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Effect of solvents on optical band gap of silicon-doped graphene oxide

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Keywords: silicon-doped graphene oxide, modified Hummer’s method, tauc plot, optical band gap

Abstract

The objective of this study was to determine the influence on the optical band gap when the same amount of silicon-doped graphene oxide was dissolved in three different solvents namely, distilled water, benzene, and dichloroethane. Ultraviolet-visible spectroscopy was used to analyse the optical properties of the solutions. Among all these solutions distilled water containing silicon-doped graphene oxide has the smallest optical band gap of 2.9 eV and is considered a semiconductor. Other solutions are not considered as semiconductors as they have optical band gaps greater than 4 eV. It was observed that there is an increase in the value of optical band gap of distilled water, benzene, and dichloroethane solutions indicating a rise in the insulating behaviour. In this experiment, graphene oxide was synthesised from graphite powder by modified Hummer’s method and was then doped with silicon. Synthesis and doping of graphene oxide were confirmed by various characterization techniques. Fourier transmission infrared spectroscopy was used for identification of surface functional groups. X-ray diffraction was carried out to confirm the formation of crystalline graphene oxide and silicon doped graphene oxide. In x-ray diffraction pattern, shifting of intensity peak from a 2θ value of 26.5° to 10° confirmed the synthesis of graphene oxide and various intensity peaks at different values of 2θ confirmed doping of graphene oxide with silicon. Scanning electron microscopy images indicated that graphene oxide sheets were decorated with spherical silicon nanoparticles. Energy dispersive x-ray spectroscopy showed that silicon doped graphene oxide powder contained 63.36% carbon, 34.05% oxygen, and 2.6% silicon.

1. Introduction

The properties of graphene have been a mystery for scientists since 2010 when Andre Geim and Konstantin Novoseloz were jointly awarded the Nobel Prize for their groundbreaking experiments on two-dimensional material graphene in the University of Manchester. Graphene is a 2D planar carbon nanostructure comprising of a one-atom thick, densely packed network of sp²-hybridized carbon atoms arranged in a hexagonal pattern with the edges of nanoparticles containing functional exogenous oxygen bearing groups such as hydroxyl, carbonyl, carboxylic, and epoxy group, which make the atomic layer hydrophilic and expand the interlayer distance [1–5].

Graphene exhibits marvellous properties. A single layer of graphene has intrinsic mobility of $2 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [6], Young’s modulus of 1.0 TPa [7], and thermal conductivity in the range of $(4.84 \pm 0.44) \times 10^2$ to $(5.36 \pm 0.48) \times 10^3 \text{ Wm}^{-1}\text{K}^{-1}$ [8]. In addition, graphene quantum dots (GQDs) show unique spin, optical, electronic, and photoelectric properties. Current methods of synthesising graphene quantum dots involve top-down and bottom-up approaches, both of which are demanding in terms of time, materials, and energy. By using top-down method, which is more advantageous, GQDs are obtained by cutting or fragmenting a single layer of graphene into particles with radii smaller than 20 nm [9–13]. GQDs thus synthesised, have higher stability, show luminescence on excitation, and edge effects [14]. Chemically modified
Graphene is used for making new materials [15–18]. Graphene oxide (GO), an oxidized derivative of graphene, has been explored in many fields, due to its hydrophilic nature and colloidal stability in aqueous environments.

The aim of this research was to synthesise oxidized derivative of graphene by improved Hummers’ method [19] in which phosphoric acid ($\text{H}_3\text{PO}_4$) was used instead of sodium nitrate ($\text{NaNO}_3$). The use of $\text{H}_3\text{PO}_4$ in this modified Hummer’s method provided a greater amount of hydrophilic oxidized graphene material than Hummer’s method. The effect of solvents on the optical band gap [20, 21] of silicon-doped graphene oxide (GO-Si) was studied, when same amount of GO-Si is dissolved in equal quantity of three different solvents; these solutions can be used as conductive materials in different kind of electric cells and batteries.

2. Materials and methods

2.1. Materials
The chemicals which were used without further purification consisted of fine powder of graphite with particle size 60 mesh, silicon powder with particle size 200 mesh from Loba Chemie, Potassium permanganate, Sulphuric acid (98%), Phosphoric acid (85%), Hydrogen peroxide (30%), Benzene, 1,2 Dichloroethane, and N, N Dimethylformamide from Scharlau.

2.2. Synthesis of graphene oxide
GO was synthesised by using modified Hummer’s method. 54 ml sulphuric acid ($\text{H}_2\text{SO}_4$) in (9:1) ratio was mixed with 6 ml of phosphoric acid. 2 g of graphite powder was added to the solvent under constant stirring. After 5 min 12 g of potassium permanganate was gradually added at a rate of 1 g/5 min. Solution was kept for constant stirring for 1 day at room temperature $\sim$20 °C until its colour turned from dark green to brown (scheme 1). After the stirring was stopped, 15 ml of hydrogen peroxide was added drop-wise. The addition of hydrogen peroxide initiated an exothermal process and changed the colour of the solution from brown to yellow (scheme 1). The solution was allowed to cool at room temperature before adding distilled water; it was then centrifuged at 4500 rpm for 30 min. It was washed with distilled water several times to remove excess of acids and then dried in oven at 80 °C for 8 h.

2.3. Preparation of silicon-doped graphene oxide
4% GO-Si was prepared by adding 1.75 g GO powder into 50 ml N, N Dimethylformamide and was sonicated at 60 °C for 30 min. Then 0.07 g silicon powder was added into the sonicated solution and the solution was stirred at 50 °C for two hours at 800 rpm after which 200 ml distilled water was added and the solution was centrifuged at 4500 rpm for 60 min. The settled down precipitate of GO-Si was washed several times with distilled water and dried in oven at 80 °C for 6 h.

2.4. Preparation of different solutions containing silicon-doped graphene oxide
1 mg of synthesized (GO-Si) was added in 5 ml of each solvent namely, distilled water, benzene, and dichloroethane and the obtained solutions were sonicated for 60 min.
3. Results and discussion

3.1. X-ray diffraction
X-ray diffraction (XRD) technique was used to study the structural properties of the pure, synthesised, and doped materials. Figure 1 illustrates the XRD pattern of pure graphite, GO, and GO-Si.

In the case of pure graphite, a narrow peak appears at a 2θ value of 26.5° which is corresponding to an interlayer spacing of 3.36 Å. A narrow peak of graphite indicates bulk crystalline size of graphite. GO peak in the XRD pattern appears at a 2θ of 10.6° corresponding to 8.32 Å interlayer distance which was resulted from intercalation of oxygen functional groups and water molecules into carbon layer structure. Shifting of the peak from 26.5° to 10.6° confirms the synthesis of GO. Unlike the graphite peak, the GO peak is not narrow indicating that the size of GO crystals has reduced. Multiple peaks in the XRD of GO-Si confirm the doping of Si in GO. In the XRD pattern of GO-Si one intensive peak is recorded at a 2θ value of 10.6° for GO and intensive peaks are recorded at 28.485°, 47.352°, and 56.157° while small peaks are recorded at 19.336°, 42.308°, 69.144°, 76.392°, 88.043°, and 94.956° for silicon [22–24].

3.2. Fourier transform infrared spectroscopy
The Fourier transform infrared spectroscopy (FTIR) is used to identify the functional groups on the surface of pure graphite. Figure 2 demonstrates FTIR of pure graphite, synthesised GO and GO-Si.

FTIR of pure graphite appears as a straight line indicating that there is no bending and stretching of bonds in the graphite structure. FTIR of GO shows stretching at 3200–3700 cm\(^{-1}\) in the single bond stretch region, corresponding to the hydroxyl group (O–H) that is attached to pure graphite [25]. The stretching in the double bond region at 1670–1820 cm\(^{-1}\), corresponds the carboxyl group (C=O) [25] indicating conversion of graphite
into GO. In the fingerprint region skeletal vibrations stretching at 500–1400 cm$^{-1}$, correspond to O–C–O bonds. The FTIR of GO-Si exhibits stretching at 2200–2500 cm$^{-1}$ that corresponds to Si–H bond [26]. The stretching at 1670–1820 cm$^{-1}$ corresponds to C=O bond [25, 26] and the bending at 1380 cm$^{-1}$ corresponds to Si-C-Si bond [26] indicating attachment of Si to GO.

3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) is used to study surface morphology of GO-Si. Figure 3 presents typical SEM images of GO-Si.

Figure 3(a) reveals that GO-Si is an amorphous mixer of GO sheets with varying size and thicknesses. Figure 3(b) shows closed view of GO-Si. It is clear from figure 3(c) that single piece of GO sheet consists of many layers of two-dimensional GO. From figure 3(d) it is observed that spherical nanoparticles of Si are embedded into GO sheets.

3.4. Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDX) is used to confirm Si doping and its atomic percentage in GO-Si. Figure 4 presents EDX spectrum of GO-Si.

The spectrum clearly shows high percentages of carbon and oxygen atoms because GO is an oxidized derivative of graphene (2D planar carbon nanostructure). Presence of Si indicates doping of GO. Detailed information of element concentration, intensity, and weight is shown in the table 1. Figure 5 shows a pie chart of weight percentages of C, O, and Si.

3.5. Quantification of optical band gap

Ultra-violet visible (UV–vis) absorption spectroscopy was used to study the optical properties of the dissolved GO-Si in the three solvents. UV–vis absorption spectra of the dissolved GO-Si in distilled water, benzene, and dichloroethane is shown in figure 6.

UV–vis absorption spectrum of the benzene solvent containing GO-Si has a broad peak at 240 nm, that of the dichloroethane solvent containing GO-Si has a narrower peak than benzene solution and it appears at 212 nm, while that of the distilled water solvent containing GO-Si has a sharp peak at 208 nm.
Willardson and Beer relationship used for quantification of optical band gaps of the three different solutions containing the same quantity of GO-Si, from the UV–vis absorption spectra, is given below:

\[ \alpha(\nu) = A(\nu - \text{E}_g)^n \]

where \( \text{E}_g \) is the energy gap, \( h \) is Planck’s constant, \( \nu \) is the frequency of incident radiation, \( A \) is a constant related to the material, the value of the exponent \( n \) denotes the nature of the transition (\( n = 1/2 \) for direct transition and \( n = 2 \) for indirect transition), and \( \alpha \) is the absorption coefficient in \( \text{cm}^{-1} \). Absorption coefficients of all solutions are calculated in \( \text{cm}^{-1} \) by using the formula: \( 2.303 \times (\text{absorption/ thickness}) \).

To find out the value of the optical band gap for semiconductor nanostructures [27, 28], thin films [29], liquids [30], and suspensions of nanoparticle [31, 32], Tauc plot is tremendously used. In the present study, Tauc plot using origin pro8 was used to find out the value of the optical band gap of solutions containing GO-Si. Tauc plot is deduced in figure 7, and linear parts of the curves are extended to intersect with energy axis; the intersection points provide the respective values of \( \text{E}_g \).

A substantial variation is observed in the value of indirect optical band gap of GO-Si, indicated in table 2, when same amount was dissolved in the equal quantity of three different solvents including distilled water, benzene, and dichloroethane. Among all solutions used in the present study; dichloroethane solution showed...
highest value of the indirect optical band gap as compared with distilled water solution which was the lowest while for benzene solution was in between these two above mentioned solutions. Thus, the value of the optical band gap is ascending in the solutions of distilled water, benzene, and dichloroethane respectively. It is concluded that solvent profitably effects on the value of the optical band gap of GO-Si.

4. Conclusion

This study was conducted in order to compare the optical band gap of three different solutions containing synthesised GO-Si. The dichloroethane solution had the highest value of Eg which is responsible for the lower conductivity; electrical conductivity is inversely proportional to the band gap as electrons require more potential to jump from valance band to conduction band when the band gap is larger. The distilled water solution is

<table>
<thead>
<tr>
<th>Solution</th>
<th>Distilled water</th>
<th>Benzene</th>
<th>Dichloroethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical band gap (eV)</td>
<td>2.9</td>
<td>4.3</td>
<td>5.1</td>
</tr>
</tbody>
</table>
considered as a semiconductor whereas the benzene and dichloroethane solutions are not because Eg value is greater than 4 eV in these two cases.

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