Evaluation of cobalt nanoparticle deposited graphene oxide and carbon nanotube supports as supercapacitor electrodes

Evaluación del óxido de grafeno depositado en nanopartículas de cobalto y soportes de nanotubos de carbono como electrodos supercondensadores

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Resumen. - *Las nanopartículas de cobalto se depositaron en soportes de carbono, nanotubos de carbono de pared múltiple (CNT) y óxido de grafeno (GO), y se evaluaron como potenciales electrodos de supercondensadores. La estructura y la morfología de las nanopartículas de cobalto depositadas sobre los soportes de carbono se estudiaron mediante XRD, TGA y espectroscopía Raman. La voltametría cíclica se utilizó para medir la carga eléctrica del electrodo en función de los materiales y se calculó su capacitancia específica (Csp). El electrodo basado en GO mostró un Csp mayor que el electrodo CNT, lo cual se atribuye a un área de superficie mayor del soporte de carbono GO. Curiosamente, el depósito de nanopartículas de Co promovió una Csp mejorada en los soportes GO y en los CNT de pared múltiple.*

Palabras clave: Supercondensador; Óxido de Grafeno; Nanotubos de Carbono; Nanopartículas de Cobalto.

Abstract. - *Cobalt nanoparticles were deposited on multi-wall carbon nanotubes (CNT) and graphene oxide (GO) carbon supports and evaluated as a potential supercapacitor electrodes. The structure and morphology of the cobalt nanoparticles deposited on carbon supports were studied using XRD, TGA, and Raman spectroscopy. Cyclic voltammetry was used to measure the electrical charge of the electrode based on the materials and their specific capacitance (Csp) were calculated. GO based electrode showed a higher Csp than CNT electrode which is attributed to a larger surface area of the GO carbon support. Interestingly, the deposition of Co nanoparticles promoted an enhanced Csp in the both GO and multi-wall CNT supports.*

Keywords: Supercapacitor; Graphene Oxide; Carbon Nanotubes; Cobalt Nanoparticles.

1. Introducción

Energy demand has always been a primary area of interest around the world and its claim has grown very fast in recent years. Considerable effort has been dedicated to the research and development of more efficient energy storage devices and systems [1].

The bulk of energy storage research has been focused on two types of electrochemical devices: batteries and capacitors. Batteries have low power density with higher energy density, while conventional capacitors exhibited high power but lower energy density. On the other hand, supercapacitors (SCs) are efficient devices that have exceeded the energy storage capacity with respect to conventional capacitors. The SCs have great advantages including their high-power density, long service life, wide operating temperature range, flexibility, and their ecofriendly nature. Some applications for these devices are in areas like consumption electronic, hybrid vehicles, and industrial power/energy managements [2]. However, SCs suffer from low energy density and high manufacturing cost.

Conventionally, the capacitive behavior can be classified into two types; (1) the double layer electric capacitance (EDLC) arising from electrostatic attraction between electrolyte and electrode surface; (2) the pseudo-capacitance associated with fast and reversible faradic reactions of the active species on the surface of the electrode.

One way to attain better performance for capacitors is to increase the capacitance (C). Capacitance is directly influenced by the dielectric constant of the electrolyte, (ε_r), the effective thickness of the double layer (d, separation between charges), the dielectric constant of the vacuum (ε_0) and the surface area (A):

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad (1)$$

The use of nanomaterials such as graphene oxide (GO) and multi-wall carbon nanotubes (CNT) can provide a synergistic effect on capacitance and thereby energy density and the deposition of nanoparticles is expected to increase this synergic effect. Typically, noble metal oxides such as RuO_2 have exhibited exceptional properties as pseudo-capacitor materials for capacitors. The high cost of Ru has thwarted its commercial acceptance as an electrode material in SCs and encouraged finding other cheaper materials with a similar capacitive behavior as RuO_2 [3]. Cobalt appears as a possibility to increase the energy storage by the phenomenon of pseudo-capacitance [reference needed]. We propose the use of GO and CNT modified deposited with Co nanoparticles in order to obtain a non-expensive and efficient material for SCs.

2. Methodology

In this work, GO was synthesized by Hummers modified method [4] and CNT were synthesized by spray pyrolysis [5]. Nanoparticles of cobalt were deposited on both carbonaceous supports by the method of reverse microemulsion [6].

2.1 Preparation of GO, CNT, Co/GO and Co/CNT

Hummers modified method consists of the exfoliation of graphite powder in strongly oxidizing media. 2 g of the natural graphite powder was added into a 250-mL beaker with 1 g of $NaNO_3$. 46 mL of H_2SO_4 were subsequently added to the graphite powder mixture under stirring in an ice-bath. Then, 6 g of $KMnO_4$ was added slowly into the beaker while stirring and the temperature of the system was maintained at 20 °C using an ice-bath. After 5 min, the ice bath was removed and the system was heated (what temperature?) for 30 min followed by an addition of 92 mL of and the mixture was stirred for 15 min. Then, 80 mL of hot water at 60 °C and H_2O_2 aqueous solution (3 wt %) were added to the mixture until the bubbling disappeared. Finally, the system was centrifuged for 30 min, and the

residue was washed with warm water until the suspension was neutralized.

In spray pyrolysis, a quartz tube was placed inside of an oven at 850 °C while a solution of 20 mM of ferrocene in toluene was sprayed out by Ar flow at 20 psi. After the reaction was allowed to proceed for 30 min, the oven cooled down to room temperature with Ar flow. CNTs were functionalized by acidic solution of H_2SO_4:HNO_3 with a ratio 1:3 M.

The deposition of Co nanoparticles was performed by reverse microemulsion method which starts with the preparation of a microemulsion solution of isopropanol/CTAB/ H_2O (56 mL/2 g/4 mL). 40 mL of microemulsion solution were taken in order to disperse the support (either CNT or GO) under sonication. Then, the dispersion was placed in a round bottom flask under stirring at 60 °C. After 15 min, a mixture of 2 mL of aqueous solution containing 100 mM of sodium borohydride and 100 mM of sodium citrate was prepared and added with 10 mL of the above microemulsion solution. After 20 min, 12 mg of cobalt (II) chloride salt dispersed in 2 mL of H_2O was slowly added into the original 10 mL of microemulsion solution by sonication and the reaction vessel was kept at reflux for 90 min. Finally, the residue was filtered and washed with DI water, isopropanol, and ketone.

2.2 Characterization

The structure and morphology of nanocomposites were characterized by Raman spectroscopy, X-ray diffraction and thermogravimetric analysis. The electrochemical properties of nanomaterials and their correlation with the nanoparticles were investigated using a three-electrode cell using techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Glassy carbon (GC) was used as working electrode (3 mm of diameter), Au wire was used as counter electrode, and Ag/AgCl/KClsat was used as reference electrode.

3. Results and Discussions

TGA curves were used to understand the thermal decomposition behavior of the two different supports used in this study. CNT showed a thermal decomposition at 633 °C, while GO exhibited the thermal decomposition at 188 °C. CNT-F (What is CNT-F? should explain that first) showed a thermal behavior similar to CNT but showed decomposition at 320 °C, due to desorption of oxygen functional groups. Besides, the metal loading of both Co/CNT and Co/GO was estimated by TGA analysis as 12% and 19% respectively.
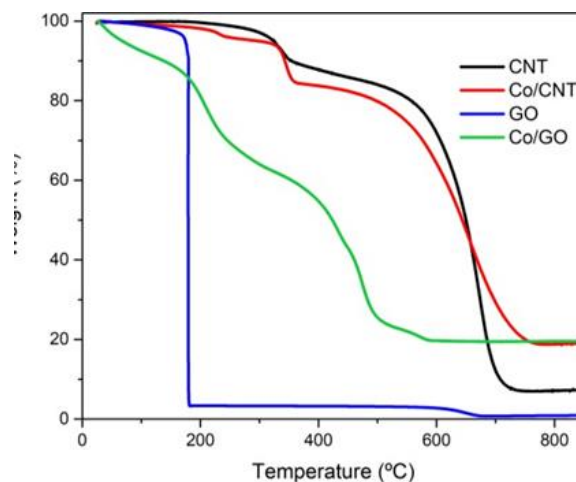

Figure 1. TGA curves of the synthesized materials.

Raman spectroscopy is useful for studying order and defects in crystal structure and is often employed to characterize carbonaceous materials [reference needed]. The G band is common for all sp2 carbon forms and it arises from the C-C bond stretch. This band is formed from first order Raman scattering and the D band is associated with disordered structural defects [7]. The ratio of the intensities of D and G bands is an indicator of the quality of bulk samples. Similar intensities of these bands indicate a high quantity of structural defects. Raman spectra of the synthetized materials exhibited a peak of D band at 1334 cm^{-1}, 1336 cm^{-1}, 1350 cm^{-1} and 1323 cm^{-1} and G band at 1586 cm^{-1}, 1582 cm^{-1}, 1603 cm^{-1} and 1594 cm^{-1} for CNT, Co/CNT, GO, and Co/GO, respectively.

The G band in GO is shifted to a higher wave number due to the oxygenation of graphite, which results in the formation of sp3 carbon atoms. The D band in GO is broadened due to the reduction in size of the sp2 domains by the creation of defects, vacancies, and distortions during oxidation. In order to confirm the formation of multi-wall carbon nanotubes, the ratio of the intensities of D and G bands present values characteristic for multi-wall carbon nanotubes. Also, the Raman spectrum from 250 nm to 350 nm does not exhibited any signal (not shown), which is typical for this structure [8].
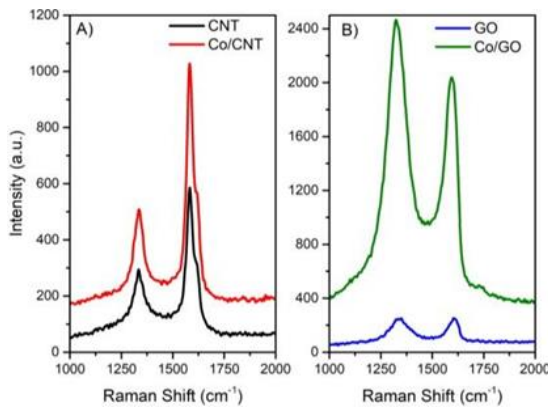
Figure 2. Raman spectra of CNT, Co/CNT (A) and GO, Co/GO (B).

The deposition of the Co nanoparticles clearly shows an increase in ID/IG ratio. The ID/IG ratio of CNT is 0.50 while that of Co/CNT 0.74. Similarly, the ID/IG ratio of GO is 0.98 while that if Co/GO is 1.21 showing that more defects appear after Co deposition.

Figure 3 showa the XRD pattern for all the material synthetized. For CNT and Co/CNT, a strongest peak appearing at the angle (2θ) of 26° is the C(002) reflection of the hexagonal graphite structure and the peak on 43° is are related with C(100) [9]. This reflection of the hexagonal graphite structure does not appear for GO or Co/GO.
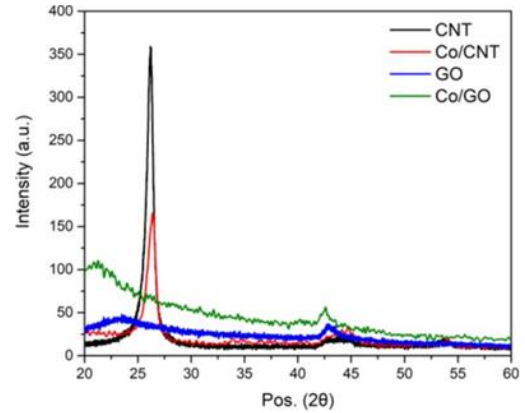

Figure 3. XRD Patterns of CNT, Co/CNT, GOx, and Co/GOx.

CV curves were performed at different potential scan rates in order to obtain the integrated charge and to calculate the specific capacitance (Csp) according to equation 2:

$$C_{sp}= \frac{Q}{2*m*\Delta V*v} \qquad (2)$$

Where, Q is the integrated charge of CV curve (mC), m is the nanomaterial loading (mg), ΔV is the potential window (mV), and v is the scan rate potential (mV s^{-1}). Figure 3 shows the Csp vs. scan rate potential of CNT, GO, Co/CNT and Co/GO.
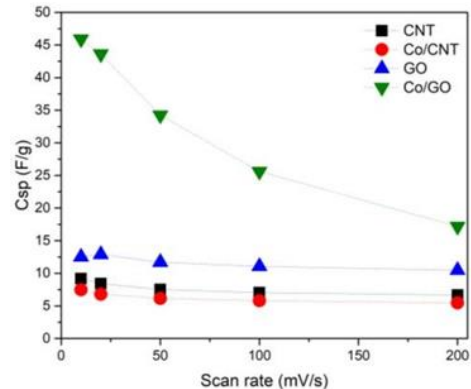
Figure 4. C$_{sp}$ vs. scan rate of the synthesized materials.

When comparing the carbon supports, GO showed higher Csp than CNT. However, when Co nanoparticles are deposited on to the supports, the Csp increases more for Co/GO but remains constant for Co/CNT. The C vs. Log frequency plot could be used to identify the geometrical capacitance and the dielectric constant of any materials [10] accordingly to Equation 1.
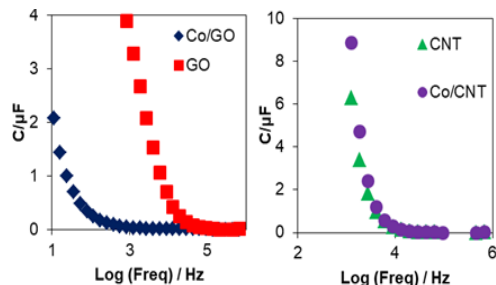
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Figure 5. Cvs. Log (Freq) of the synthesized materials.

The capacitance of all the materials were estimated from Figure 5 and the dielectric constant of the materials are of the same order.

4. Conclusions

Co nanoparticles were deposited onto CNT and GO supports. The nanomaterials synthesized were characterized using XRD, TGA, and Raman showed a higher surface area for Co/GO. Based on the CV results, Co/GO exhibited the highest Csp among all the materials studied which is attributed the large surface area of GO and the contribution of pseudo- capacitance from Co nanoparticles.

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