IRAQI JOURNAL OF APPLIED PHYSICS
Vol. 22, No. 2, April-June 2026, pp. 191-195

Collaborative Effect of Si and N Co-Doping in Graphene Oxide for Superior Counter Electrode Performance in DSSC

Falah D. Sulaiman
Moaaed Motlak[*]

Department of Physics,
College of Science,
University of Anbar,
Ramadi, IRAQ
* Corresponding author email:
moaaed.motlak@uoanbar.edu.iq

The study presents a strong synthesis of Si and N co-doped graphene oxide (GO) by a simple and efficient approach. Comprehensive structural and chemical characterizations established the uniform incorporation of both dopants into the GO matrix. X-ray diffraction and Raman spectroscopy evidenced discrete peak displacements and a rise in defect density, which signify a rearranged microstructure and strengthened sp^2/sp^3 interactions. Core-level X-ray photoelectron spectroscopy further confirmed the presence of N–C and Si–O–C coordination, thereby validating the co-doping mechanism. When integrated as the counter electrode in dye-sensitized solar cells, the co-doped GO sheet demonstrated markedly improved electronic conductivity and catalytic activity relative to either pristine or singly doped counterparts. The resulting device reached a power conversion efficiency of 3.613%, which we attribute to accelerated charge transport and a higher density of catalytic sites. These results emphasize the promise of Si, N co-doped GO as a metal-free, economical electrode material in advanced photovoltaic applications.

Keyword: Impurity implantation; Electronic structure; Graphene; Photoelectric conversion
Received: 10 July 2025; Revised: 7 September 2025; Accepted: 14 September 2025

1. Introduction

Research on reasonable, earth-abundant materials for dye-sensitized solar cells (DSSCs) has increased due to the growing demand for sustainable energy technologies. The standard counter-electrode catalyst, platinum, has good electrocatalytic activity but is nevertheless expensive and environmentally unfeasible for widespread use [1,2]. In recent years, graphene oxide (GO) has attracted noteworthy attention because of its exceptional physicochemical characteristics, extremely large surface area, and abundant surface chemistry, making it a potential contender for energy storage and conversion applications [3–5]. However, pure GO's photovoltaic efficiency is hampered by its low conductivity and lack of active catalytic sites. In order to overcome these obstacles, heteroatom doping has become an effective method to modify the electronic structure, improve conductivity, and generate carbon-based compounds with active sites, enhancing their overall performance [6,7]. The incorporated approach was proposed to enhance charge carrier-harvesting efficiency, offering an extra efficient location site for the charge carrier transference [8]. In previous works, researchers found that incorporated metal in the GO structure significantly changes the electronic structures and optical properties. In this regard, some researchers utilized experimental investigations to show that the Si incorporation GO structure specifically adjusted conductivity is essential for GO systems. These materials display distinct, fascinating features, such as excellent stability and the potential to control these properties through structural and composition modification [9,10]. Nitrogen (N) doping has been widely explored among various heteroatoms because it can change graphene's electrical characteristics through electron donation and structural modification [11–15]. Conversely, silicon (Si) has distinct benefits, such as tunable chemical reactivity, compatibility with carbon lattices, and the potential to form stable Si–C, and Si–O–C bonds that can significantly influence material behavior [16,17]. The synergistic effect of simultaneous Si and N doping can improve charge transport characteristics and structural flaws and increase electrochemical activity, which is highly desirable for applications such as counter electrodes in dye-sensitized solar cells (DSSCs) [17,18].

This study reports the successful synthesis of Si and N co-doped GO via a facile doping process. Structural and morphological characterizations verify the effective incorporation of Si and N into the GO framework, forming new bonding configurations such as N–C and Si–O–C. Electrochemical impedance spectroscopy (EIS) and J–V characteristics of DSSCs demonstrate that Si,N co-doped GO exhibits superior electrical conductivity and electrocatalytic performance compared to pristine and single-doped GO counterparts. These findings highlight the potential of Si, N co-doped GO as a high-performance, metal-free counter electrode material for next-generation solar cells and other electrochemical devices.

2. Experimental Part

For the preparation of the electrode, all chemicals including silicon tetrachloride ($SiCl_4$), urea, graphite, and potassium permanganate ($KMnO_4$) were purchased from Sigma Aldrich. The synthesis process began by slowly dissolving 0.2 g of $SiCl_4$ in 20 mL of distilled water. The $SiCl_4$ used was of 99% purity, and the urea was of 99.5% purity. At the same time, 0.15 g of urea was separately dissolved in 20 mL of distilled water with continuous stirring for 20 minutes. These two solutions were then combined and stirred magnetically for one hour. $SiCl_4$ is extremely moisture-reactive; therefore, all manipulations were carried out in an inert dry environment with the aid of a fume hood, and glassware was pre-dried prior to use. Personal protective equipment, including goggles and gloves, were worn at all times. All reactions were carried out under standard laboratory conditions at approximately 25 °C and 40–50% relative humidity unless otherwise stated [19]. Graphene oxide (GO) was synthesized using a modified version of the Hummers' method. In the next step, 0.2 g of GO was dispersed in 100 mL of distilled water and subjected to ultra-sonication for 40 minutes. This GO dispersion was added to the previously prepared solution under continuous stirring. Before the hydrothermal treatment, 200 mL of hydrazine hydrate was added to the mixture. The solution was then transferred into a Teflon-lined autoclave and heated at 180 °C for 10 hours. After hydrothermal treatment, the resulting product was filtered, washed thoroughly, and dried overnight at 60 °C to obtain the final Si, N co-doped GO material.

The fabrication of dye-sensitized solar cells involved three main steps: preparation of the photoanode, fabrication of the counter electrode, and assembly of the cell with electrolyte. Fluorine-doped tin oxide (FTO) glass substrates (with a sheet resistance of 10 Ω/sq.) were used for the photoanode. Using the doctor-blade technique, a thin film of TiO_2 nanoparticles (Degussa P25) was coated onto the FTO glass. Each photoanode had an active area of 0.25 cm^2 and a film thickness of approximately 8–10 μm. The coated substrates were then annealed at 450 °C for 30 minutes to ensure proper adhesion and crystallinity. The TiO_2 films were subsequently immersed in a 0.3 mM N719 ruthenium dye (Solaronix) solution for 24 hours. After dye adsorption, the photoanodes were rinsed with ethanol and dried under a nitrogen stream. The synthesized Si, N co-doped GO material for the counter electrode was applied onto another piece of FTO glass using the same doctor-blade method. The coated film was then cleaned with ethanol and dried at 60 °C for 30 minutes. Finally, the counter electrode was aligned over the dye-sensitized TiO_2 photoanode, with a Surlyn gasket (60 μm thick, SX 1170-60, Solaronix) placed between them to prevent leakage. The electrolyte - comprising 0.5 M lithium iodide (LiI), 0.05 mM iodine (I_2), and 0.2 M tert-butylpyridine in acetonitrile - was injected into the assembled cell through pre-drilled holes in the counter electrode using a syringe. The injection holes were then sealed to complete the DSSC assembly.

3. Results and Discussion

In Fig. (1a), the XRD analysis shows substantial alterations to the graphene oxide (GO) structure following co-doping with Si and N. In the pristine GO sample, a prominent and sharp diffraction peak is seen at about $2\theta = 11°$, which aligns with the material's (001) plane. The diffraction pattern varies significantly when Si and N are doped. The (001) peak broadens and changes its angle to one higher, around $2\theta = 21°$. This change indicates that the gap between layers has reduced, likely due to the partial removal of oxygen-containing functional groups or a reorganization of the GO layers due to the doping procedure.

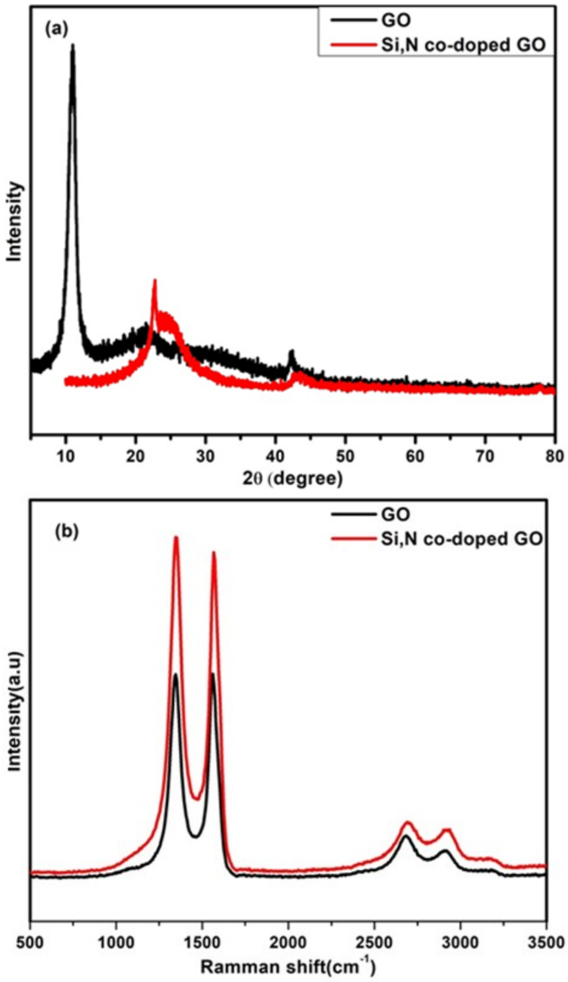


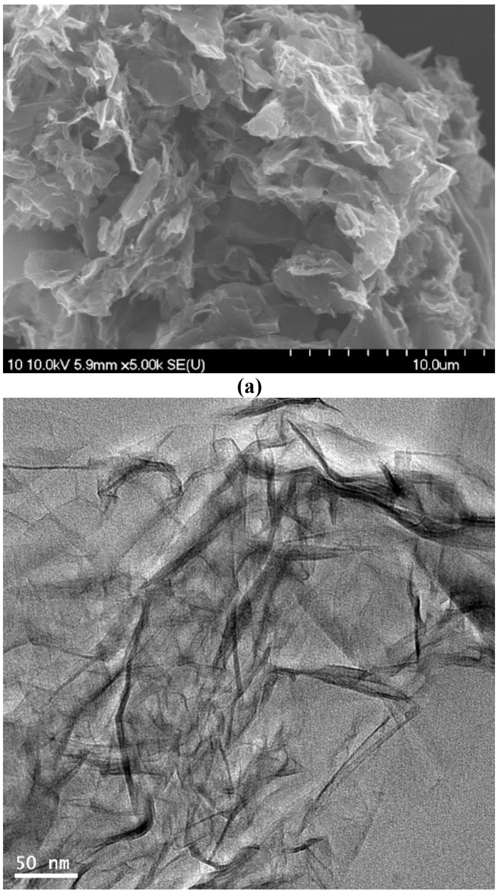
Fig. (1) (a) XRD patterns of GO and Si,N co-doped GO and (b) Raman spectra of GO and Si,N co-doped GO

XRD pattern of Si and N co-doped GO suggests (001) peak shifting towards higher 2θ value, signifying decrease in interlayer spacing. The peak broadening also suggests increased structural disorder. The decrease in d-spacing results from partial removal of oxygen-containing groups and introduction of Si and N atoms into the GO lattice, which reduce the interlayer distance but induce structural distortions. Additional structural changes may be indicated by large humps and small variations in the 20°-40° range, possibly arising from new bonding environments or interactions between the dopants and the GO matrix. Notably, no sharp peaks indicative of crystalline silicon or silicon dioxide are observed, implying that the dopants might be amorphous or well-dispersed within the GO framework. The combined effects of peak shifting, broadening, and background changes give solid proof that Si and N have successfully altered the structural arrangement of GO [20,21].

Raman spectra of the investigated samples (Fig. 1b) reveal prominent D and G bands positioned near 1350 eV and 1580 eV, respectively. The D band indicates structural imperfections and disruptions in the carbon lattice, while the G band arises from the vibrational modes of sp^2-hybridized carbon atoms within graphitic domains. In the case of the N,Si co-doped graphene oxide, the D-band intensity is greatly improved as contrasted with the undoped counterpart, suggesting a higher density of defects. This increase, reflected in the elevated I_D/I_G ratio, proves that doping with silicon and nitrogen was successful. Moreover, the spectral region between 2700 and 3100 eV shows broader and more intense features, corresponding to higher-order Raman modes, such as the 2D and D+G bands, which appear stronger and slightly shifted by dopant incorporation. These shifts suggest the formation of new chemical bonds, particularly Si–O–C and N–C linkages, which alter the bonding environment of carbon atoms. The results confirm that nitrogen and silicon have been successfully introduced into the GO framework.

The FE-SEM and TEM studies (Fig. 2) validate the synthesis of Si,N co-doped GO, which maintains its sheet-like shape while exhibiting enhanced wrinkling and localized structural disorder. These features are indicative of effective dopant incorporation. The results of the Raman and XRD analyses agree with the morphological characteristics. That provides evidence that the co-doping method affects the GO structure and texture significantly without compromising the integrity of the GO framework.

The XPS spectra in Fig. (3a) show clear signals for carbon (C 1s), nitrogen (N 1s), silicon (Si 2p), and oxygen (O 1s). The strong C 1s peak at around 285 eV indicates a high carbon content (87.05 at.%), where the carbon-based structure of GO is well-reflected. N 1s at approximately 400 eV (2.6 at.%) and Si 2p near 104 eV (0.81 at.%) indicate that both dopants were added to the substance. The O 1s peak at ~533 eV (9.53 at.%) corresponds to oxygen-containing groups, typical of GO, enhancing its chemical activity and hydrophilicity. In the high-resolution Si 2p spectrum (Fig. 3b), a broad peak at 104.08 eV suggests oxidized silicon species like Si–O–C or SiO_2, suggesting that the GO structure is silicon-bound chemically. The N 1s spectrum in Fig. (3c) displays a 399.86 eV peak attributed to nitrogen in graphitic or pyrrolic configurations (N–C bonding), confirming that the carbon lattice now contains nitrogen. The XPS spectra at high resolution indeed confirm the presence of Si–O–C and N–C bonds in co-doped GO, which are key to enhanced electrocatalytic activity. Pyridinic and graphitic nitrogen in N–C bonds improve charge conduction and offer more active sites, resulting in better reaction kinetics. Si–O–C bonds introduce structural faults, change the electronic surroundings of carbon atoms, and enhance hydrophilicity at the surface, ensuring better adsorption of the reactants.



(a)

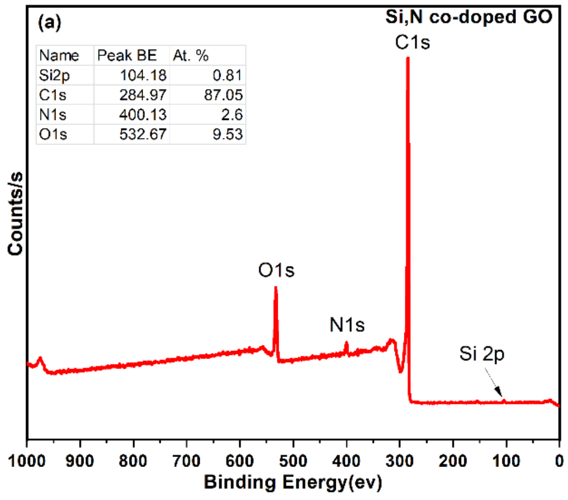
(b)

Fig. (2) (a) FE-SEM image and (b) TEM image of the prepared sample

The synergistic effect of these specific bonds increases active site density, enables electron transfer, and thus leads to the observed enhancement in electrocatalytic performance. This doping method improves electronic and catalytic characteristics and correlates with increased structural defects observed in Raman analysis. The separated O 1s exhibit five separated peaks in Fig. (3d), revealing the complex oxygen chemistry and in favor of Si–O–C bonds. The XPS data verify the successful co-doping of GO with silicon and nitrogen.

The photocurrent density–voltage (J–V) characteristics of dye-sensitized solar cells (DSSCs) employing different counter electrodes were evaluated under standard AM 1.5G simulated sunlight at an intensity of 100 mW/cm². The data presented in Fig. (4) reveals how the choice of counter electrode significantly influences device performance. The DSSC using a Si-doped GO-based counter electrode generated 0.635 V open-circuit voltage (V_{oc}) and 7.84 mA/cm² short-circuit current density (J_{sc}), 0.513 a fill factor (FF), and 2.558% a power conversion efficiency (η). These values reflect better performance than the cell with a pristine GO counter electrode. In contrast, the DSSC incorporating pure GO showed a slightly higher J_{sc} of 9.58 mA/cm² but exhibited a much lower FF of 0.42 and reduced V_{oc} of 0.431 V, leading to a much-reduced total efficiency of just 1.72%.

The best performance was observed for the DSSC with the Si, N co-doped GO counter electrode. This device revealed a J_{sc} of 10.34 mA/cm², a V_{oc} of 0.787 V, an FF of 0.444, and the highest efficiency of 3.613% among all samples. Although the Si,N co-doped GO counter electrode possesses the optimal PCE (3.613%), its FF (0.444) is less than that of the monolithic Si-doped GO (0.513). This loss in FF is attributable to enhanced structure disorder resulting from co-doping, as indicated by Raman examination. While such defects increase conductivity and electrocatalytic performance, they also create extra recombination channels, slightly degrading charge collection and increasing the internal resistance. Therefore, the increased PCE is due to the increased photocurrent, and the decreased FF is a product of the trade-off between electrocatalytic efficacy and charge transport efficiency. The increased performance is attributed to the synergistic effect of silicon and nitrogen doping, which enhances the material's electrical conductivity and electrocatalytic activity. In summary, DSSCs' photovoltaic performance is significantly enhanced when replacing conventional GO with Si,N co-doped GO as a counter electrode. With its ability to support higher current and voltage outputs, this co-doped material shows strong potential for use in high-efficiency, stable dye-sensitized solar cells.



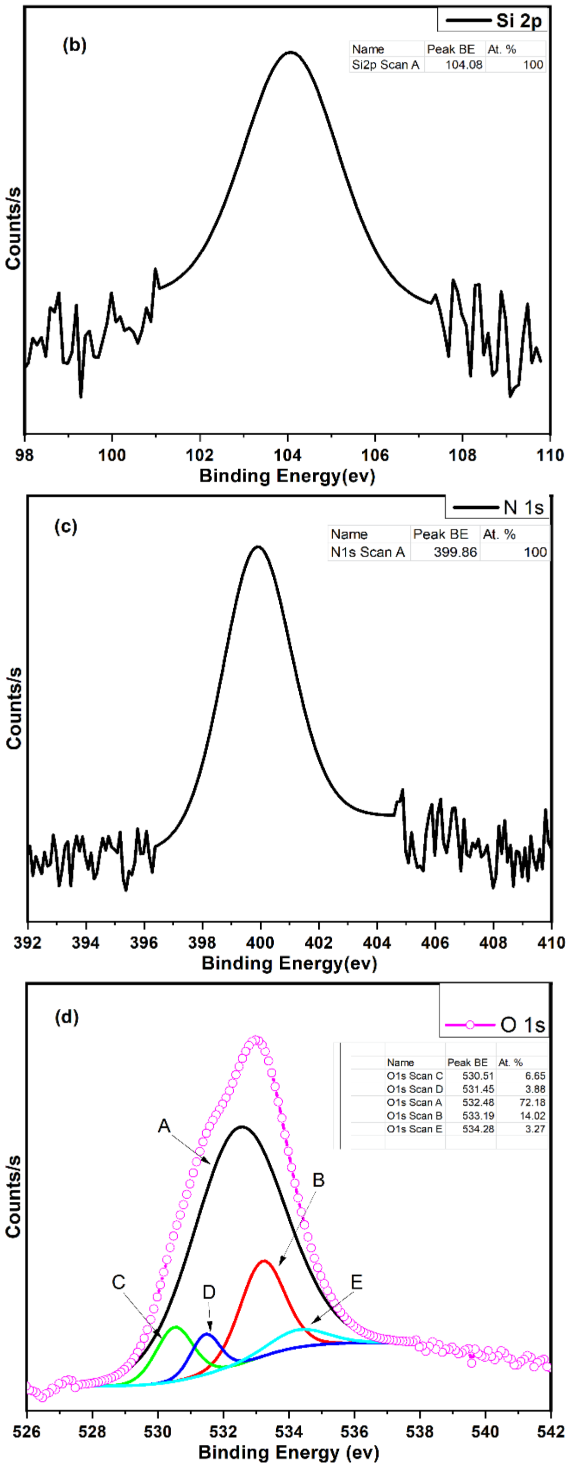


Fig. (3) (a) XPS survey spectrum of Si,N co-doped GO,(b) High-resolution Si 2p spectrum,(c) High-resolution N 1s spectrum, and Deconvoluted O 1s spectrum

4. Conclusion

This study proves that Si,N co-doping of graphene oxide dramatically improves its efficiency as a counter electrode in DSSCs. The co-doped GO had a 3.613% power conversion efficiency higher than other material testing. This increase is primarily due to enhanced charge transfer and higher active site density due to the synergistic effect of Si and N doping. These findings indicate the potential of Si,N co-doped GO as an efficient, metal-free alternative in high-performance energy conversion devices, particularly solar cells.

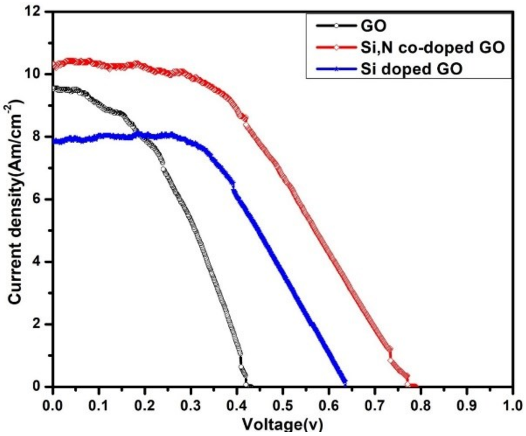


Fig. (4) J-V curves performance behavior of GO, Si-doped GO, and Si, N co-doped GO

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