silver chloride ($\text{Ag}|\text{AgCl}$) and a platinum wire were used as the working, reference and counter electrodes, respectively. All potential reported refers to this $\text{Ag}|\text{AgCl}$ (sat. KCl) reference electrode. Cyclic voltammograms were recorded from -0.20 to $0.72\ \text{V}$ at a scan rate of $0.1\ \text{Vs}^{-1}$.

And finally the silicon wafer deposited with PANI/MWNT composite film was dipped into the solution of HAuCl_4 , and gold nanoparticles were prepared by pulse voltammetry with a pulse width of 5 s and the high potential and low potential were 1.1 V and $-0.2\ \text{V}$, respectively, which resulted in the PANI/MWNT/Au composite film.

3. Results and discussion

3.1. Electropolymerization of PANI/MWNT/Au composite film

Modification of the surface of working electrode was performed in two steps. First, PANI/MWNT composite film was deposited onto the working electrode using cyclic voltammetry. Second, Au nanoparticles were incorporated into PANI/MWNT composite film by pulse voltammetry.

Fig. 1 displays a cyclic voltammogram (CV) recorded in a solution of 1 M H_2SO_4 without addition of aniline monomer after the electrochemical polymerization in the solution containing 10 mg MWNT and 5 mL aniline (5 potential cycles) at $0.1\ \text{Vs}^{-1}$. The formation of PANI/MWNT film was evident from the CV findings. In the first potential cycle, a significantly high peak current at the potential of aniline oxidation was noted for the solution of MWNT–aniline. This gives a clue that the amine group in MWNT–aniline was oxidized at the potential of aniline oxidation. Moreover, the current values at the redox peaks corresponding to PANI showed the continuous increases with the number of potential cycles. These observations indicate that the formation of PANI/MWNT composite film.

At the same time, the result of Raman spectra (Fig. 2) further confirms the formation of PANI on MWNT. For comparison, this figure also includes the spectra of pure MWNT, PANI, and PANI/Au composite. The pattern of

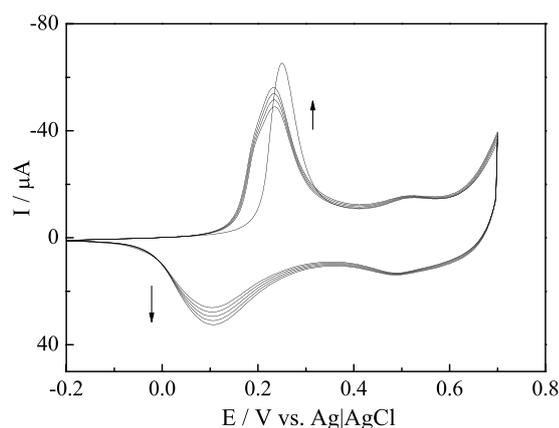


Fig. 1. Cyclic voltammogram (5 cycles) recorded in a solution of 1 M H_2SO_4 without addition of aniline monomer after the electrochemical polymerization in the solution containing 10 mg MWNT and 5 mL aniline (scan rate: 0.1 V s^{-1}).

MWNT indicates that the surface derivatization does not affect the graphite structure of the MWNT and the reaction can be used to produce carboxylic acid groups at local defects in the curved graphite sheets and tube ends [12]. Two strong peaks at 1584 cm^{-1} (G mode) which is the Raman-allowed phonon high-frequency mode and a disordered-induced peak at 1350 cm^{-1} (D mode) which may originate from the defects in the curved graphite sheets and tube ends. Comparing the I_G/I_D ratio of the MWNT with those without carboxylic acid group, which is much

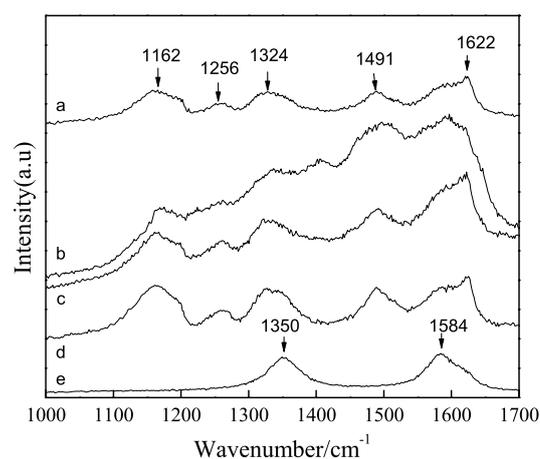


Fig. 2. Raman spectra of (a) PANI, (b) PANI/Au composite, (c) PANI/MWNTs composite, (d) PANI/MWNTs/Au composite, and (e) pure MWNTs.

lower than that in previous report [12] (1.11 versus 1.72), it reveals that the chemical derivatization increases the degree of disorder. This finding indicates the presence of defects at both the ends and the sidewalls of the MWNT [13]. But, these two peaks do not appear in PANI/MWNT and PANI/MWNT/Au composites. For PANI/MWNT and PANI/MWNT/Au composites, C–H bending of the quinoid ring at 1162 cm^{-1} , C–H bending of the benzenoid ring at 1256 cm^{-1} , C–N⁺ stretching at 1324 cm^{-1} , and C–C stretching of the benzene ring at

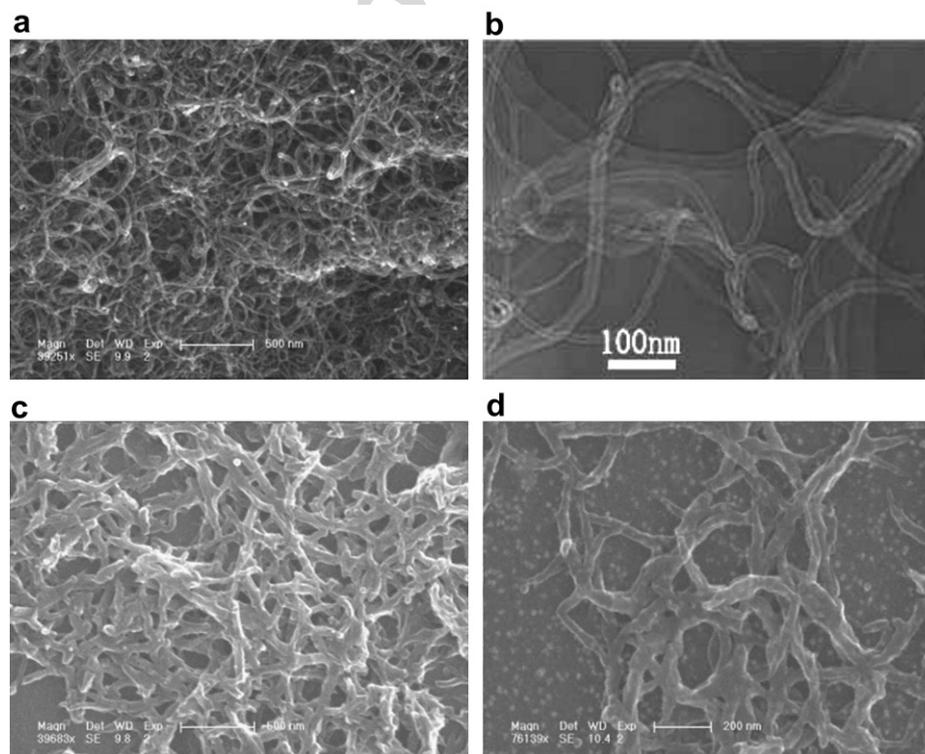


Fig. 3. SEM images of (a) the MWNTs film, (b) the PANI/MWNTs composite film, (c) the PANI/MWNTs/Au composite film, and (d) TEM image of MWNTs–aniline solution diluted with acetone. Scale bars: (a) 500 nm, (b) 500 nm, (c) 200 nm, (d) 100 nm.

1491 cm^{-1} and at 1622 cm^{-1} are observed, revealing the presence of the doped PANI structure [12]. The Raman spectra indicate that the MWNT serve as the core in the formation of a tubular shell of PANI/MWNT and PANI/MWNT/Au composites. In other words, in these two composite films, PANI film is present on the MWNT surface.

Also, the morphology of the products was tested by SEM and TEM. The SEM images of MWNT, PANI/MWNT, and PANI/MWNT/Au composite film and TEM image of MWNT–aniline solution diluted with acetone are shown in Fig. 3. Clearly, the SEM image of the purified MWNT shows that the MWNT are very long and present as highly entangled network structure, which are responsible for the difficulty to disperse the MWNT in the polymer matrix and the relatively low solubility of the MWNT in most solvents (Fig. 3a). In addition, the MWNT are not uniform and the diameter of the MWNT ranges from ca. 13 to 50 nm. The TEM image of MWNT–aniline solution diluted with acetone (Fig. 3b) shows that the tubes are still hollow, which indicates that aniline monomers have been adsorbed entirely on the surface of MWNT. This result is in consistent with the result of Raman. Moreover, Fig. 3c shows that a tubular layer of a highly uniform PANI-coated film is present on the MWNT surface. After the deposition of gold nanoparticles (Fig. 3d), it can be clearly seen that most of gold nanoparticles dispersed uniformly into the PANI/MWNT composite film and the diameter of these particles is ca. 19 nm. These particles are separated from each other, but not aggregation.

Further, XPS was applied to determine the oxidation state of gold nanoparticles. Fig. 4 shows the Au 4f_{7/2} and Au 4f_{5/2} doublet with the binding energies of 84.2 and 87.8 eV, respectively. These are typical values for Au⁰, indicating the formation of Au⁰ nanoparticles.

3.2. Electrocatalysis of PANI/MWNT/Au

In order to examine the property of the composite film, the PANI/MWNT/Au-functionalized electrode was used

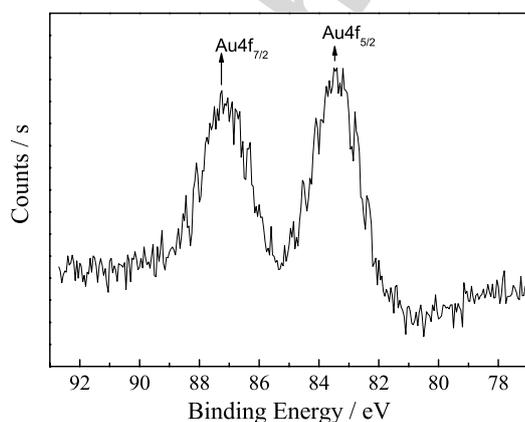


Fig. 4. XPS spectrum of Au of the PANI/MWNT/Au composite.

to the electrochemical oxidation towards ascorbic acid (AA) in 0.1 M phosphate buffer solution (pH 7.0). For comparison, we also studied the oxidation of AA by the MWNT/Au-functionalized and bare Au electrodes were also examined in the control experiments (as shown in Fig. 5A), respectively. As seen in Fig. 5A, AA shows a sluggish and much smaller CV peak response with an oxidation wave at ca. 0.51 V at a bare Au electrode while the PANI/MWNT/Au and MWNT/Au-modified electrodes lead to obvious negative shifts of AA oxidation overpotential ($E_{\text{pa}} = 0.41$ V and $E_{\text{pa}} = 0.47$ V, respectively) and increases of the oxidation peak current. Moreover, the PANI/MWNT/Au electrode has significantly greater activity than MWNT/Au electrode towards the oxidation of AA. The greatly enhanced peak current and the negative shift of oxidation overpotential indicate strong electrocatalytic activity of Au nanoparticles distributed in PANI/MWNT or MWNT matrices towards the AA. Further, the presence of PANI which stabilized the Au nanoparticles and prevented the particles from aggregation may account for the stronger activity of PANI/MWNT/Au than that of MWNT/Au [10]. Fig. 5B shows the CVs of different con-

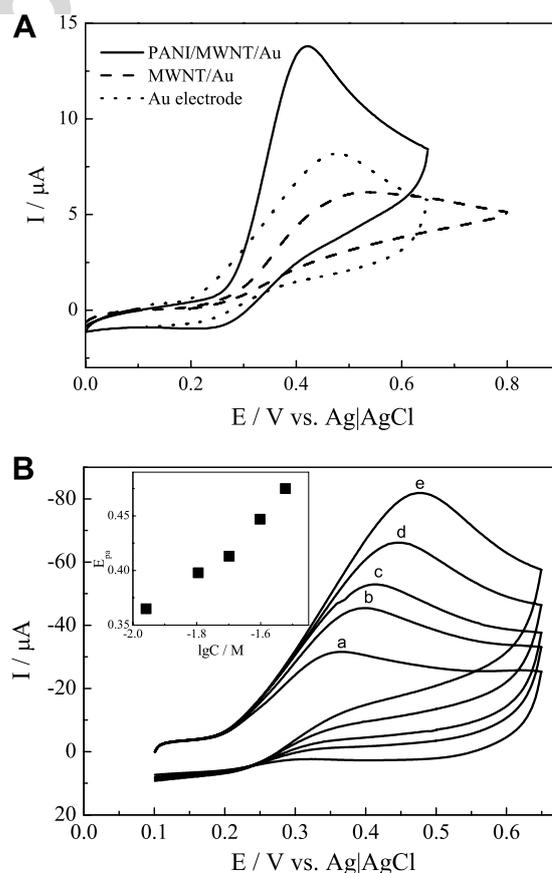


Fig. 5. (A) Cyclic voltammograms of 10 mM AA at bare Au electrode (dot line), MWNT/A-functionalized electrode (dashed line) and PANI/MWNT/Au-modified electrode (solid line) in PBS buffer (pH 7.0) (B) AA concentration from (a) to (e) are 11, 16, 20, 25, and 30 mM, respectively. Scan rate: 0.05 Vs^{-1} . Inset: the relationship between peak potentials and concentration.

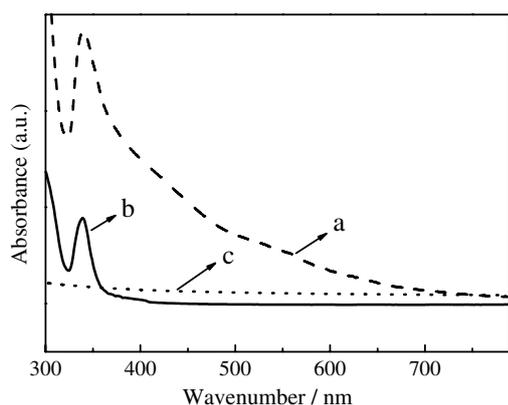


Fig. 6. UV-vis absorption spectra of MWNT-aniline (a), aniline (b), and MWNT (c) solution diluted with acetone.

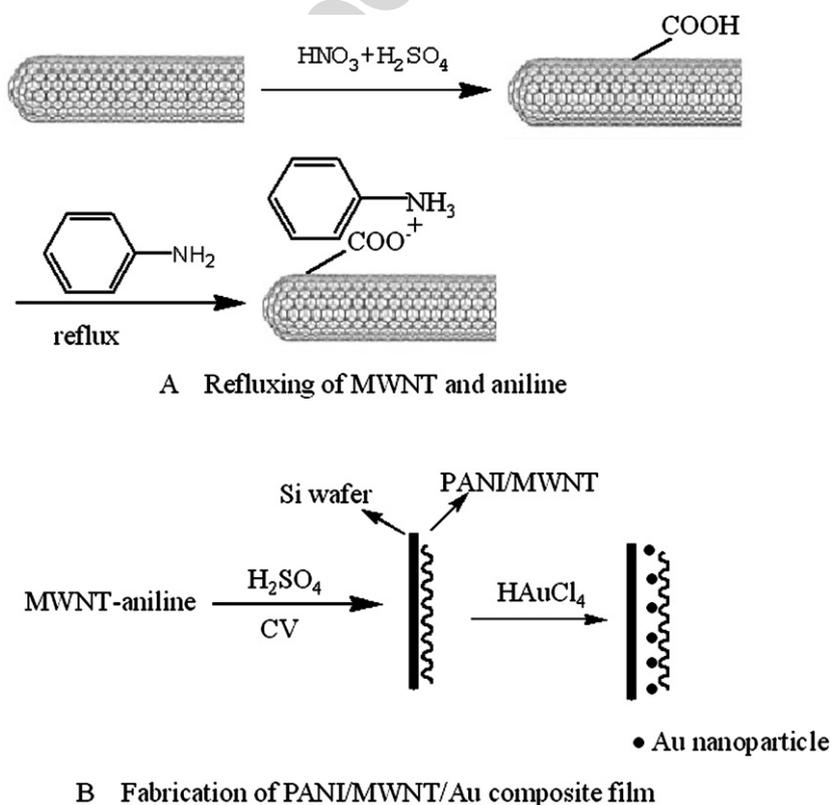
concentrations of AA at the PANI/MWNT/Au-functionalized Au electrode. It is clear that the oxidation peak current is increasing with the increase of AA concentration. The inset in Fig. 5B shows the relationship between shift in peak potentials and concentration. The peak potential is proportional to the log of the AA concentration.

The shift in peak potentials with concentration (Fig. 5B) may result from the two possible reasons. First, the product of ascorbic acid, according to previous reports [17], can easily adsorb on the electrode surface and fouled the surface, which can depress the effect of catalyst. Second, the concentration of ascorbic acid we used in this case,

>10 mM, was considered too high due to quite limited active sites (Au sites) on the electrode surface. Then, a depression in electrocatalytic response at higher concentrations of ascorbic acid was resulted.

3.3. Reaction mechanism

Fig. 6 shows UV-vis absorption of (a) MWNT-aniline solution, (b) aniline, and (c) MWNT diluted with acetone. No absorption peak was observed in the spectrum of MWNT. A single peak appeared around 350 nm in the spectrum of aniline. In the spectrum of MWNT-aniline solution, absorption between 310 and 400 nm is very strong while a new peak at 550 nm suggests the formation of an aniline-MWNT charge-transfer complex [16]. As in our system, it can be considered that the carboxyl groups of MWNT and the amino groups of aniline monomers can form an anilinium carboxylate salt (MWNT-CO_2^-) ($^+\text{NH}_3\text{Ph}$) from aniline and the defect carboxylic acid groups of the MWNT [14]. And it is also helpful to form the complex due to the hydrogen bonding interaction between them each other. During the CV cycling, the aniline monomers polymerize on the surface of MWNTs while the tubes of MWNTs remain pristine. After that, the repulsion between the oxidized units of PANI and ingoing of counterions at a high potential make the films become loosen [15]. And at this time, AuCl_4^- can enter easily into the loosen film. And then the low potential was applied and



Scheme 1. Reaction mechanism of PANI/MWNT/Au composite film.

the AuCl_4^- is reduced into Au^0 nanoparticles, and synchronously, the films become much tight, and the gold nanoparticles can be enwrapped entirely in this film (as illustrated in Scheme 1).

4. Conclusions

In summary, PANI/MWNT/Au composite film was prepared via a simple electropolymerization. And the result of SEM indicated that the composite film was composed of nanotubes and uniformly dispersed gold nanoparticles in the film. Raman measurement indicated a well electropolymerization of PANI on MWNT, and XPS result confirmed the formation of Au^0 nanoparticles. In addition, cyclic voltammograms showed that the film exhibited good electrocatalysis towards AA oxidation. This investigation indicates that catalytic electrodes based on a combination of substrate, carbon nanotubes, polymers, and electrochemically dispersed metals, mixed metals, or metal oxides can be generated by the same way.

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References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] G.L. Che, B.B. Lakshmi, E.R. Fischer, C.R. Martin, *Nature* 393 (1998) 346.
- [3] C. Nutzenadel, A. Zuttel, D. Chartouni, L. Schlapbach, *Nature* 2 (1999) 30.
- [4] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, F. Béguin, *Carbon* 37 (1999) 61.
- [5] E. Frackowoak, K. Méténier, T. Kyotani, S. Bonnamy, F. Béguin, *Am. Carbon Soc. II* (1999) 544.
- [6] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, *Science* 297 (2002) 787.
- [7] J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier, P.M. Ajayan, *J. Am. Chem. Soc.* 116 (1994) 7935.
- [8] C. Pham-Huu, N. Keller, M.J. Ledoux, L.J. Charbonniere, R. Ziessel, *Chem. Commun.* (2000) 1871.
- [9] C.H. Liang, Z.L. Li, J.S. Qiu, C. Li, *J. Catal.* 211 (2002) 278.
- [10] P. Santhosh, A. Gopalan, K.P. Lee, *J. Catal.* 238 (2006) 177.
- [11] C.A. Foss, G.L. Hornyak, J.A. Stockert, C.R. Martin, *J. Phys. Chem.* 96 (1992) 7497.
- [12] J. Sanchez-Gonzalez, A. Macias-Garcia, M.F. Alexandre-Franco, *Carbon* 43 (2005) 741.
- [13] Z.X. Wei, M.X. Wan, T. Lin, L.M. Dai, *Adv. Mater.* 15 (2003) 136.
- [14] D.F. Perepichka, F. Wudl, S.R. Wilson, Y. Sun, D.I. Schuster, *J. Mater. Chem.* 14 (2004) 2749.
- [15] S.A. Curran, P.M. Ajayan, W.J. Blau, D.L. Carroll, J.N. Coleman, A.B. Dolton, A.P. Davey, A. Drury, B. McCarthy, S. Maier, A. Strevens, *Adv. Mater.* 10 (1998) 1091.
- [16] Y. Sun, S.R. Wilson, D.I. Schuster, *J. Am. Soc. Chem.* 123 (2001) 5348.
- [17] J. Zhang, P.H. Deng, Y.L. Feng, Y.F. Kuang, J.J. Yang, *Microchim. Acta* 147 (2004) 279.