

Hydrothermal synthesis of NiO/carbon nanotubes nanocomposite for energy production and storage devices.

R. Pinedo^a, I. Ruiz de Larramendi^a, D. Jimenez de Aberasturi^a, M. Insausti^a,
J. I. Ruiz de Larramendi^a, and T. Rojo^{a,b,*}

^aDepartamento de Química Inorgánica, Facultad de Ciencia y Tecnología (UPV/EHU),
Apdo 644, 48080, Bilbao (Spain) and ^bCIC energiGUNE, Parque Tecnológico de Alava,
Albert Einstein 46 - ED. E7, 01510 Miñano, Álava (Spain)

teo.rojo@ehu.es

Because of their unique one-dimensional (1D) geometric and electronic structure, large surface area, good chemical and thermal stability, and excellent mechanical properties, carbon nanotubes (CNTs) provide a new model system for basic scientific study of materials science [1]. The modification of the CNTs with functional materials opens a wide range of applications which covers from microelectronics and energy devices to the biology and medicine [2,3]. There have been several researches concerning the attachment of various inorganic oxides onto single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). For example, oxide nanoparticles such as SiO₂ [4,5] SnO₂ [6], ZnO [7,8], TiO₂ [9-13] have been coated onto CNTs by impregnation, sol-gel, hydrothermal synthesis, thermal evaporation-deposition and so on. In order to facilitate the adsorption of the oxide particles onto the surface of the CNTs, several modification of the CNTs can be employed, such as their oxidation by strong acids, which introduces carboxyl groups and prevents the agglomeration of oxide nanoparticles, because of the strong interactions between the hydroxyl groups and the metallic oxide nanoparticles [14]. Other metal oxides have been coated on CNTs by redox reactions between CNTs and KMnO₄ [15-18]. In addition, the surface of these nanostructured materials has been also modified by other reactants s polymers or surfactants [5, 12, 13, 19]

The aim of our research is focused on the search of nanostructured materials for application in energy devices, such as solid oxide fuel cells (SOFCs), lithium-air batteries or supercapacitors. In this work a composite system based on NiO particles coating the CNTs with possible application in the mentioned three fields is studied. The NiO is already used as anode for SOFC systems, however this composite system could enhance its properties providing a large increase of the surface area of the electrode which would promote the creation of reaction points, improving therefore its electrochemical performance [20 JACS argentinos]. However, in order to be used in SOFC devices it is necessary to reduce the operating temperature of these cells to 500 °C were the nanotubes remain stable. Another interesting application is its use as cathode for lithium-air batteries, where some other similar materials such as the MnO₂/CNT have been found to be interesting [21, 22]. Moreover, this type of materials have shown excellent properties for energy storage devices, such as supercapacitors [23]

In order to obtain this composite system an easy, non-expensive, two step hydrothermal route has been followed, using MWCNT and NiCl₂ as starting reactants and sodium dodecyl sulfate (SDS) as surfactant agent. The obtained aqueous suspension was heated at 80 °C for 4 hours. Once the sample was washed and dried, a thermal treatment at 400 °C for 2 hours was necessary to reach to the NiO. In order to confirm this fact an X-ray diffraction analysis was carried out (see Figure 1).

The scanning electron microscopy (SEM) images reveal the nanostructured shape of the synthesized material with a large surface area with potential properties for its use in energy material devices (see Figure.2.).

The thermal stability of the nanocomposite system has been studied by thermogravimetric analysis, and the electrochemical measurements show an interesting performance for its use as supercapacitor, cathode in lithium-air batteries and anode in intermediate temperature SOFCs (IT-SOFCs).

References:

- [1]. R. Saito, G. Dresselhouse and M. S. Dresselhouse, **Physical Properties of Carbon Nanotubes**, (1998), Imperial College Press, London.
- [2]. J. A. Fagan , B. J. Bauer , E. K. Hobbie , M. L. Becker , A. R. Hight Walker , J. R. Simpson , J. Chun , J. Obrzut , V. Bajpai , F. R. Phelan , D. Simien , J. Y. Huh and K. B. Migler, **Advanced Materials**, (2011), 23, 338–348.

- [3]. Yue, G. Z.; Qiu, Q.; Gao, Bo; Cheng, Y.; Zhang, J.; Shimoda, H.; Chang, S.; Lu, J. P.; Zhou, O., **Applied Physics Letters**, (2002), 81(2), 355-357.
- [4]. T. Seeger, T. Köhler, T. Frauenheim, N. Grobert, M. Rühle, M. Terrones and G. Seifert, **Chem. Commun.**, (2002), 34.
- [5]. E. A. Whitsitt and A. R. Barron, **Nano Lett.**, (2003), 3, 775.
- [6]. W. Q. Han and A. Zettl, **Nano Lett.**, (2003), 3, 681.
- [7]. W. D. Zhang, **Nanotechnology**, (2006), 17, 1036.
- [8]. S. Y. Bae, H. W. Seo, H. C. Choi, J. Park and J. Park, **J. Phys. Chem. B**, (2004), 108, 12318.
- [9]. B. Liu and H. C. Zeng, **Chem. Mater.**, (2008), 20, 2711.
- [10]. Q. Huang and L. Gao, **J. Mater. Chem.**, (2003), 13, 1517.
- [11]. A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Beguin and S. Bonnamy, **Carbon**, (2004), 42, 1147.
- [12]. S. W. Lee and W. M. Sigmund, **Chem. Commun.**, (2003), 780.
- [13]. T. Sainsbury and D. Fitzmaurice, **Chem. Mater.**, (2004), 16, 3780.
- [14]. X. Li, J. Niu, J. Zhang, H. Li and Z. Liu, **J. Phys. Chem. B**, (2003), 107, 2453.
- [15]. X. Jin, W. Zhou, S. Zhang and G. Z. Chen, **Small**, (2007), 3, 1513.
- [16]. S. B. Ma, K. Y. Ahn, E. S. Lee, K. H. Oh and K. B. Kim, **Carbon**, (2007), 45, 375.
- [17]. W. D. Zhang and J. Chen, **Pure Appl. Chem.**, (2009), 81, 2317.
- [18]. J. Yan, Z. J. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. P. Song and M. L. Zhang, **J. Power Sources**, (2009), 194, 1202.
- [19]. A. Gonzalez-Campo, K. L. Orchard, N. Sato, M. S. P. Shaffer and C. K. Williams, **Chem. Commun.**, (2009), 4034.
- [20]. M. G. Bellino, J. G. Sacanell, D. G. Lamas, A. G. Leyva, N. E. Walsoe de Reza, **J. Am. Chem. Soc.**, (2007), 129, 3066-3067.
- [21]. J. Xiao, W. Xu, D. Wang and J.-G. Zhang, **Journal of The Electrochemical Society**, (2010), 157, 3, A294-A297.
- [22]. L. Jin, L. Xu, C. Morein, C. Chen, M. Lai, S. Dharmarathna, A. Doble, and S. L. Sui, **Adv. Funct. Mater.** (2010), 22, 3373–3382.
- [23]. W. Zhang, B. Xu and L. Jiang, **J. Mater. Chem.**, (2010), 20, 6383–6391.

Figures

Figure caption1. Obtained diffractogram for the NiO-MWCNTs nanocomposites system

Figure caption2. SEM images of the nanocomposite system NiO/MWCNTs

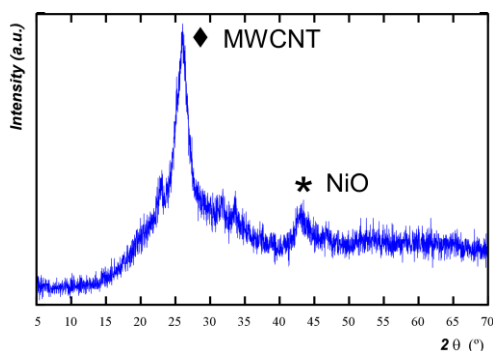


Figure 1. Obtained diffractogram for the NiO-MWCNTs nanocomposites system

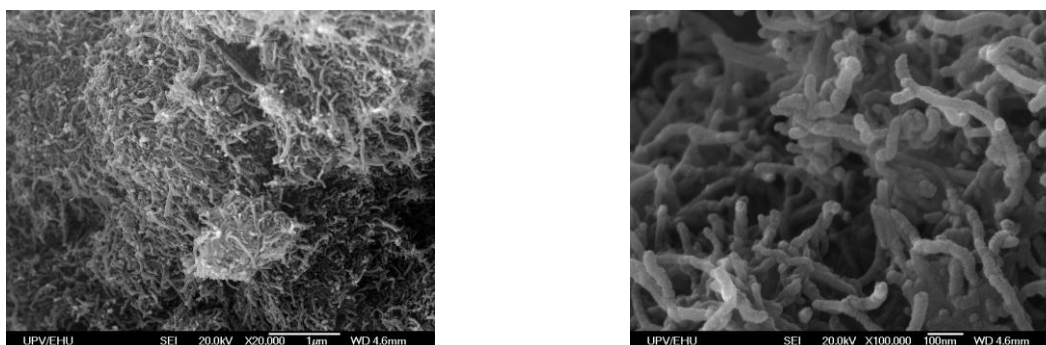


Figure 2. SEM images of the nanocomposite system NiO/MWCNTs