Facile sonochemical synthesis of artichoke-like Co$_3$O$_4$-graphene nanocomposites

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Abstract. Facile sonochemical technique was used for the first time to synthesize Co$_3$O$_4$-graphene nanocomposites at room temperature. The nanocomposites under investigation were prepared with different Co$_3$O$_4$ molar ratios of nanoparticles. The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FT-IR) and UV-vis spectroscopy. The results show that Co$_3$O$_4$ nanoparticles were distributed uniformly on the surface of graphene sheet. This work reports a simple preparation approach and recommends the described methodology for the decoration of graphene sheet surface with miscellaneous metal oxide nanoparticles.

Keywords: Graphene; Co$_3$O$_4$ nanoparticles; nanocomposite; morphology; FESEM

1. Introduction

Graphene is one of the most attractive materials being widely researched in recent times. The increased popularity of graphene originates from its wondrous properties, which include, but are not limited to, excellent electron mobility through its atom-thick sp$^2$ bonded 2-D structure, its large current density, optical transmittance, very good mechanical properties and remarkable thermal conductivity [1–5]. Significant synergistic effects often occur in graphene/metal oxide composites owing to size effects and interfacial interactions.

The synergistic effects in graphene/metal oxide composites can be underlined as follows: (i) graphene is a novel 2D support for homogeneously nucleating, growing or assembling metal oxides with distinguished size, shape, and crystallinity; (ii) metal oxides amongst the layers of graphene can proficiently defeat the re-stacking of graphene; (iii) graphene can act as a 2D conductive model for construction of a 3D interlocked conductive porous network to enhance both electrical conductivity and charge transportation of pure oxides; (iv) graphene can suppress the volume change and particle agglomeration of metal oxides during the charge–discharge process; (v) oxygen-containing functional groups on graphene guarantees respectable interfacial interactions as well as electrical contacts between graphene and metal oxides. Due to these good special effects, integration of metal oxides nanoparticles and graphene in a composite fully uses each active component and subsequently realizes outstanding electrochemical performance.

The potential applications of metal oxide–graphene nanocomposites include super capacitors, anodes for Li-ion batteries, electrocatalysts, and biosensors where several structural models of graphene-cobalt oxide composites are already proposed [6–12].
Herein, we report a facile strategy to synthesize nano composite of Co$_3$O$_4$ anchored on conducting graphene as an advanced anode for Li-ion batteries. The objective of this work was to prepare and to characterize the (G-Co$_3$O$_4$) nanocomposites in different proportions in order to verify their physicochemical properties. Moreover, one of our goals is to explore the effect of Co$_3$O$_4$ weight ratio on the properties of nanocomposites to highlight the applications of such new nanocomposites and to open a new era for another potential uses.

2. Materials and method

2.1 Synthesis of Co$_3$O$_4$ nanoparticles
All chemical reagents (analytical grade) were used as received without further purification. Deionized water was used throughout this study. Simply, an aqueous solution of ammonium carbonate (1.86 g) was added to a stirring solution of Co (CH$_3$COO)$_2$.4H$_2$O; (0.8g). The reaction was transferred into a Teflon lined stainless steel autoclave which was hydrothermally treated at 160 °C for 24 hrs. The pink precipitate of CoCO$_3$ was thoroughly washed and dried at 60°C for 24h. The obtained powder was calcined in air at 300 °C for 2 h in air to obtain Co$_3$O$_4$ nanoparticles [13].

2.2 Synthesis of Co$_3$O$_4$- graphene nanocomposites
Nanocomposites of Co$_3$O$_4$-graphene were prepared using modified sonochemical technique. The details were as follows: Preparation of graphene sheets (G) using graphene powder dispersed in deionized water using ultrasonic bath at a power 700W for 1h to fully exfoliate the graphene until a homogeneous sheet was observed. All nanocomposites were prepared by adding 5, 10 and 20% of Co$_3$O$_4$ directly into 20mL of the dispersed graphene using ultrasonication for 90 min, then dried at 40 °C in air for 48hrs.

2.3 Characterizations
X-ray diffraction (XRD) patterns were examined using Bruker X-ray powder diffractometer (model D8 Advance) with (Cu K$_{α1}$, λ=1.5417 Å). The morphology of the nanocomposites was characterized by field emission scanning electron microscopy (FESEM, Model Quanta 250 FEG). Fourier transform infrared spectroscopy (FT-IR) were obtained using Bomem; model MB1575. The UV-vis spectra were recorded on a UV-vis spectrophotometer (Jasco; model 530).

3. Results and discussion

3.1 XRD diffraction
The XRD patterns of graphene, Co$_3$O$_4$, and the as-prepared nanocomposites (Co$_3$O$_4$-graphene) were illustrated in figure 1 (a-e) For graphene, a very sharp peak was observed at 26.52°, which is attributed to the C (002) plane [14,15]. The data were indexed according to the reported pattern. of the ICDD card 08-0415 which assures the hexagonal crystal symmetry belonging to the P6$_3$/mmc space group. Co$_3$O$_4$ nanoparticles were crystallized in single phase cubic spinel structure as compared and indexed with ICDD card no (78-1970). All peaks appear to be broad with small intensities pointing to nanoscale particles. All planes concerning the Co$_3$O$_4$ were indexed on the basis of the cubic spinel structure of space group Fd3m. The key planes in the XRD pattern of pure Co$_3$O$_4$ were assigned to (111), (220), (311), (400), (422), (511) and (440) respectively. The lattice parameter was computed based on cubic structure and is a= 8.0804 Å. The theoretical density was calculated from $D_\text{th} = ZM/NV$, where Z counts for the number of molecules per unit cell (Z=8), M is the molecular weight, N is Avogadro’s number and V is the unit cell volume. It was found to be =6.063g/cm$^3$ which agree well with that reported in the corresponding ICDD card. The X-ray...
Figure 1. XRD patterns of graphene, \( \text{Co}_3\text{O}_4 \) nanoparticles and \( \text{Co}_3\text{O}_4 \)-graphene nanocomposite at different weight ratios of \( \text{Co}_3\text{O}_4 \) nanoparticles.

diffraction patterns of the cobalt oxide nanoparticles (\( \text{Co}_3\text{O}_4 \)), graphene and composites with different molar ratios of \( \text{Co}_3\text{O}_4 \) nanoparticles display the reflections at \( 2\theta = 19.018^\circ, 31.177^\circ, 36.884^\circ, 44.817^\circ, 55.729^\circ, 59.314^\circ \) and \( 65.472^\circ \). These peaks are associated with the crystallographic planes (111), (220), (311), (400), (422), (511) and (440) which agree with the typical spinel \( \text{Co}_3\text{O}_4 \) cubic structure [16]. The average crystallite size of cobalt oxide nanoparticles was estimated from Scherrer equation using the corrected full width at half maximum (FWHM). As reported in the literature [17], the Scherrer’s equation is described as follows: \( L = (k\lambda)/(\beta \cos \theta) \), where \( L \) is the average crystallite size (nm), \( \lambda \) is the X-ray wavelength (0.1540593 nm), \( \theta \) is the corresponding Bragg angle, \( k = 0.9 \) is the shape factor and \( \beta \) is the corrected FWHM.
Table 1. Structural parameters of graphene- Co$_3$O$_4$ nanocomposites

| Sample     | a (Å)  | V (Å$^3$) | D$_x$ (g/cm$^3$) of Co$_3$O$_4$ | L$_{avg.}$ (nm) |
|------------|--------|-----------|-------------------------------|-----------------|
| Pure Co$_3$O$_4$ | 8.0804 | 527.32    | 6.063                         | 17.65           |
| 5% Co$_3$O$_4$    | 8.1248 | 536.34    | 5.960                         | 19.06           |
| 10% Co$_3$O$_4$   | 8.1269 | 536.57    | 5.958                         | 20.46           |
| 20% Co$_3$O$_4$   | 8.1301 | 537.36    | 5.949                         | 24.06           |

Figure 2. FESEM of Co$_3$O$_4$- graphene nanocomposites at different Co$_3$O$_4$ weight ratios, (a) Co$_3$O$_4$, (b and c) 5%, (d, e and f) 10%, (g) 20%.
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Figure 3. (a-c) FTIR spectra of Co$_3$O$_4$- graphene nanocomposites

The lattice parameters unit cell volume, theoretical density and average crystallite size for G-Co$_3$O$_4$ nanoparticles are reported in table 1. The data in the table assure that Co$_3$O$_4$ crystallite increased significantly in size when decorating graphene sheets, this means that the existence of the graphene layers didn’t impede the crystal growth completely and Co$_3$O$_4$ nanoparticles were used successfully to prevent the stacking of graphene sheets and to offer an excellent conducting matrix and/ or template anchored with metal oxide nanoparticles. Moreover, the lattice parameter of the cubic unit cell as well as its volume increased with increasing Co$_3$O$_4$ weight percent in the nanocomposite. The lattice expansion; here in; depended strongly on the Co$_3$O$_4$ ratio which takes the upper hand in controlling the spacing between the graphene layers.

3.2. Field emission scanning electron microscopy (FESEM)

Figure 2 (a) illustrates the FESEM of Co$_3$O$_4$ nanoparticles. Nanospheres appeared homogenously distributed with uniform size, stacked together without significant coalescence despite the absence of surfactant. The observed grain size ranged from 90 to 100nm.

In Fig. (2:b,c) the sample with 5% Co$_3$O$_4$ nanoparticles morphology looks like homogenously distributed nanospheres anchored on the graphene nanosheets. The graphene nanosheets are well separated and the Co$_3$O$_4$ nanoparticles prevented their overlap.

From a closer look to the FESEM micrograph, it is obviously remarked that Co$_3$O$_4$ nanoparticles here didn’t predominate due to their small content weight ratio. Graphene nanosheets appeared to be curved in a flower like morphology as clear in Figure 2 (d-f) representing 10% Co$_3$O$_4$. The layers of graphene appears as artichoke like carnations homogenously distributed. The nanosheets appeared to be as flower petals decorated with Co$_3$O$_4$ nanospheres. The micrographs give insight about more information useful in many applications. The graphene acted successfully as 2D template for enhanced crystal growth of Co$_3$O$_4$ nanospheres.

Herein and from the micrographs 20% of the Co$_3$O$_4$; Figure 2 (g) by increasing Co$_3$O$_4$ nanoparticles, they become more distributed and interesting features are clearly seen. The Co$_3$O$_4$ nanoparticles
prevent the intercalation of the graphene and their overlay while the later helps in more homogenous dispersion of the former. This excellent morphology presented in a decorative manner where the graphene were arranged in flower like morphology and curved layers assure the strong interaction between \( \text{Co}_3\text{O}_4 \) and graphene nanosheets with good mechanical flexibility. These nanocomposites are now recommended in energy storage applications owing to their large surface active area, since the anchoring of \( \text{Co}_3\text{O}_4 \) successed effectively to reduce the restacking of graphene sheets.

3.3 FTIR spectra
The infrared spectra of the produced \( \text{Co}_3\text{O}_4 \)-graphene, nanocomposite samples, are presented in Figure 3 (a-c). The data show absorption bands at 668 and 571 cm\(^{-1} \) which confirms the spinel structure of \( \text{Co}_3\text{O}_4 \). This absorption band is not clear in the sample (a) due to small amount of \( \text{Co}_3\text{O}_4 \) band (5%). The first peak is specifically assigned to the stretching vibration mode of \( \nu_{\text{Co}-\text{O}} \) for \( \text{Co}^{2+} \), while the band appeared at 571 cm\(^{-1} \) is attributed to the \( \text{Co}-\text{O} \) bond for \( \text{Co}^{3+} \) [18,19]. The IR spectra, of the \( \text{Co}_3\text{O}_4 \) - graphene, nanocomposite samples exhibited a broad band at 3428, 3425 and 3424 cm\(^{-1} \), respectively corresponding to the frequency vibrations of \((\text{OH})\) group of the water molecules due to drying process where the temperature was 40\(^\circ\)C only. The bands appeared at 1627, 1619 and 1626 cm\(^{-1} \) are assigned to the stretching vibration of \( \nu_{\text{C}=\text{O}} \) groups for graphene- \( \text{Co}_3\text{O}_4 \), nanocomposite samples, respectively. The band intensities are certainly dependent on the \( \text{Co}_3\text{O}_4 \) content ratio in the nanocomposite.

3.4 Optical properties of \( \text{Co}_3\text{O}_4 \)-graphene nanocomposites
The optical absorption properties of the as-prepared \( \text{Co}_3\text{O}_4 \)-graphene nanocomposite (20% weight ratio of \( \text{Co}_3\text{O}_4 \) was investigated at room temperature by UV–vis spectroscopy figure 4. When incorporating \( \text{Co}_3\text{O}_4 \) on to graphene surface, the small content 5% and 10% weight ratios didn’t reveal absorbance owing to the excellent conductivity of graphene. At 20% \( \text{Co}_3\text{O}_4 \), the band gap was calculated to have two obvious absorption peaks. The optical band gap \( E_g \) of the \( \text{Co}_3\text{O}_4 \)-graphene nanocomposite (20%) was calculated using the equation (1) [20,21]:

\[
\alpha = A(\nu - E_g)^n / \nu
\]  

Where \( \alpha \) is the linear absorption coefficient, \( \nu \) is the photon energy, \( A \) is a constant involving properties of the bands, and \( n \) is \( \frac{1}{2}, \frac{3}{2}, 2, \) and \( 3 \) for directly allowed, directly forbidden, indirectly allowed, and indirectly forbidden transitions, respectively.

![Figure 4. UV-Vis absorption spectra of 20% Co$_3$O$_4$-graphene nanocomposite.](image)

The \( (\alpha \nu)^2 \) versus \( \nu \) curve is shown in the inset of figure 4. The value of \( \nu \) extrapolated to \( (\alpha \nu)^2 = 0 \) gives the absorption band gap energy. Two regions with a linear relationship are observed and giving two energy gap (\( E_g \)) values of 3.4 and 2.5 eV. It is known [22] that the band gap of \( \text{Co}_3\text{O}_4 \) nanoparticles reveal two \( E_g \) values of 3.2 and 2.3 eV . The band gap of 2.3 eV can be associated with
the $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ charge transfer process, while the 3.2 eV band gap relates to the $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ charge transfer [23]. The increase in the band gap of the Co$_3$O$_4$-graphene nanocomposite (20%) may be ascribe to the quantum confinement effects or small size effects of the Co$_3$O$_4$ nanoparticles [24].

4. Conclusion

Co$_3$O$_4$ nanoparticles with average diameter of 90-100 nm were homogeneously adhered to the surface of graphene via a simplified sonochemical technique. The highly conductive matrix of graphene enabled the anchoring of Co$_3$O$_4$ nanoparticles in a well dispersed manner. The ratio of Co$_3$O$_4$ nanoparticles play the hero role in controlling the morphology of the graphene-Co$_3$O$_4$ composites, where we can tailor the physiochemical properties associated with the obtained morphology to achieve potential applications. Here, we concluded that graphene sheets acted as template for hosting metal oxide nanoparticles to be used in the optimization of the storage capacity of super capacitors. Moreover, increasing Co$_3$O$_4$ content could help in the use of these nanocomposites as modified anode for Li-ion batteries owing to the excellent conductivity offered by graphene itself. Our future work will be involved in exploring this methodology for the preparation of novel nanocomposites to offer multifunctional platform.

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References

[1] Choi W, Lahiri I, Secelaboyiina R and Kang Y S 2010 Synthesis of graphene and its applications: a review Crit. Rev. Solid State Mater. Sci. 35 52–71
[2] Soldano C, Mahmood A and Dujardin E 2010 Production, properties and potential of graphene Carbon N. Y. 48 2127–50
[3] Rao C N R, Sood A K, Voggu R and Subrahmanyam K S 2010 Some novel attributes of graphene J. Phys. Chem. Lett. 1 572–80
[4] Kuilla T, Bhadra S, Yao D, Kim N H, Bose S and Lee J H 2010 Recent advances in graphene based polymer composites Prog. Polym. Sci. 35 1350–75
[5] Fuhrer M S, Lau C N and MacDonald A H 2010 Graphene: materially better carbon MRS Bull. 35 289–95
[6] Wu Z-S, Ren W, Wen L, Gao L, Zhao J, Chen Z, Zhou G, Li F and Cheng H-M 2010 Graphene Anchored with Co3O4 Nanoparticles as Anode of Lithium Ion Batteries with Enhanced Reversible Capacity and Cyclic Performance ACS Nano 4 3187–94
[7] Chen S Q and Wang Y 2010 Microwave-assisted synthesis of a Co 3 O 4 – graphene sheet-on-sheet nanocomposite as a superior anode material for Li-ion batteries † J. Mater. Chem. 20 9735–9
[8] Wang G, Liu J, Tang S, Li H and Cao D 2011 Cobalt oxide–graphene nanocomposite as anode materials for lithium-ion batteries J. Solid State Electrochem. 15 2587–92
[9] Kim H, Seo D-H, Kim S-W, Kim J and Kang K 2011 Highly reversible Co3O4/graphene hybrid anode for lithium rechargeable batteries Carbon N. Y. 49 326–32
[10] Li B, Cao H, Shao J, Li G, Qu M and Yin G 2011 Co3O4@graphene Composites as Anode Materials for High-Performance Lithium Ion Batteries Inorg. Chem. 50 628–32
[11] Zhu J, Sharma Y K, Zeng Z, Zhang X, Srinivasan M, Mhaisalkar S, Zhang H, Hng H H and Yan Q 2011 Cobalt Oxide Nanowall Arrays on Reduced Graphene Oxide Sheets with Controlled Phase, Grain Size, and Porosity for Li-Ion Battery Electrodes J. Phys. Chem. C 115 8400–6
[12] Wang B, Wang Y, Park J, Ahn H and Wang G 2011 In situ synthesis of Co3O4/graphene nanocomposite material for lithium-ion batteries and supercapacitors with high capacity and supercapacitance J. Alloys Compd. 509 7778–83
[13] Nassar M Y 2013 Size-controlled synthesis of CoCO3 and Co3O4 nanoparticles by free-
surfactant hydrothermal method \textit{Mater. Lett.} \textbf{94} 112–5

[14] Zhou W, Liu J, Chen T, Tan K S, Jia X, Luo Z, Cong C, Yang H, Li C M and Yu T 2011 Fabrication of Co3O4-reduced graphene oxide scrolls for high-performance supercapacitor electrodes \textit{Phys. Chem. Chem. Phys.} \textbf{13} 14462–5

[15] Cobalt G A, Electrode O, Supercapacitor H and Detection E G 2012 3D Graphene Á Cobalt Oxide Electrode for High-Performance Supercapacitor and Enzymeless Glucose Detection \textit{ACS Nano} \textbf{6} 3206–13

[16] Wang X, Liu S, Wang H, Tu F, Fang D and Li Y 2012 Facile and green synthesis of Co3O4 nanoplates/graphene nanosheets composite for supercapacitor \textit{J. Solid State Electrochem.} \textbf{16} 3593–602

[17] R. Jenkins R L S 1996 \textit{Chemical Analysis: Introduction to X-ray Power Diffractometry} (John Willy and Sons, Inc., New York)

[18] Tatzber M, Stemmer M, Spiegel H, Katzberger C, Haberhauer G and Gerzabek M H 2007 An alternative method to measure carbonate in soils by FT-IR spectroscopy \textit{Environ. Chem. Lett.} \textbf{5} 9–12

[19] Šoptrajanov B, Stefov V, Kuzmanovski I, Jovanovski G, Lutz H D and Engelen B 2002 Very low H–O–H bending frequencies. IV. Fourier transform infrared spectra of synthetic dittmarite \textit{J. Mol. Struct.} \textbf{613} 7–14

[20] Salavati-Niasari M, Davar F, Mazaheri M and Shaterian M 2008 Preparation of cobalt nanoparticles from [bis(salicylidene)cobalt(II)]–oleylamine complex by thermal decomposition \textit{J. Magn. Magn. Mater.} \textbf{320} 575–8

[21] Herrero M, Benito P, Labajos F M and Rives V 2007 Nanosize cobalt oxide-containing catalysts obtained through microwave-assisted methods \textit{Catal. Today} \textbf{128} 129–37

[22] Farhadi S, Safabakhsh J and Zaringhadam P 2013 Synthesis, characterization, and investigation of optical and magnetic properties of cobalt oxide (Co3O4) nanoparticles \textit{J. Nanostructure Chem.} \textbf{3} 69

[23] He T, Chen D, Jiao X, Wang Y and Duan Y 2005 Solubility-controlled synthesis of high-quality Co3O4 nanocrystals \textit{Chem. Mater.} \textbf{17} 4023–30

[24] Kumar R V, Diamant Y and Gedanken A 2000 Sonochemical synthesis and characterization of nanometer-size transition metal oxides from metal acetates \textit{Chem. Mater.} \textbf{12} 2301–5