

# Synthesis of graphene/cobalt oxide nanocomposite by pulsed laser ablation in water and its characteristics

Adeleh Granmayeh Rad<sup>1,\*</sup> , Elham Darabi<sup>2</sup> , Alaa Kadhim Manea<sup>2</sup>

<sup>1</sup>Department of Basic Science, Roudehen Branch, Islamic Azad University, Roudehen, Iran.

<sup>2</sup>Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran.

\*Corresponding author: [geranmayeh.r@gmail.com](mailto:geranmayeh.r@gmail.com)

## Original Research

## Abstract:

Received:  
2 January 2024  
Revised:  
10 February 2024  
Accepted:  
14 February 2024  
Published online:  
10 March 2024

This work aims to provide an overview of the synthesis and characterization method employed for the graphene/cobalt nanocomposite, along with highlighting its applications. In this research, we report the synthesis of graphene/cobalt nanocomposite using two-steps laser ablation technique. The experiments were performed with the first harmonic (1064 nm, 10 ns, 6 Hz) output of a Nd:YAG laser varying the operative energy of 100 mJ for graphene synthesis and 80 mJ for cobalt synthesis. The structural, morphological and optical characteristics of the prepared samples have been investigated using X-ray diffraction (XRD) analysis, field effect electron microscope (FESEM), energy dispersive spectrum (EDX) and UV-Visible spectrophotometry. All characteristic peaks of XRD and EDX results agreed well with those of graphene and cobalt oxide. The FESEM images showed the formation of graphene nano sheets and Co or Co Oxide nanoparticles. The average grain size of these nanoparticles was estimated about 25 nm.

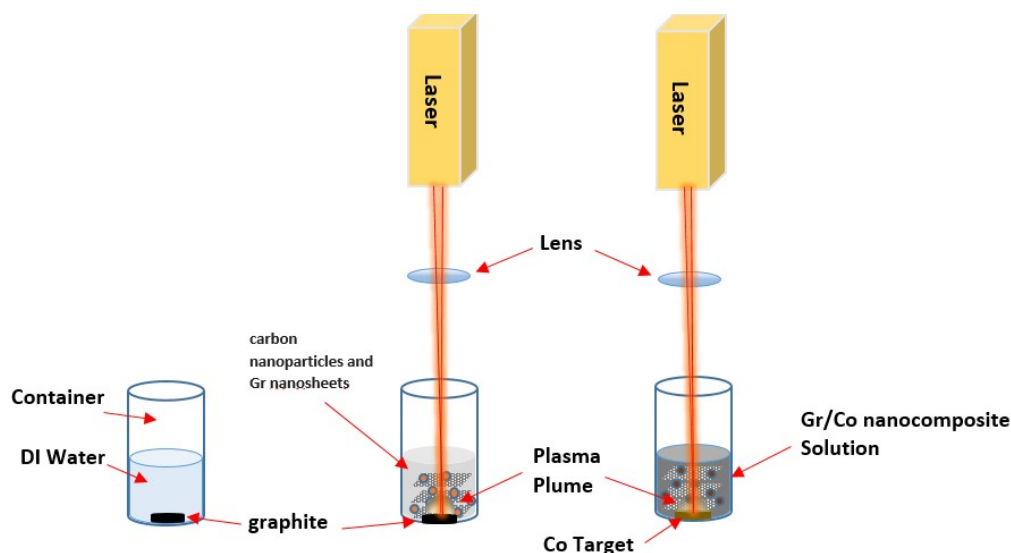
© The Author(s) 2024

**Keywords:** Graphene/cobalt oxide nanocomposite; Pulsed laser ablation; Morphological properties; Optical properties

## 1. Introduction

Field of nanotechnology has witnessed significant advancements in recent years, with researchers exploring various synthesis and characterization techniques to develop novel materials for various applications. One such material of interest is the graphene/cobalt (Gr/Co) or graphene/cobalt oxide nanocomposite. Metal nanoparticles and other inorganic/organic species can be grown, doped, or adsorbed on the surface of graphene to alter, enhance, and manipulate its properties. If these particles are magnetic, the entire nanocomposite may be magnetic as well, providing additional possibilities and uses for the created hybrids. Liu et al. [1] present a unique method involving the use of a sacrificial template and glucose molecules to form sandwiched graphene @ (Li<sub>0.893</sub>Fe<sub>0.036</sub>) Co(PO<sub>4</sub>) nanoparticles. Robinson et al. [2] described the synthesis of cobalt nanoparticles using pulsed laser irradiation of cobalt carbonyl in a solution of stabilizing ligands. Dong et al. [3] discussed the chemical vapor condensation method for synthesizing cobalt nanoparticles using cobalt carbonyl as the precursor. Wu et al. [4] focused on the sol-gel method for prepar-

ing Sm-Co nanoparticles using metal salts and complexing agents. For Co-G composites (cobalt-vacancy defect [5] or a single Co atom combined with vacancy in an armchair graphene nanoribbon [6]), plane-wave Density Functional Theory (DFT) studies were conducted. In this instance, it was discovered that the metal donation gave the produced composite magnetic characteristics. The subject of cobalt-graphene nanocomposites was covered in several studies. STM spin-excitation spectroscopy was used to examine individual Co atoms on graphene on Pt (111) and their magnetic properties. Three different hydrogenated species, each with very different magnetic properties from the cobalt element, were found to exist upon hydrogen adsorption [7]. It was proposed that large magnetic anisotropy results from strong ligand field effects that occur as a result of the interaction of Co-G orbitals. Several papers investigated the cobalt intercalation between graphene and Ir (111) using various methods. As a result, X-ray magnetic circular dichroism and photoemission were used to describe the cobalt layers intercalated between graphene and Ir (111) [8]. In particular, a magnetic moment was created in the graphene layer that was antiparallel to the cobalt's magnetic moment. It



**Figure 1.** Experimental setup for graphene/cobalt nanocomposite synthesis by laser ablation.

was discovered that magnetic ordering extended beyond monolayer intercalation. Cobalt-intercalated graphene on Ir (111) was examined using spin-polarized scanning tunneling microscopy and DFT computations in a similar research [9]. The lattice mismatch between the graphene and the Co on Ir (111) was found to be the cause of the high corrugation within the Moiré pattern, which is caused by the strong bonding between cobalt and graphene.

Overall, the literature on novel applications of graphene/cobalt nanostructure highlights their immense potential in various fields. These nanoparticles, which are a combination of graphene and metal oxide nanocomposites, exhibit unique properties that make them highly suitable for a wide range of applications. From biomedical to electronics, energy to environmental science, the research conducted thus far demonstrates the significant impact that graphene/cobalt nanostructure can have on society. In the field of biomedicine, graphene/cobalt nanostructures have emerged as promising tools for drug delivery systems. The high surface area and tunable properties of these nanoparticles enable efficient loading and controlled release of therapeutic agents. Moreover, their biocompatibility and low toxicity make them ideal candidates for targeted drug delivery, minimizing side effects and increasing therapeutic efficacy [10]. This research has the potential to revolutionize the treatment of various diseases, providing more targeted, effective, and personalized therapies.

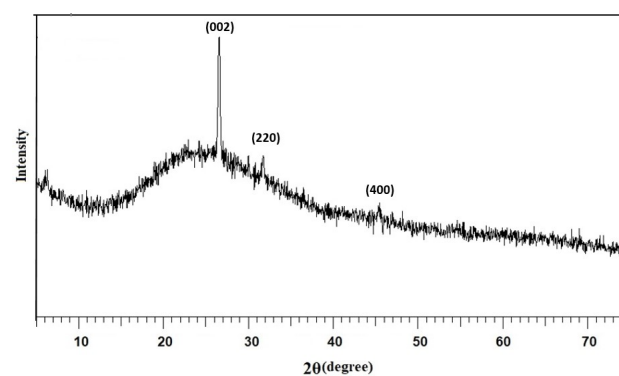
Several studies have demonstrated the potential of these nanoparticles to improve drug solubility, enhance drug targeting, and increase therapeutic efficacy. However, there are debates regarding the long-term safety and biocompatibility of these nanoparticles, as well as challenges in achieving controlled release and overcoming potential drug resistance [11].

Graphene/cobalt nanostructure have shown promise in this area by simultaneously delivering therapeutic agents while providing real-time imaging of treatment efficacy. However, challenges remain in terms of biocompatibility, targeted delivery, and scalability for clinical applications.

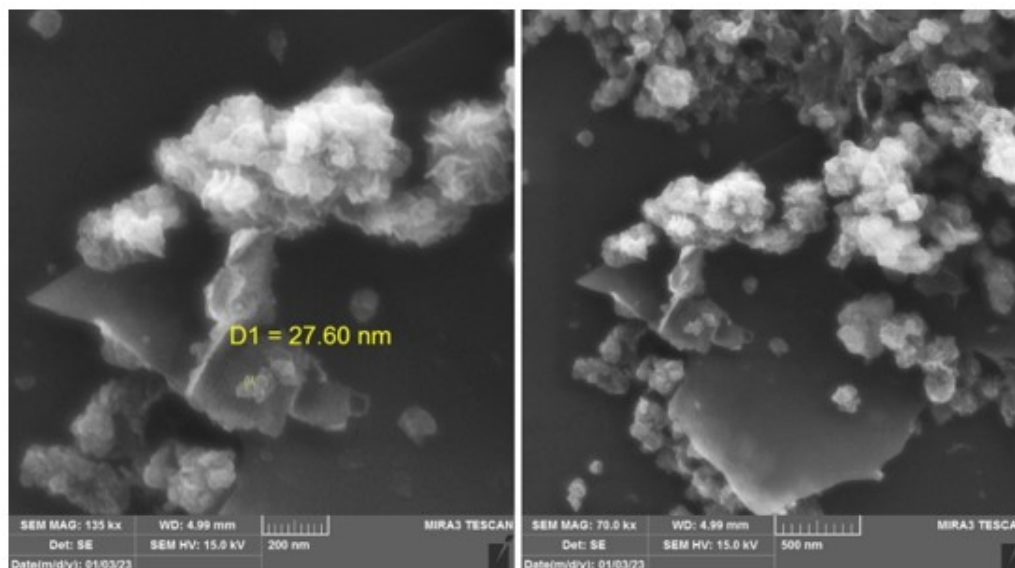
From an energy perspective, the use of graphene/cobalt nanostructure has demonstrated promising results in the field of solar cells and energy conversion systems [12, 13]. The efficient light absorption, long charge carrier lifetime, and excellent electron transport properties of these nanoparticles enable enhanced photovoltaic performance. Additionally, graphene/cobalt nanostructures have been utilized as catalysts in various energy conversion reactions, such as hydrogen evolution and oxygen reduction, due to their high catalytic activity and stability. These findings contribute to the development of sustainable and efficient energy conversion technologies.

Graphene/cobalt nanostructures have attracted attention in the field of energy storage and conversion. This theme explores their potential in areas such as lithium-ion batteries, super capacitors, and catalysis for fuel cells. Significant improvements in battery performance, capacitive properties, and catalytic activity have been reported. However, challenges persist in terms of cost-effectiveness, long-term stability, and scalability for industrial applications.

In terms of environmental science, the utilization of graphene/cobalt nanostructure has shown potential for pollution remediation and water treatment. This composition



**Figure 2.** X-ray diffraction spectrum of graphene/cobalt nanocomposite.



**Figure 3.** Field effect scanning electron microscope image of Gr/Co nanocomposite.

can efficiently remove organic pollutants, heavy metals, and other contaminants from wastewater due to their high adsorption capacity and catalytic properties [14, 15]. Additionally, their antimicrobial properties make them effective for disinfection purposes. The application of graphene/cobalt nanostructure in environmental remediation can contribute to the mitigation of water pollution and the preservation of natural resources.

These nanoparticles have demonstrated effectiveness in the removal of pollutants, heavy metals, and organic compounds from water and soil systems. However, there are concerns regarding potential ecological impacts and the scalability of nanoparticle production for large-scale remediation.

## 2. Experimental details

### 2.1 Synthesis of graphene/cobalt nanocomposite

A circular piece of high purity graphite, with a diameter of 6 mm and a thickness of 1.5 mm was used as the first target. Another target was a circular piece of cobalt with a diameter of 5 mm and a thickness of 1 mm (99.9% purity). Prior to the experiment the targets underwent polishing using paper and then were ultrasonically cleaned to remove any contaminants. Following that they were subjected to distilled water with pH value of 7 and resistance equal to  $5 \times 10^6 \Omega/\text{cm}$ .

In this study we employed the laser ablation technique to produce nanocomposites of graphene/cobalt (Figure 1). To accomplish this we utilized a Q Switched Nd:YAG laser (ISO 3485 CE certified, trademarked HUAFEI, China) operating at a wavelength of 1064 nm. The laser pulse width was 10 ns, repeated at a rate of 6 Hz. Before passing through the lens the diameter of the laser beam was measured as 2 mm. After passing a lens with the focal length of 100 mm it was estimated to be 28  $\mu\text{m}$ , on the target surface. Graphite and cobalt coins were irradiated with 250 pulses and 500 pulses of 100 mJ and 80 mJ energy, respectively. The reason for using different energies for graphite and cobalt targets was

that the ablation threshold energy of cobalt is higher than graphite.

A laser beam with a wavelength of 1064 nm was irradiated to a graphite target immersed in 3 mL of distilled water in a beaker to form both carbon nanoparticles and graphene nanosheets in the water. Then, the graphite coin was removed to replace the cobalt coin in the nano-graphene solution, and the laser ablation process was performed. Therefore, graphene/cobalt nanocomposites were prepared.

### 2.2 XRD analysis

To determine the structure of graphene/cobalt nanocomposite, the X-ray diffraction spectrum of the samples was prepared. An X-ray diffractometer, D8 Advance Bruker YT device under  $\text{CuK}\alpha$  radiation with a wavelength of  $\lambda = 1.5418 \text{ \AA}$  was used to study the crystallinity of the samples. The common method of analyzing materials based on XRD pattern is using picks of XRDs graph and calculating, to find out what materials exist in the sample. A simpler and faster method of analyzing materials based on XRD pattern is using software. In present work this has been done by X'Pert high score software. The features of the diffractometer were: focusing size of  $1.0 \times 10.0 \text{ mm}$ , scanning mode of  $2\theta$ , scanning interval of  $5^\circ - 75^\circ$ , scanning speed ( $2\theta$ ) of  $0.1^\circ/\text{min}$ , and scanning step ( $2\theta$ ) of  $0.01^\circ$ . Specimen preparation for XRD analysis was done as follows. 30 drops of aqueous sample with suspended particles were deposited over glass substrate and left it to dry.

### 2.3 FESEM analysis

Field Effect Scanning Electron Microscope (FESEM) images were used to analyze the morphological aspects and particle size distribution of graphene/cobalt nanocomposites. Examination of the surface morphology of the samples was done using a field emission scanning electron microscope (FESEM) model MIRA3TESCAN-XMU microscope, the voltage used to take these images was 15 kV.

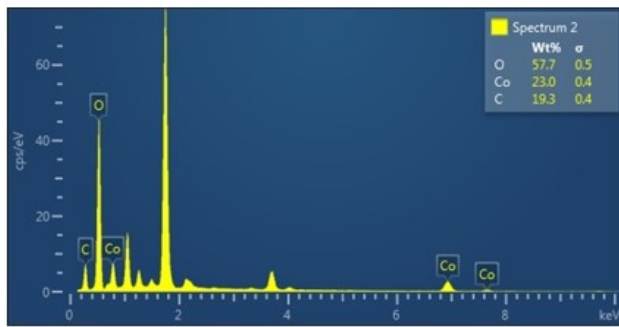


Figure 4. EDX image of Gr/Co nanocomposite.

## 2.4 Optical properties

The UV-VIS-IR optical absorption spectra of Gr, Co and graphene/cobalt nanocomposites were recorded in the region 190 – 900 nm by a spectrophotometer (CECIL 2700). A dual beam spectrometer uses a reference beam and a sampling beam that travels through the sample. Absorption spectra were collected at room temperature. Optical constants were calculated using a computer program.

## 3. Results and discussion

### 3.1 XRD analysis of graphene/cobalt nanocomposite

The XRD pattern of the synthesized sample, deposited on glass substrate is shown in Figure 2. The characteristic peak located at around  $26.48^\circ$  is related to the graphene nanosheets (JCPDS No. 01-0646) [16]. The observed diffraction peak position at  $2\theta = 31.25$  and  $44.9^\circ$  were completely matched with the JCPDS card No: 073:1701 for the  $\text{Co}_3\text{O}_4$  structure. The broad peak appearing at  $20^\circ$  to  $30^\circ$  is due to the glass substrate. These results propose the successful synthesis of graphene/cobalt oxide nanocomposite.

### 3.2 Texture and morphology

#### 3.2.1 FESEM microscopy

Figure 3 shows the FESEM images of prepared nanocomposite. In this figure, with different magnifications (scales of 200 nm (left) and 500 nm (right)), few nano sheets and many spherical nano shapes can be clearly observed which corresponds to layers of graphene and Co or Co oxide nanoparticles, respectively. The average grain size of nanoparticles is estimated about 25 nm. This morphology is well agreement with the results of XRD pattern.

#### 3.2.2 Energy dispersive X-ray spectroscopy

The chemical composition of Gr/Co nanocomposite was analyzed using energy dispersive spectroscopy (EDX) and the results are presented in Figure 4. The voltage used to perform this test was between zero and 10 kV. In Figure 4, the presence of carbon, oxygen and cobalt elements confirms the formation of graphene and probably cobalt oxide in our nanocomposite. The emission peaks were observed at 0.9, 6.9, 7.6 (eV) corresponds to Co. Hence, the emission peak noted at 0.2 (eV), and 0.5 (eV) represent the element C and O respectively. The absence of other elements in the energy dispersion spectrum confirms the absence of

impurity in these structures. According to the spectrum, it can be seen that in the Gr/Co oxide nanocomposite, the weight percentage of cobalt and carbon is 23% and 19.3%, respectively. Due to the high weight percentage of oxygen (%57.7) and the results of XRD pattern it can be concluded that the formation of graphene/Co oxide nanostructure is most probable than graphene/Co nanostructure.

### 3.3 Optical properties

The amount of light beam absorption by the sample depends on the energy of the incident photon, the type of material and the nature of its crystal structure. The absorption spectrum for pure solutions of graphene (a), cobalt (b) and the prepared nanocomposite (c) is illustrated in Figure 5 in the range of 180 – 900 nm. The pure solutions of graphene and cobalt were separately prepared by laser ablation technique under applying 80 mJ energy for graphene sample and 100 mJ energy for cobalt sample synthesis. As shown in Figure 5(a) and (b), the absorption peaks can be observed at 270 nm and 266 nm for graphene and cobalt samples, respectively. As can be seen, the absorption intensity for graphene sample is higher than that of cobalt. This could be due to the fact that the binding energy of cobalt particles is stronger than graphene. It is also shown in the graphene sample, the absorption intensity is lower than Gr/Co nanocomposite, and

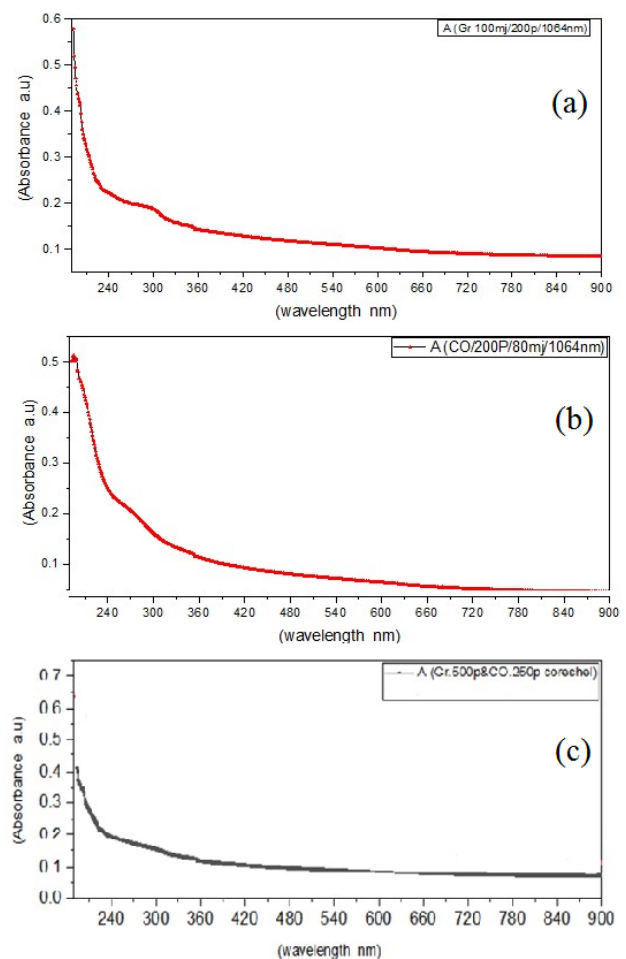


Figure 5. Absorption spectra for (a) graphene, (b) cobalt and (c) Gr/Co nanocomposite.



in the cobalt nanoparticles, the absorption intensity is higher than Gr/Co nanocomposite. This is due to the superposition between graphene and cobalt, this nanocomposite process leads to different absorption, as shown in Figure 5(c).

#### 4. Conclusion

Laser ablation method has been used to prepare Gr/Co nanocomposite. The synthesized sample has been analyzed by XRD, UV-Vis, SEM, EDX methods. XRD analysis confirmed the formation of graphene and cobalt oxide. Graphene nanosheets morphology and Co or Co Oxide nanoparticles were clearly seen in FESEM images. The average grain size of nanoparticles was in the range of 25 nm. All results demonstrated the successful synthesis of graphene/cobalt oxide nanocomposite.

The research on novel applications of Gr/Co nanocomposite provides immense value to society. Their potential in biomedicine, electronics, energy, and environmental science is highly promising, offering advancements in healthcare, electronics, energy efficiency, and pollution control. However, further research is needed to better understand the long-term effects and potential risks associated with the use of Gr/Co nanocomposite. Additionally, the scalability and cost-effectiveness of mass production methods should be considered to ensure their widespread implementation. Exploring the challenges and opportunities in these areas will further enhance the understanding and application of Gr/Co nanocomposite, leading to more sustainable and impactful technological solutions for the betterment of society.

##### Ethical approval

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

##### Authors Contributions

All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

##### Availability of data and materials

Data presented in the manuscript are available via request.

##### Conflict of Interests

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

##### Open Access

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and

reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the OICCPress publisher. To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0>.

#### References

- [1] L. Liu, H. Zhang, X. Chen, L. Fang, Y. Bai, R. Liu, and Y. Wang. "Unique synthesis of sandwiched graphene@ $(\text{Li}_{0.893}\text{Fe}_{0.036})\text{Co}(\text{PO}_4)$  nanoparticles as high-performance cathode materials for lithium-ion batteries." *J. Mater. Chem. A*, **3**:12320–12327, 2015. DOI: <https://doi.org/10.1039/C5TA02058A>.
- [2] I. Robinson, M. Volk, L. D. Tung, G. Caruntu, N. Kay, T. Nicola, and N. T. K. Thanh. "Synthesis of Co nanoparticles by pulsed laser irradiation of cobalt carbonyl in organic solution." *Journal of Physical Chemistry C*, **113**:9497–9501, 2009. DOI: <https://doi.org/10.1021/jp9014564>.
- [3] X. L. Dong, C. J. Choi, and B. K. Kim. "Chemical synthesis of Co nanoparticles by chemical vapor condensation." *Scripta Materialia*, **47**:857–861, 2002. DOI: [https://doi.org/10.1016/S1359-6462\(02\)00304-4](https://doi.org/10.1016/S1359-6462(02)00304-4).
- [4] W. Wu, J. Zhang, P. Cao, J. Dong, and H. Ding. "Synthesis of Sm–Co nanoparticles by sol–gel method." *Modern Physics Letters B*, **32**:1840069, 2018. DOI: <https://doi.org/10.1142/S0217984918400699>.
- [5] A. T. Raji and E. B. Lombardi. "Stability, magnetic and electronic properties of cobalt–vacancy defect pairs in graphene: A first-principles study." *Physica B*, **464**:28–37, 2015. DOI: <https://doi.org/10.1016/j.physb.2015.02.017>.
- [6] B. Li, D. Xu, J. Zhao, and H. Zeng. "First principles study of electronic and magnetic properties of Co-doped armchair graphene nanoribbons." *J. Nanomater.*, **2015**:538180, 2015. DOI: <https://doi.org/10.1155/2015/538180>.
- [7] F. Donati, Q. Dubout, G. Autes, F. Patthey, F. Calleja, P. Gambardella, O. V. Yazyev, and H. Brune. "Magnetic moment and anisotropy of individual Co atoms on graphene." *Phys. Rev. Lett.*, **111**:236801, 2013. DOI: <https://doi.org/10.1103/PhysRevLett.111.236801>.

- [8] H. Vita, S. Bottcher, P. Leicht, K. Horn, A. B. Shick, and F. Maca. “Electronic structure and magnetic properties of cobalt intercalated in graphene on Ir(111).”. *Phys. Rev. B*, **90**:165432, 2014. DOI: <https://doi.org/10.1103/PhysRevB.90.165432>.
- [9] R. Decker, J. Brede, N. Atodiresei, V. Caciuc, S. Blugel, and R. Wiesendanger. “Atomic-scale magnetism of cobalt-intercalated graphene.”. *Phys. Rev. B*, **87**:041403(R), 2013. DOI: <https://doi.org/10.1103/PhysRevB.87.041403>.
- [10] D. K. Kim and J. Dobson. “Nanomedicine for targeted drug delivery.”. *J. Mater. Chem.*, **19**:6294, 2009. DOI: <https://doi.org/10.1039/B902711B>.
- [11] H. Ragelle, F. Danhier, V. Préat, R. Langer, and D. G. Anderson. “Nanoparticle-based drug delivery systems: A commercial and regulatory outlook as the field matures.”. *Expert Opin Drug Deliv.*, **14**:851–864, 2017. DOI: <https://doi.org/10.1080/17425247.2016.1244187>.
- [12] B. Tale, K. R. Nemade, and P. V. Tekade. “Graphene based nano-composites for efficient energy conversion and storage in Solar cells and Supercapacitors: A review.”. *Polymer-Plastics Technology and Materials*, **60**:784–797, 2021. DOI: <https://doi.org/10.1080/25740881.2020.1851378>.
- [13] R. Paul. “Prospects of carbon nanomaterials for energy storage and conversion.”. *Carbon Based Nanomaterials for Advanced Thermal and Electrochemical Energy Storage and Conversion.*, :423–430, 2019. DOI: <https://doi.org/10.1016/B978-0-12-814083-3.00018-4>.
- [14] G. A. V. Magalhães-Ghiotto, A. M. de Oliveira, J. P. S. Natal, R. Bergamasco, and R. G. Gomes. “Green nanoparticles in water treatment: A review of research trends, applications, environmental aspects and large-scale production.”. *Environmental Nanotechnology, Monitoring & Management journal*, **16**:100526, 2021. DOI: <https://doi.org/10.1016/j.enmm.2021.100526>.
- [15] L. Handoyo, D. Pramudita, D. Mangindaan, and A. Indarto. “Application of nanoparticles in environmental cleanup: Production, potential risks and solutions.”. *Emerging Eco-friendly Green Technologies for Wastewater Treatment*, :45–76, 2020. DOI: <https://doi.org/10.1007/978-981-15-1390-9-3>.
- [16] W. C. Oh, F. J. Zhang, and M. L. Chen. “Characterization and photodegradation characteristics of organic dye for Pt–titania combined multi-walled carbon nanotube composite catalysts.”. *J Ind Eng Chem.*, **16**:321, 2010. DOI: <https://doi.org/10.1016/j.jiec.2010.01.032>.