ELSEVIER



Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Pd nanoparticles deposited on poly(lactic acid) grafted carbon nanotubes: Synthesis, characterization and application in Heck C–C coupling reaction

Gururaj M. Neelgund, Aderemi Oki*

Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA

ARTICLE INFO

ABSTRACT

Article history: Received 8 December 2010 Received in revised form 21 March 2011 Accepted 28 March 2011 Available online 1 April 2011

Keywords: Carbon nanotubes Poly(lactic acid) Palladium Catalytic activity Heck reaction

1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have generated tremendous interest in the area of nanotechnology [1]. With the simple chemical composition and atomic bonding configuration, CNTs exhibit extreme diversity and richness in their structure dependent properties [2,3]. The considerable interest in CNTs is strongly related to their fascinating and unique optical, electrical, mechanical, and thermal properties. Consequently, the exceptional properties of CNTs made them as the ideal candidates for numerous applications in nanoelectronics [4,5], catalysis [6–8], diagnostics [9,10] and drug delivery [11,12]. Owing to the high aspect ratio and specific surface area, CNTs are excellent supporting material for catalyst, especially in heterogeneous catalysis [13,14]. Since the support with a high specific surface area is ideal for deposition of catalytically active metal nanoparticles, such nanoparticles exhibit greater catalytic efficiency than their bulk counterpart due to high surface-to-volume ratio [15]. In order to control the CNTnanoparticles interface and to favor a high loading of nanoparticles, coordinating polymer grafts can act as macromolecular coupling agents as they carry multiple binding sites.

Palladium nanoparticles are of current interest due to their superior catalytic performance and these nanoparticles are finding enormous industrial applications in both heterogeneous and homogeneous catalytic reactions [16,17]. Supported Pd nanopar-

ticles. The formation of *f*-CNTs-Pd nanocatalyst was analyzed by UV–vis, FTIR and Raman spectroscopy, powder XRD, energy dispersive spectroscopy and thermogravimetric analysis. The morphologies of the nanocatalyst were characterized using scanning and transmission electron microscopes. The *f*-CNTs stabilized Pd nanoparticles are found to be more effective in the promotion of Heck cross-coupling reaction between aryl halides and n-butyl acrylate. The *f*-CNTs-Pd nanocatalyst was regenerated for three cycles of reaction without any significant loss in its activity. Published by Elsevier B.V.

Herein we described the synthesis of a novel f-CNTs-Pd nanocatalyst by covalent grafting of poly(lactic

acid) (PLA) onto carbon nanotubes (CNTs) and subsequent deposition of Pd nanoparticles. Prior to graft-

ing of PLA, CNTs were oxidized with a mixture of HNO₃/H₂SO₄ and successively activated with thionyl

chloride. The PLA grafted CNTs (f-CNTs) were then used as platform for in situ deposition of Pd nanopar-

ticles catalysts posses high catalytic activity, good stability, ease separation and satisfactory reusability compared to traditional homogeneous Pd(OAc)₂, PdCl₂ catalysts. Owing to these interests here we report the synthesis of a heterogeneous palladium nanocatalyst supported on poly(lactic acid) (PLA) functionalized carbon nanotubes (CNTs) and its efficiency in the promotion of Heck coupling reaction.

2. Experimental

2.1. Materials

All the reagents were purchased from Aldrich and used without any purification. All aqueous solutions were prepared with ultrapure water obtained from the Milli-Q Plus system (Millipore). The tetrahydrofuran (THF) was dried over sodium benzophenone under nitrogen and freshly distilled prior to use.

2.2. Synthesis of PLA

PLA was synthesized according to previously reported method [18,19] and the molecular weight measured from gel permeation chromatography (GPC) was found to be 50,000 g/mol.

2.3. Covalent grafting of PLA to CNTs

Pristine CNTs (*p*-CNTs) were refluxed under stirring in the mixture of 1:3 (v/v) HNO₃ and H₂SO₄ at 70 °C for 24 h, which was followed by centrifugation and repeated washings with DI water

^{*} Corresponding author. Fax: +1 936 261 3117. *E-mail address:* aroki@pvamu.edu (A. Oki).



Scheme 1. Covalent grafting of PLA onto CNTs and successive deposition of Pd nanoparticles.

[20]. The carboxylated CNTs (CNTs-COOH) thus obtained were dried under vacuum at 40 °C and reacted with excess of SOCl₂ at room temperature for 24 h. The acylated CNTs (CNTs-COCl) were separated by centrifugation, subsequently washed with anhydrous THF and dried in vacuum at 40 °C for 12 h. The CNTs-COCl were then dispersed in CH₂Cl₂ by sonication for 10 min, mixed with a solution of PLA in CH₂Cl₂ and allowed to react with flowing nitrogen at 35 °C for 12 h. The resulting PLA functionalized CNTs (*f*-CNTs) were centrifuged, washed with CH₂Cl₂ and dried in vacuum.

2.4. Preparation of nanocatalysts

2.4.1. Preparation of f-CNTs-Pd nanocatalyst

The *f*-CNTs (40 mg) were dispersed in 15 mL DI water by sonication for 10 min and a aqueous solution of PdCl₂ (10 mL, 0.01 mol L⁻¹) was added to dispersion of *f*-CNTs. The mixture was stirred for 2 h in room temperature to complete attainment of coordination, which follows slow addition of a freshly prepared solution of NaBH₄ (10 mL, 0.05 mol L⁻¹) in DI water. The reaction mixture was then stirred under ambient conditions for 4 h. Thus yielded *f*-CNTs-Pd nanocatalyst was subjected to centrifugation, washed with DI water and dried in vacuum at 40 °C for 12 h. The overall synthesis of *f*-CNTs-Pd nanocatalyst is schematically demonstrated in Scheme 1.

2.4.2. Preparation of CNTs-COOH-Pd nanocatalyst

The CNTs-COOH–Pd nanocatalyst was prepared similar to the procedure mentioned above for *f*-CNTs-Pd nanocatalyst using CNTs-COOH instead of *f*-CNTs.

2.4.3. Preparation of PLA-Pd nanocatalyst

PLA (40 mg) was dissolved in CH_2Cl_2 and a solution of PdCl₂ in methanol (10 mL, 0.01 mol L⁻¹) was added. This mixture was stirred at room temperature for 2 h followed by addition of NaBH₄ solution (10 mL, 0.05 mol L⁻¹). Then the reaction was allowed to proceed at room temperature for 4 h. The resulting PLA-Pd nanocatalyst was separated by centrifugation, successively washed with CH_2Cl_2 and water and dried under vacuum for 8 h.

In all the nanocatalysts, a total Pd loading of 40% was obtained by controlling the concentration of PdCl₂.

2.5. Catalytic activity

In order to evaluate the catalytic activity of immobilized Pd nanoparticles, the heterostructured *f*-CNTs-Pd nanocatalyst was used in the important carbon–carbon bond forming Heck coupling reaction. The cross-coupling of arylhalide with n-butyl acrylate in the presence of *f*-CNTs-Pd nanocatalyst (Scheme 2) was accomplished as follows. The mixture containing arylhalide (5 mmol), n-butyl acrylate (5.5 mmol), triethylamine (5.5 mmol)



Scheme 2. Heck reaction between arylhalide and n-butylacrylate catalyzed by *f*-CNTs-Pd nanocatalyst.

in 10 mL*N*,*N*-dimethyl formamide (DMF) was stirred at 100 °C in the presence of *f*-CNTs-Pd nanocatalyst (10 mg). Then a solution of Na₂CO₃ (0.25 g) in 10 mL Dl water was added to reaction mixture, stirred at room temperature for 15 min and subjected to centrifugation. The resulting reaction mixture was treated with 10 mL 2% HCl solution, which yields to precipitation of the reaction product. The crude product was then purified by recrystallization.

2.6. Characterization

The molecular weight of PLA was measured by Waters GPC system using polystyrene as the standard and THF as eluent. The UV-vis absorption spectra were recorded on Varian Carry 50 Bio UV-vis spectrophotometer and Fourier transform infrared (FTIR) spectra were recorded using Thermo-Nicolet IR 2000 spectrometer (KBr pellet). Thermogravimetric analyses (TGA) were performed with a Perkin Elmer Diamond TG/DTA instrument at a heating rate of 10 °C/min under flow of nitrogen. Raman spectra were recorded using Renishaw R-3000QE system in the backscattering configuration using an Argon ion laser with wavelength of 785 nm. XRD patterns were recorded on Scintag X-ray diffractometer (PAD X), equipped with Cu K α photon source (45 kV, 40 mA) at a scanning rate of 3°/min. Scanning electron microscopy (SEM) measurements were performed on a JEOL JXA-8900 microscope and the X-ray energy dispersive spectroscopy (EDS) measurements were made with a ThermoNoran EDS System 6 attached to SEM. Transmission electron microscopy (TEM) images were obtained with a Hitachi H-8100 microscope at 200 kV.

3. Results and discussion

The UV–vis spectrum of CNTs-COOH (Fig. 1a), dispersed in water displayed the characteristic absorption band with decreasing absorptivity at 249 nm [20]. This characteristic band in the spectrum of *f*-CNTs (Fig. 1b) displaced to 273 nm after function-



Fig. 1. UV-vis absorption spectra of (a) CNTs-COOH, (b) *f*-CNTs and (c) *f*-CNTs-Pd nanocatalyst.

alizing CNTs-COOH with PLA. The substantial red shift of 24 nm in the spectrum of *f*-CNTs and the differences observed in the spectra of *f*-CNTs and mixture of PLA and CNTs-COOH (see the Supporting Information, Fig. S1) exhibits existence of strong interactions between PLA chains and CNTs, which favors the efficient dispersibility of *f*-CNTs in both organic and aqueous media. No distinctive surface plasmon resonance for Pd nanoparticles could be observed in the spectrum of *f*-CNTs-Pd nanocatalyst (Fig. 1c), which is inline with the previous reports that Pd nanoparticles are known to absorb in the UV region with virtually no structure [21,22]. While the characteristic band of CNTs further red shifted to 279 nm by deposition of Pd nanoparticles onto *f*-CNTs. There is no new absorption features emerged after deposition of Pd nanoparticles, which implies that there is no charge diffusion or electronic interaction between *f*-CNTs and Pd nanoparticles.

The composition of *f*-CNTs-Pd nanocatalyst was analyzed by FTIR spectroscopy. Fig. 2a-c represent the IR spectra obtained for PLA, f-CNTs and f-CNTs-Pd nanocatalyst, respectively. The spectrum of *f*-CNTs displayed all the important characteristic bands associated with PLA, the most obvious changes are diminished intensity in bands and displacement of position. The ester C-O stretching band for PLA was appeared at 1760 cm⁻¹ and for f-CNTs it was at 1750 cm^{-1} , this blue shifting of band in *f*-CNTs is owing to grafting of PLA chains onto CNTs. The broad feature at 3500 and 3430 cm⁻¹ for PLA and *f*-CNTs, respectively corresponds to the absorption of -OH stretching of hydroxyl groups. The resonances due to C-CH₃ stretching and -CH₃ asymmetric bending mode were appeared at 1090 and 1460 cm⁻¹, respectively [23]. The absorption around 1180 cm⁻¹ corresponds to C–C–O stretching [24]. Another important observation is the appearance of doublet at 3000 and 2950 $\rm cm^{-1}$ due to –CH twisting vibrations. In addition, the spectrum of *f*-CNTs exhibited C–C absorption at 1576 cm^{-1} , which indicates that the graphene structures of CNTs were not disturbed by functionalizing with PLA [25]. The spectrum of f-CNTs-Pd nanocatalyst appeared with few characteristic bands with low intensity. The conformational changes occurred by the deposition of Pd nanoparticles demonstrates the strong interaction exists between f-CNTs and Pd nanoparticles, which causes for higher stabilization of f-CNTs-Pd nanocatalyst. Therefore, it is valid to contend the successful grafting of PLA chains onto CNTs and subsequent deposition of Pd nanoparticles.

The phase structure of the nanocatalyst was revealed through powder XRD. The XRD patterns acquired for pristine CNTs (p-CNTs), f-CNTs and f-CNTs-Pd nanocatalyst is shown in Fig. 3. The diffraction peaks at 26.3° and 42.6° for p-CNTs (Fig. 3a) are attributed to (002) and (100) planes of hexagonal graphite and appearance of these



Fig. 2. FTIR spectra of (a) PLA, (b) f-CNTs and (c) f-CNTs-Pd nanocatalyst.



Fig. 3. Powder XRD patterns of (a) p-CNTs, (b) f-CNTs and (c) f-CNTs-Pd nanocatalyst.

peaks with high intensity suggests that *p*-CNTs have a high graphitic structure [20]. After functionalization, the diffraction peaks corresponding to (002) and (100) planes of CNTs were appeared at 26° and 42.5° for *f*-CNTs (Fig. 3b). A minute blue shift in the bands was observed for *f*-CNTs, which signifies that functionalization of CNTs with PLA did not destroy or alter the original structure of *p*-CNTs. The *f*-CNTs-Pd nanocatalyst (Fig. 3c) clearly exhibited (111), (200)

and (220) crystallographic planes of face-centered cubic (fcc) palladium at 39.8°, 46° and 67.2°, respectively (JCPDS No. 89-4897). The additional two peaks in Fig. 3c at 26.3° and 46° were from CNTs. Thus the XRD results indicate efficient immobilization of fcc structured Pd nanoparticles on *f*-CNTs.

The Raman spectra of *p*-CNTs (Fig. 4a), *f*-CNTs (Fig. 4b) and *f*-CNTs-Pd nanocatalyst (Fig. 4c) revealed the existence of charac-



Fig. 4. Raman spectra of (a) *p*-CNTs, (b) *f*-CNTs and (c) *f*-CNTs-Pd nanocatalyst.



Fig. 5. SEM images of (a) and (b) f-CNTs and (c) and (d) f-CNTs-Pd nanocatalyst.

158

Table 1	
Raman bands displayed for <i>p</i> -CNTs, <i>f</i> -CNTs and <i>f</i> -CNTs-Pd nanocatalyst.	

	Position of band (cm ⁻¹)				ID/IG
	D-band	G-band	D ₂ -band	D*-band	
p-CNTs	1306	1587	-	2583	0.40
<i>f</i> -CNTs	1312	1579	1607	2624	1.23
f-CNTs-Pd nanocatalyst	1313	1591	1616	2631	1.14

(-) denotes that D₂-band was not displayed for *p*-CNTs.

teristic D- and G-bands around 1310 and 1585 cm^{-1} , respectively. In addition, the D*-band was displayed for all the samples around 2610 cm⁻¹ and the D₂-band, which is a shoulder of the G-band was observed only for *f*-CNTs and *f*-CNTs-Pd nanocatalyst around 1610 cm⁻¹. The location of all bands is summarized in Table 1. The D- and D₂-bands were attributed to defects in the hexagonal framework of graphite and G-band to in-plan vibrations of the graphite (sp²-hybridized carbons) [26]. Thus the intensity ratio of D-band to G-band (ID/IG) provides information about defects caused by functionalization. The value of ID/IG for *p*-CNTs, *f*-CNTs, *f*-CNTs-Pd nanocatalyst was 0.4, 1.23 and 1.14 respectively. The significant increase in the value of ID/IG for *f*-CNTs was primarily attributed to conversion of carbon atoms from sp^2 to sp^3 hybridization, which indicates existence of more number of surface defects in *f*-CNTs generated by the treatment of *p*-CNTs with acids and SOCl₂ (see the Supporting Information, Fig. S2). The value of *ID*/IG for *f*-CNTs-Pd nanocatalyst was lower than that of the *f*-CNTs, which reflects that the disorder in nanotubes was not directly affected by the deposition of Pd nanoparticles. Considering these conformational changes in the Raman spectra, we can reasonably conclude that CNTs are effectively functionalized through grafting of PLA and further deposition of Pd nanoparticles.

The surface morphology of *f*-CNTs and *f*-CNTs-Pd nanocatalyst were characterized through SEM and TEM. The SEM images of *f*-CNTs (Fig. 5a and b) exhibit effective grafting of PLA onto CNTs and the efficient entanglement of CNTs by functionalization. This



Fig. 6. TEM images of (a) and (b) f-CNTs and (c) and (d) f-CNTs-Pd nanocatalyst.

demonstrates that strong interaction exists between CNTs and PLA chains, which facilitates the high dispersing ability of f-CNTs in both organic and aqueous media. The existence of Pd nanoparticles, deposited on *f*-CNTs was clearly distinguishable as bright spots in Fig. 5c and d. The density of Pd nanoparticles in f-CNTs-Pd nanocatalyst is abundant and these nanoparticles together formed some clusters. The formation of clusters might have originated by twinned or multiple twinned seeding of Pd nanoparticles, which is in accordance with previous reports [27,28]. The interpretations made on the basis of SEM images were further supported by the TEM images shown in Fig. 6. In the images of f-CNTs (Fig. 6a and b) the graphitic frame of CNT is easily distinguishable below PLA layer. That is, a core shell structure of CNTs at the center can be seen clearly, which indicates that the CNTs were covalently grafted by PLA chains. The thickness of PLA layer grafted onto the surface of the CNTs was around 4 nm and the PLA chains provided an effective steric barrier against bundling of CNTs. The thickness of grafted PLA on some places of CNTs was found to be non-uniform. The images of f-CNTs-Pd nanocatalyst (Fig. 6c and d) exhibits that Pd nanoparticles are randomly dispersed on *f*-CNTs and some of them appeared twinned together. The random distribution of Pd nanoparticles may be attributed to the large number of defect sites produced by the harsh treatment of acids. The mean diameter of Pd nanoparticles immobilized on f-CNTs was found to be around 12 nm. The existence of metallic Pd in f-CNTs-Pd nanocatalyst was further revealed by EDS shown in Fig. 7. The peak corresponding to C was originated by CNTs with a small contribution from PLA chains. The signal corresponding to O was also generated by PLA and the signal Pd was originated by Pd nanoparticles. The peaks derived from Cu were from the copper grid used in TEM measurements.

To obtain more quantitative information about extent of functionalization and contents of PLA, TGA analysis was performed and the profiles obtained are exhibited in Fig. 8. The profile of CNTs-COOH showed a minute weight loss of about 3% at 500 °C owing to decomposition of carboxyl groups (Fig. 8a). In addition, there is a major weight loss of 16.4% displayed for CNTs-COOH in the temperature range of 500–615 °C due to combustion of CNTs [29] and the residual weight remained from CNTs-COOH at 800 °C was 81.5%. The profile of PLA exhibited a single and complete weight loss in the temperature range of 280–390 °C because of degradation of PLA (Fig. 8b). While *f*-CNTs exhibited a weight loss of 23% in the temperature range from 300–600 °C due to degradation of PLA grafted onto CNTs, which indicates that the amount of PLA grafted to CNTs was 23 wt% (Fig. 8c) [30]. An increment of about 20 °C in the degradation of PLA was observed in *f*-CNTs, which exhibits existence of strong



Fig. 7. EDS of *f*-CNTs-Pd nanocatalyst.



Fig. 8. TGA profiles of (a) CNTs-COOH, (b) PLA, (c) *f*-CNTs and (d) *f*-CNTs-Pd nanocatalyst.

interaction between PLA chains and CNTs. The second weight loss observed at higher temperature range of 600-720 °C for *f*-CNTs was due to combustion of CNTs. The degradation behavior of *f*-CNTs-Pd nanocatalyst (Fig. 8d) is entirely different from that of *f*-CNTs and the residual weight measured at 800 °C was 23.4%, these observations demonstrates that Pd nanoparticles are well anchored onto *f*-CNTs.

To evaluate the catalytic activity of *f*-CNTs-Pd nanocatalyst, we studied the Heck reaction between bromobenzene and methyl acrylate in the absence of any catalyst and observed that there was no formation of product after 15 h. Similarly, use of f-CNTs as a catalyst also did not exhibit any catalytic activity. However, the reaction was carried out in the presence of f-CNTs-Pd nanocatalyst demonstrated efficient conversion of reactants to product. To further confirm the generality in the activity of *f*-CNTs-Pd nanocatalyst, the Heck reaction was studied with different arylhalides and n-butyl acrylates, the results are shown in Table 2. The reactants, arylhalides and n-butyl acrylates efficiently converted to their respective coupling product with good yield in the presence of f-CNTs-Pd nanocatalyst. The high catalytic activity of f-CNTs-Pd nanocatalyst is attributed to the large active surface area of Pd nanoparticles. To find the stability, f-CNTs-Pd nanocatalyst separated by centrifugation from the reaction mixture between bromobenzene and methyl acrylate was washed with DI water, subsequently with acetone and dried at 110 °C for 2 h. The recycled f-CNTs-Pd nanocatalyst was then used in other three cycles of reaction, which resulted in the formation of methyl cinnamate with $\approx 2\%$ lower yield than previous cycle, which indicates that the *f*-CNTs-Pd nanocatalyst is an excellent catalyst to use in multiple cycles of reactions.

Further the performance of *f*-CNTs-Pd nanocatalyst was compared with CNTs-COOH–Pd (without PLA) and PLA-Pd (without CNTs) nanocatalysts by Heck reaction between bromobenzene and methyl acrylate. Both, the control experiments using CNTs-COOH–Pd and PLA-Pd nanocatalysts and the typical experiment with *f*-CNTs-Pd nanocatalyst were conducted under identical conditions. The duration for completion of reaction between bromobenzene and methyl acrylate in the presence of *f*-CNTs-Pd nanocatalyst was found to be 8 h, while the duration for completion of same reaction using CNTs-COOH–Pd and PLA-Pd nanocatalysts was found to be 11 h and 15 h, respectively. Hence the combination of PLA and CNTs provides favorable environment for enhancement in catalytic activity of Pd nanoparticles. Overall, the PLA functionalized CNTs are ideal platforms for better immobilization of Pd nanoparticles and to gain their enhanced performance.

Table 2

Heck reaction between aryl halide and n-butyl acrylate catalyzed by f-CNTs-Pd nanocatalyst.



4. Conclusions

The acyl groups were successfully introduced on the surface of CNTs by treating them with a mixture of HNO₃/H₂SO₄ and subsequently with SOCl₂. The COCl groups generated on the surface of CNTs were consequently utilized for grafting of PLA chains. The retention of PLA on the surface of CNTs after extensive washings with CH₂Cl₂ was evidenced by FTIR, TGA and TEM, which reveals that PLA chains are covalently grafted onto CNTs and a strong interaction exists between them. The *f*-CNTs were effectively employed as substrate for in situ generation of Pd nanoparticles. The deposition of Pd nanoparticles on *f*-CNTs was confirmatively studied by XRD and TEM. The coupling between arylhalides and n-butyl acrylates using f-CNTs-Pd as a catalyst was successfully accomplished through well know Heck reaction. The activity of f-CNTs-Pd nanocatalyst was significantly influenced by the presence of CNTs. Moreover, the novel nanocatalyst, f-CNTs-Pd is stable, easily recoverable and maintains its high activity over a number of cycles. The further efforts to extend application of this system in other reactions are currently progress in our laboratory.

Acknowledgements

The authors acknowledge the support from NIH-NIGMS grant #1SC3GM086245, NIH-NIGMS RISE grant #1R25GM078361 and the Welch foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.03.050.

References

- [1] S. Iijima, Nature 354 (1991) 56–58.
- [2] P.M. Ajayan, Chem. Rev. 99 (1999) 1787–1799.
- [3] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787-792.
- [4] Y. Saito, S. Uemura, Carbon 38 (2000) 169–182.
- [5] A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. Mcintyre, P. Mceuen, M. Lundstrom, H. Dai, Nat. Mater. 1 (2002) 241–246.
- [6] S. Wang, E. Humphreys, S. Chung, D. Delduco, S. Lustig, H. Wang, K. Parker, N. Rizzo, S. Subramoney, Y. Chiang, A. Jagota, Nat. Mater. 2 (2003) 196–200.
- [7] G. Dieckmann, A. Dalton, P. Johnson, J. Razal, J. Chen, G. Giordano, E. Munoz, I. Musselman, R. Baughman, R. Draper, J. Am. Chem. Soc. 125 (2003) 1770– 1777.
- [8] G.G. Samsonidze, E.D. Semke, M. Usrey, D.J. Walls, Science 302 (2003) 1545–1548.
- [9] Y. Wang, X. Wang, B. Wu, Z. Zhao, F. Yin, S. Li, X. Qin, Q. Chen, Sens. Actuators B 130 (2008) 809–815.
- [10] H. Zhao, H. Ju, Anal. Biochem. 350 (2006) 138-144.
- [11] E. Miyako, H. Nagata, K. Hirano, Y. Makita, K. Nakayama, T. Hirotsu, Nanotechnology 18 (2007) 475103–475109.
- [12] M.J. O'Connell, S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, R.E. Smalley, Science 297 (2002) 593–596.
- [13] S.M. Chergui, A. Ledebt, F. Mammeri, F. Herbst, B. Carbonnier, H.B. Romdhane, M. Delamar, M.M. Chehimi, Langmuir 26 (2010) 16115–16121.
- [14] S. Song, H. Yang, R. Rao, H. Liu, A. Zhang, Appl. Catal. A 375 (2010) 265– 271.
- [15] C. Burda, X.B. Chen, R. Narayanan, M.A. El-Sayed, Chem. Rev. 105 (2005) 1025–1102.
- [16] R.B. Bedford, Chem. Commun. (2003) 1787–1796.
- [17] R. Amengual, E. Genin, V. Michelet, Adv. Synth. Catal. 344 (2002) 393-398.
- [18] G.X. Chen, H.S. Kim, B.H. Park, J.S. Yoon, J. Phys. Chem. B 109 (2005) 22237–22243.
- [19] G.X. Chen, H.S. Kim, E.S. Kim, J.S. Yoon, Eur. Polym. J. 42 (2006) 468-472.
- [20] G.M. Neelgund, A. Oki, J. Nanosci. Nanotechnol. 11 (2011) 3621-3629.
- [21] B. Yoon, H. Kim, C.M. Wai, Chem. Commun. (2003) 1040-1041.
- [22] Z. Li, J. Gao, X. Xing, S. Wu, S. Shuang, C. Dong, M.C. Paau, M.M.F. Choi, J. Phys. Chem. C 114 (2010) 723–733.
- [23] A.N. Chakoli, J. Wan, J.T. Feng, M. Amirian, J.H. Sui, W. Cai, Appl. Surf. Sci. 256 (2009) 170–177.
- [24] Y.C. Jung, H. Muramatsu, T. Hayashi, J.H. Kim, Y.A. Kim, M. Endo, M.S. Dresselhaus, Eur. J. Inorg. Chem. 2010 (2010) 4305–4308.
- [25] J.T. Yoon, Y.G. Jeong, S.C. Lee, B.G. Min, Polym. Adv. Technol. 20 (2009) 631– 638.
- [26] J.J. Park, D.M. Park, J.H. Youk, W.R. Yu, J. Lee, Carbon 48 (2010) 2899-2905.
- [27] Y. Xiong, Y. Xia, Adv. Mater. 19 (2007) 3385-3391.
- [28] O. Winjobi, Z. Zhang, C. Liang, W. Li, Electrochim. Acta 55 (2010) 4217– 4221.
- [29] B. Olalde, J.M. Aizpurua, A. Garcia, I. Bustero, I. Obieta, M.J. Jurado, J. Phys. Chem. C 112 (2008) 10663-10667.
- [30] W. Song, Z. Zheng, W. Tang, X. Wang, Polymer 48 (2007) 3658-3663.