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A Facile Green Synthesis of Polyethyleneimine-Functionalized Graphene Oxide Frameworks with Enhanced CO₂ Capture and Selectivity

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Abstract

The development of efficient and sustainable materials for carbon dioxide (CO₂) capture remains a critical challenge in mitigating greenhouse gas emissions. Amine-functionalized carbon materials have emerged as promising candidates due to their strong affinity for CO₂; however, their performance is governed by the complex interplay between amine accessibility, interfacial interactions, and structural properties. In this work, polyethyleneimine (PEI)-functionalized graphene oxide frameworks (GOFs) were synthesized via solvent-controlled and chemically modified strategies to systematically elucidate the role of synthesis pathways in determining CO₂ adsorption behavior. An aqueous-based synthesis provides a highly polar environment that promotes increased PEI loading and stabilizes an extended polymer conformation, resulting in enhanced dipole moments and greater exposure of accessible amine sites. As a result, the optimized material achieves a CO₂ uptake of 35 cc g⁻¹ with near-complete CO₂/N₂ selectivity (~100%) predicted by the IAST model, significantly outperforming pristine GO (5.8 cc g⁻¹). In contrast, ethanol-mediated synthesis, characterized by lower solvent polarity, induces a more compact PEI conformation with reduced dipole moment and limited amine accessibility, leading to decreased PEI incorporation and a lower CO₂ uptake of 22.5 cc g⁻¹. Alternatively, acyl chloride (–COCl) functionalization, followed by PEI grafting in dimethylformamide (DMF), facilitates the covalent anchoring of PEI chains. However, the partial depletion of oxygen-containing functional groups during the –COCl functionalization step limits PEI loading, resulting in a comparatively lower CO₂ uptake of 12.6 cc g⁻¹. Collectively, these results identify solvent-mediated interfacial interactions and

polymer conformational behavior as key determinants of developing PEI-functionalized graphene oxide frameworks with a high CO₂ capture performance.

Introduction

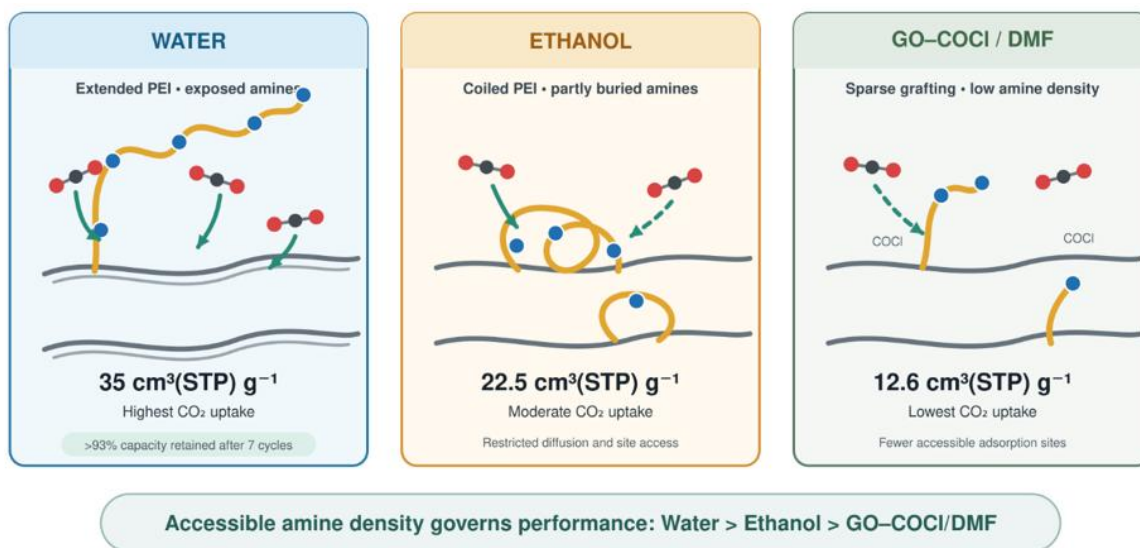
The continuous increase in anthropogenic carbon dioxide (CO₂) emissions arising from fossil fuel combustion and industrial activities represents one of the most pressing environmental challenges of the twenty-first century, contributing substantially to global warming and climate change.¹⁻³ Atmospheric CO₂ concentrations have increased markedly in recent decades, underscoring the urgent need for efficient, sustainable carbon capture technologies that mitigate greenhouse gas emissions while maintaining low energy consumption and operational stability.⁴⁻⁶ Among the available CO₂ mitigation strategies, solid adsorbent technologies have attracted considerable attention as promising alternatives to conventional solvent-based absorption systems because of their lower regeneration energy requirements, improved corrosion resistance, and superior long-term stability.⁷⁻¹⁰ Nevertheless, the efficiency of adsorption-based systems is strongly governed by the physicochemical characteristics of the adsorbent, including surface chemistry, pore structure, functional group accessibility, and gas selectivity.^{11, 12} Therefore, the rational development of adsorbent materials exhibiting high CO₂ affinity and excellent CO₂/N₂ selectivity remains a major objective in carbon capture research.

Carbon-based materials, particularly graphene oxide (GO), have emerged as attractive candidates for gas adsorption applications owing to their tunable surface chemistry, high chemical stability, and abundance of oxygen-containing functional groups, including hydroxyl, epoxy, carbonyl, and carboxyl moieties.¹³⁻¹⁶ These functional groups provide reactive sites for subsequent chemical modification and promote interactions with polar

gas molecules. However, pristine GO generally exhibits limited CO₂ adsorption capacity and weak selectivity toward CO₂ over N₂ because gas adsorption is predominantly governed by nonspecific physisorption interactions.^{17, 18} To address these limitations, GO has been functionalized with amine groups, ionic liquids, nitrogen-containing species, and metal–organic framework (MOF) hybrids to introduce stronger chemisorption sites, enhance CO₂/N₂ selectivity, and improve adsorption capacity through synergistic acid–base interactions and increased porosity.^{19–24} Among these modification strategies, polyethyleneimine (PEI) has been extensively investigated as an amine-rich polymer because of its high density of primary, secondary, and tertiary amine groups, which can reversibly interact with CO₂ through carbamate and bicarbonate formation mechanisms.^{25, 26} Previous studies have demonstrated that incorporation of PEI into porous supports can significantly enhance CO₂ adsorption capacity and selectivity under low-pressure and flue-gas conditions.^{27–31} However, excessive PEI loading may result in pore blockage, reduced surface area, and mass-transfer limitations, thereby adversely affecting adsorption kinetics and the accessibility of amine active sites.³² Consequently, optimizing the interfacial interactions between PEI and the supporting substrate is essential for maximizing adsorption performance. Recently, graphene oxide-based hybrid frameworks functionalized with amine-containing polymers have attracted increasing interest because the two-dimensional architecture of GO enables homogeneous distribution of amine functionalities while preserving accessible diffusion pathways for gas transport.³³ The adsorption performance of these hybrid materials depends not only on the quantity of incorporated amine groups but also on the nature of interfacial interactions, dispersion behavior, and structural organization within the framework.^{34, 35}

In the present study, polyethyleneimine-functionalized graphene oxide frameworks (PEI-GOFs) were synthesized using three different approaches, namely aqueous-assisted assembly (GOF (W)), ethanol-mediated synthesis (GOF (E)), and acyl chloride functionalization followed by PEI grafting in dimethylformamide (GOF (COCl)), to systematically investigate the influence of the synthesis route on CO₂ adsorption performance and CO₂/N₂ selectivity (**Scheme 1**). Comprehensive structural and surface characterization, including FTIR, XPS, XRD, BET, SEM, and TEM, was performed to elucidate relationships among interfacial interactions, chemical functionality, porosity, and adsorption behavior. To provide molecular-level insight into the experimentally observed solvent-dependent performance, density functional theory (DFT) calculations were further employed to examine the effect of the solvent environment on PEI conformation, dipole moment, and the accessibility of amine adsorption sites, while non-covalent interaction analysis was used to elucidate the intermolecular interactions governing GO–PEI assembly. The combined experimental and theoretical results demonstrate that the aqueous-assisted synthesis route promotes a more polar environment and stronger hydrogen bonding between GO and PEI, stabilizing an extended PEI configuration with more accessible amine groups, thereby enhancing CO₂ uptake and CO₂/N₂ selectivity. In contrast, ethanol-mediated synthesis reduces PEI incorporation due to its lower polarity and induces a more compact PEI conformation with a reduced dipole moment and limited amine accessibility, thereby decreasing CO₂ uptake. Although acyl chloride functionalization in DMF promotes covalent grafting, partial depletion of oxygen-containing functional groups during the functionalization experiment restricts PEI loading, resulting in inferior CO₂ adsorption performance. Overall, this study establishes solvent-mediated interfacial interactions as the

primary factor governing the adsorption properties of PEI-GOFs and demonstrates how integrating experimental characterization with DFT calculations provides a comprehensive understanding for the rational design of high-performance CO₂ capture materials.



Scheme 1: Schematic illustration of solvent-dependent PEI configuration and accessible amine sites governing CO₂ adsorption, with performance following the order Water > Ethanol > DMF.

Methodology

Synthesis of Polyethyleneimine-based GOF

Synthesis of Polyethyleneimine-functionalized Graphene Oxide Frameworks (GOFs) as presented in (Scheme 2).

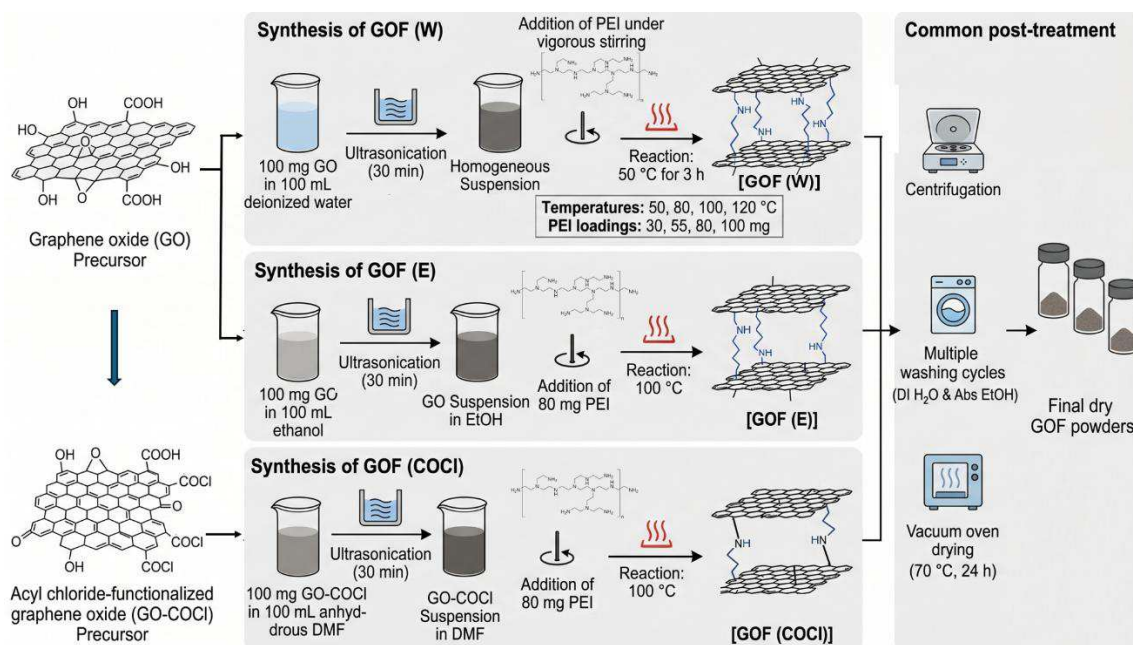
Synthesis of GOF (W); To prepare the aqueous-based graphene oxide framework (GOF-W), 100 mg of GO was dispersed in 100 mL of deionized water and exfoliated via ultrasonication for 30 min to ensure a homogeneous suspension. Subsequently, 30 mg of polyethylenimine (PEI) was introduced into the dispersion under vigorous stirring. The reaction mixture was maintained at 50 °C for 3 h. To investigate the influence of reaction parameters on the framework properties, the synthesis was repeated at varying

temperatures (50, 80, 100, and 120 °C) and PEI loadings (30, 55, 80, and 100 mg). The resulting samples were designated as W-x, where x represents the mass of PEI used (e.g., W-30, W-55, W-80, and W-100).

Synthesis of GOF (E); For the synthesis of GOF (E), the procedure described above was adapted by replacing the aqueous medium with 100 mL of ethanol. The reaction was conducted using 80 mg of PEI at a fixed temperature of 100°C.

Synthesis of GOF (COCl); GOF (COCl) was synthesized by utilizing acyl chloride-functionalized GO (GO-COCl) as the precursor. In this instance, 100 mg of GO-COCl was dispersed in 100 mL of anhydrous N,N-dimethylformamide (DMF). The functionalization was carried out with 80 mg of PEI at 100°C under an inert atmosphere.

Following the reaction, all modified GO products were recovered via centrifugation. The precipitates were subjected to multiple washing cycles with deionized water and absolute ethanol to remove unreacted PEI and residual solvents. Finally, the obtained powders were dried in a vacuum oven at 70°C for 12 h before further characterization and adsorption testing.



Scheme 2: Schematic illustration of the synthesis routes for PEI-GOFs composites prepared in water [GOF (W)], ethanol [GOF (E)], and DMF using acyl chloride-functionalized GO [GOF (COCl)], followed by common post-treatment procedures.

Results and Discussion

Structural Characterization

FTIR and ¹³C NMR

The structure of the synthesized composite and the interaction between GO and PEI under different synthesis conditions were first characterized by Fourier Transform Infrared (FTIR) spectroscopy.

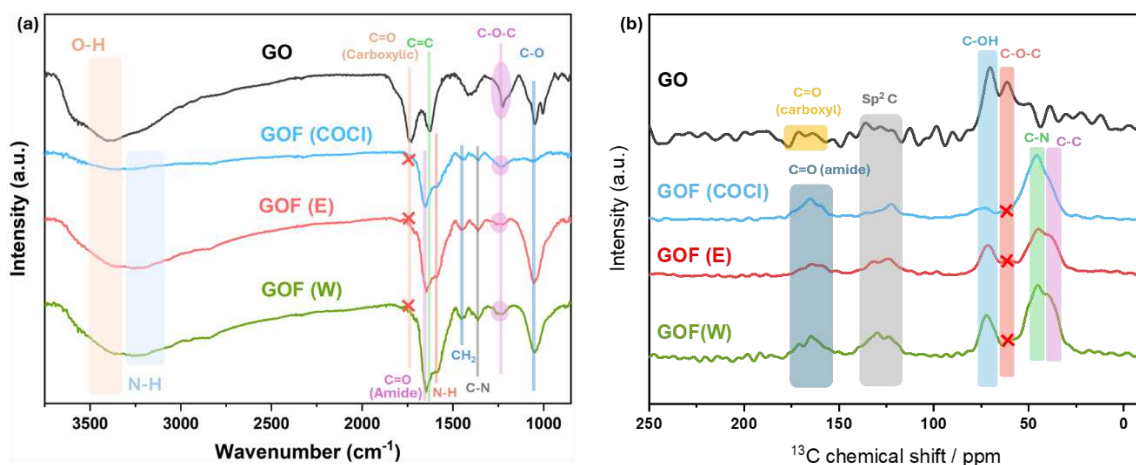


Figure 1: (a) FTIR spectra and (b) XPS survey spectra of pristine GO and PEI-functionalized graphene oxide composites synthesized via different routes: GOF (W), GOF (E), and GOF (COCl).

As shown in **Figure 1a**, the FTIR spectrum of pristine GO exhibits characteristic absorption bands corresponding to its highly oxidized structure. The broad band observed around 3200-3500 cm⁻¹ is attributed to O-H stretching vibrations from hydroxyl groups and adsorbed water molecules. The prominent peak at ~1733 cm⁻¹ corresponds to C=O stretching of carboxylic acid groups, while the band near ~1620 cm⁻¹ is associated with C=C stretching from the unoxidized graphitic domains. Additional peaks in the range of 1000-1300 cm⁻¹ arise from C-O-C (epoxy) and C-O (alkoxy) functionalities.^{19, 36} These oxygen-containing groups provide active sites for chemical modification. Upon functionalization with PEI, notable spectral changes are observed in all GOF samples, indicating successful incorporation of nitrogen-containing species. In GOF (W), GOF (E), and GOF (COCl) the intensity of the carboxyl C=O peak (~1733 cm⁻¹) decreases significantly, suggesting the involvement of these groups in interactions with PEI. Concurrently, new absorption bands appear around ~1650 cm⁻¹ and ~1590 cm⁻¹, which are assigned to amide I (C=O stretching) and amide II (N-H bending) vibrations, respectively

(**Figure 1a**).^{37,38} The aberrance of bands in the region of $\sim 1350\text{--}1450\text{ cm}^{-1}$ further supports the presence of C–N stretching vibrations. In addition, the significant reduction in the epoxy C–O–C peak ($\sim 1228\text{ cm}^{-1}$) suggests that epoxy groups also contribute to the interaction with PEI.³⁷ These features indicate that PEI has been successfully attached to the GO surface. However, the nature and extent of interaction differ depending on the synthesis conditions. Interestingly, GOF (COCl) shows a significant reduction in the O–H band ($3500\text{--}3400\text{ cm}^{-1}$) and the C–O peak ($\sim 1100\text{ cm}^{-1}$).³⁹ This reduction can be attributed to the prolonged reaction time and elevated temperature ($80\text{ }^{\circ}\text{C}$) used for converting GO into its acyl chloride derivative (GO (COCl)), which may partially reduce GO and remove oxygen functionalities. As a result, fewer reactive sites are available for PEI attachment, leading to a lower degree of functionalization. **Figure 1b** presents the solid-state ^{13}C NMR spectra of pristine GO and the PEI-functionalized GO samples. Pristine GO exhibits characteristic resonances at $\sim 170\text{ ppm}$ (carboxyl C=O), $\sim 130\text{ ppm}$ (sp^2 -hybridized C), $\sim 70\text{ ppm}$ (C–OH), and $\sim 60\text{ ppm}$ (epoxy C–O–C), confirming the presence of abundant oxygen-containing functional groups.⁴⁰ Following PEI functionalization, the carboxyl signal at $\sim 170\text{ ppm}$ reduced markedly, while a new resonance appears at $\sim 165\text{ ppm}$, assigned to the amide carbonyl (C=O), indicating the formation of amide linkages between GO and PEI. In addition, new signals at $\sim 40\text{--}50\text{ ppm}$, corresponding to C–N and PEI methylene (C–C) carbons, further confirm the successful incorporation of PEI onto the GO surface. Consistent with the FTIR results, GOF (W) exhibits the most pronounced PEI-related signals, indicating the highest degree of functionalization, whereas GOF (COCl) shows relatively weaker amide and PEI methylene (C–C) carbons resonances, suggesting a lower grafting efficiency due to the partial loss of oxygen-containing functional groups

(significant reduction in the C–OH resonance at ~70 ppm is observed) during the acyl chloride preparation step.

XPS analysis further confirms the successful functionalization of GO. The survey spectrum of pristine GO (**Figure 2a**) displays only C1s and O1s peaks, consistent with its oxygen-rich composition.⁴⁵ After functionalization, all GOF samples exhibit an N1s peak at ~399–400 eV, confirming the incorporation of nitrogen from PEI.⁴⁶ As summarized in **Table S1**, the nitrogen content indicates that the degree of PEI functionalization is highest for the water-treated sample, followed by the ethanol- and acyl chloride-mediated samples. To further elucidate the chemical interactions between GO and PEI, high-resolution C1s, O1s, and N1s spectra were deconvoluted. The deconvoluted C1s spectrum of pristine GO (**Figure 2b**) exhibits characteristic components of its highly oxidized structure, including a dominant peak at ~284.6 eV assigned to sp²-hybridized C–C/C=C bonds, together with peaks at ~286.9 eV (C–O–C/C–OH), ~287.9 eV (C=O), and ~288.9 eV (O–C=O), confirming the high abundance of epoxy, hydroxyl, carbonyl, and carboxyl groups.^{19, 47} The O1s spectrum (**Figure 2c**) further supports these assignments, showing contributions at ~531.0 eV (C=O), ~532.8 eV (C–O), and ~533.7 eV (O–C=O), confirming the presence of abundant oxygen functionalities that serve as reactive sites for subsequent modification.⁴⁸ Following conversion of GO to its acyl chloride derivative, GO(COCl), the intensity and area of the oxygen-containing carbon peaks, including C–O–C, C–OH, and C=O, decrease markedly (**Figure 2d**), indicating the consumption of oxygenated groups during chlorination. This reduction is attributed to the prolonged reaction time and elevated temperature (80 °C) used to prepare GO(COCl). The O1s spectrum (**Figure 2e**) also shows a pronounced decrease in the C–O and carbonyl oxygen components. In addition, two new

peaks at ~ 197.4 and ~ 200.0 eV, assigned to Cl $2p_{3/2}$ and Cl $2p_{1/2}$, respectively, confirm the formation of acyl chloride ($\text{O}=\text{C}-\text{Cl}$) groups.

Upon functionalization in aqueous and ethanol medium, the XPS spectra of GOF (W) and GOF (E) reveal significant chemical transformation, as evidenced in the C1s region (**Figure 2g, and Figure S1a**) by the emergence of a new component at ~ 285.8 eV corresponding to C-N bonding and a distinct peak at ~ 288.2 eV attributed to $\text{N}-\text{C}=\text{O}$,⁴⁹ confirming the formation of amide linkages between GO and PEI; concurrently, the relative intensity of oxygenated carbon peaks decreases, indicating their involvement in the interaction process.^{50, 51} The O1s spectrum of GOF (W) and GOF (E) (**Figure 2h, and Figure S1b**) further demonstrates the appearance of a new contribution at ~ 531.4 - 531.7 eV assigned to amide oxygen, alongside a reduction in C-O-related intensity and the presence of a higher binding energy component (~ 534.6 eV) associated with adsorbed water.^{49, 52} The N1s spectrum (**Figure 2i, and Figure S1c**) provides decisive evidence of PEI incorporation, showing three distinct nitrogen environments at ~ 399.1 eV ($-\text{NH}_2/\text{C}-\text{N}$), ~ 400.6 eV ($\text{N}-\text{C}=\text{O}$), and ~ 401.7 eV ($-\text{NH}_3^+$),^{50, 53} with the relatively high intensity of the protonated amine peak indicating that electrostatic attraction between positively charged PEI and negatively charged GO sheets plays a dominant role, contributing to the highest degree of functionalization observed in this system.

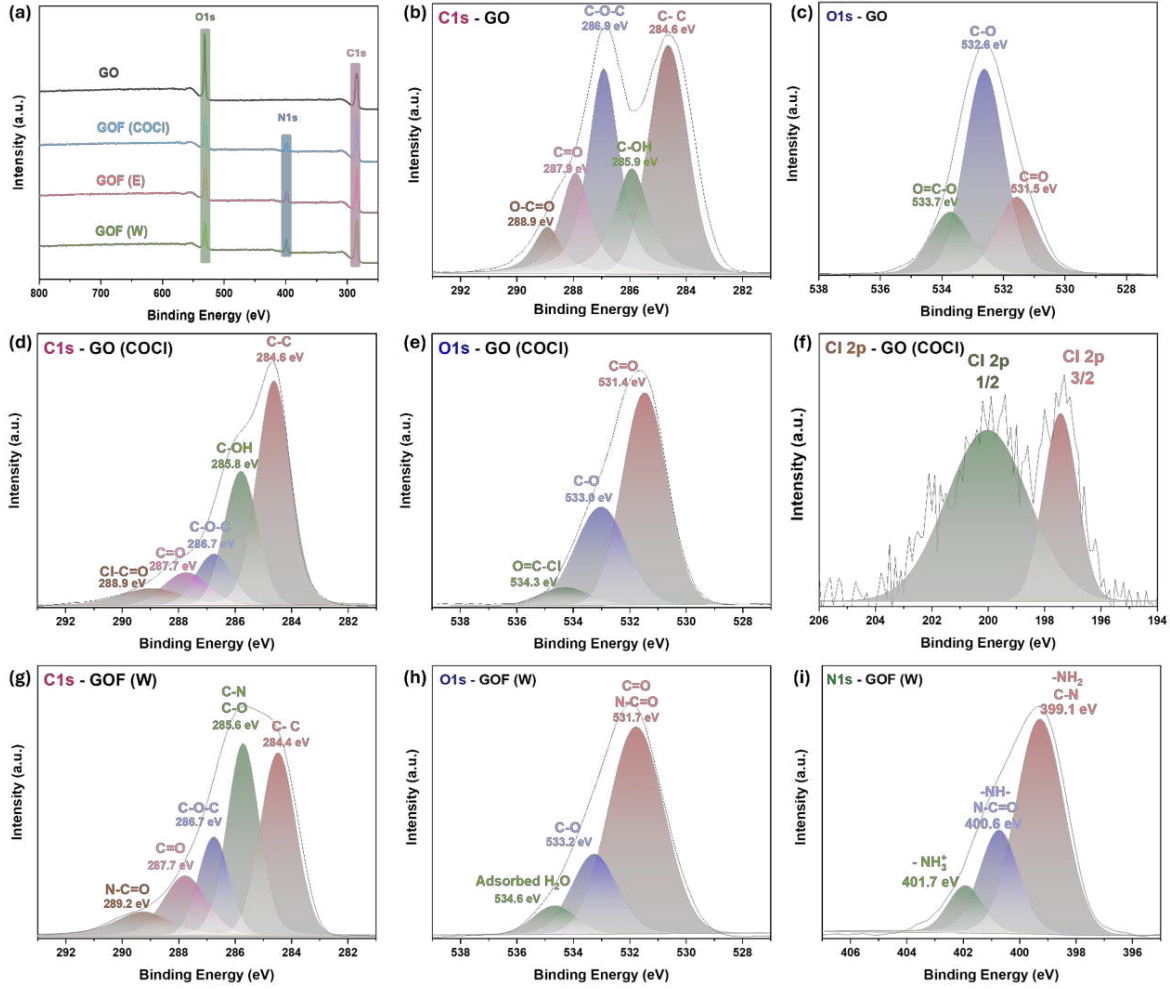


Figure 2: High-resolution XPS spectra of various samples: (a-b) C 1s and O 1s spectra of GO; (c-e) C 1s, O 1s, and N1s spectra of GOF (E); (f-h) C 1s, O 1s, and N1s spectra of GOF (W).

XRD Analysis

The structural evolution of graphene oxide (GO) and its functionalized derivatives was further analyzed using X-ray diffraction (XRD) and Raman spectroscopy, providing complementary insights into interlayer spacing, crystallinity, and defect density. The XRD pattern of pristine GO (**Figure 3**) exhibits a characteristic sharp diffraction peak at $2\theta \approx 11.5^\circ$, corresponding to the (001) plane, which reflects the expanded interlayer spacing resulting from the presence of abundant oxygen-containing functional groups and

intercalated water molecules. Following conversion to GO (COCl), a decrease in the intensity and slight broadening of the (001) peak are observed (**Figure 3b**), accompanied by the appearance of a broad peak around $2\theta \approx 24-26^\circ$ assigned to the (002) plane of graphitic carbon, indicating partial removal of oxygenated functional groups and structural modification during the acyl chloride formation process. This observation is consistent with FTIR, ^{13}C -NMR, and XPS results showing a reduction in O-H and C-O bands and suggests partial reduction of GO under prolonged reaction at elevated temperature. In the case of GOF (COCl), the XRD pattern becomes significantly broadened with reduced peak intensity, indicating increased structural disorder and disruption of the regular stacking of graphene layers (**Figure 3b**). In contrast, GOF (W) and GOF (E) exhibit a pronounced weakening of the (001) peak along with a shift toward lower diffraction angles (**Figure 3a**), appearing at approximately 9.7° and 10° , respectively, which indicates effective exfoliation and expansion of the interlayer spacing due to intercalation of PEI chains between GO sheets.³³ Notably, GOF (W) shows a more significant peak shift and intensity reduction compared to GOF (E), suggesting a higher degree of exfoliation and stronger interlayer interaction, which correlates well with XPS results indicating higher nitrogen content in the aqueous system. Raman spectroscopy further supports these structural modifications (**Figure S2**), where GO and modified materials display the characteristic D band ($\sim 1350\text{ cm}^{-1}$) associated with structural defects and disorder and the G band ($\sim 1580\text{ cm}^{-1}$) corresponding to the in-plane vibration of sp^2 carbon atoms, with a moderate $I_{\text{D}}/I_{\text{G}}$ ratio indicative of defects introduced during oxidation.

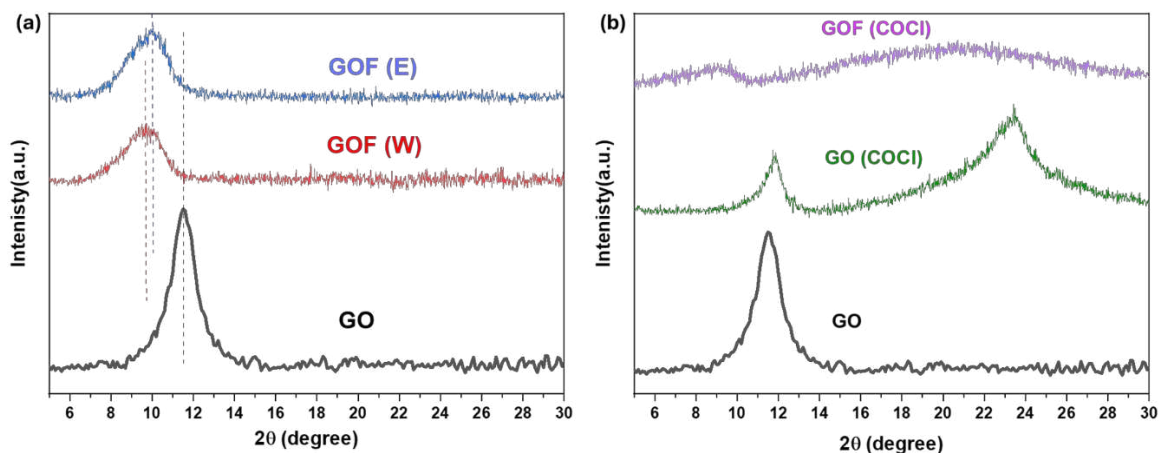


Figure 3: (a) XRD patterns of synthesized GOF (W) and GOF (E) compared to that of pristine GO. (b) XRD patterns of synthesized GO (COCl) and GOF (COCl) compared to that of pristine GO.

Surface Area and Porosity Analysis (BET/BJH)

The textural properties of graphene oxide (GO) and its functionalized derivatives were systematically analyzed using nitrogen adsorption–desorption isotherms (BET), surface area measurements, and pore size distribution profiles, as presented in **Figure 4** and summarized in **Table S2**, providing detailed insight into the structural modifications induced by polyethyleneimine (PEI). Pristine GO exhibits a typical Type IV adsorption isotherm with a pronounced H3 hysteresis loop (**Figure 4a**), characteristic of mesoporous materials with slit-shaped pores formed by the aggregation and stacking of GO sheets, which is consistent with the expanded interlayer spacing observed in XRD and the presence of abundant oxygen-containing functional groups confirmed by FTIR. The corresponding pore size distribution (**Figure 4a inset**) shows a broad mesoporous profile without a sharp peak, indicating heterogeneous pore structures arising from irregular stacking and structural defects. Upon functionalization with PEI, all modified samples (GOF (W), GOF (E), and GOF (COCl)) retain the general Type IV isotherm shape (**Figure 4b–d**) but exhibit

significantly reduced nitrogen uptake across the entire relative pressure range along with a less pronounced hysteresis loop, indicating a decrease in accessible porosity; this observation is quantitatively supported by the decrease in specific surface area reported in **Table S2**, confirming that PEI incorporation leads to substantial occupation and blockage of existing pores and surface sites. Among the functionalized samples, GOF (W) shows the most pronounced reduction in the surface area value in **Table S2**, indicating the highest degree of pore filling and surface coverage by PEI. In contrast, GOF (E) exhibits an increase in the surface area compared to that of GOF (W)(**Table S2**), indicating partial pore blocking and lower PEI loading. For GOF (COCl), the isotherm (**Figure 4d**) also shows reduced adsorption capacity, but the extent of reduction differs, as reflected in **Table S2**, due to the distinct functionalization pathway; the partial reduction of GO during acyl chloride formation decreases the number of oxygen-containing functional groups, leading to lower nitrogen incorporation compared to GOF (W), resulting in less uniform pore filling and reduced but differently distributed porosity.

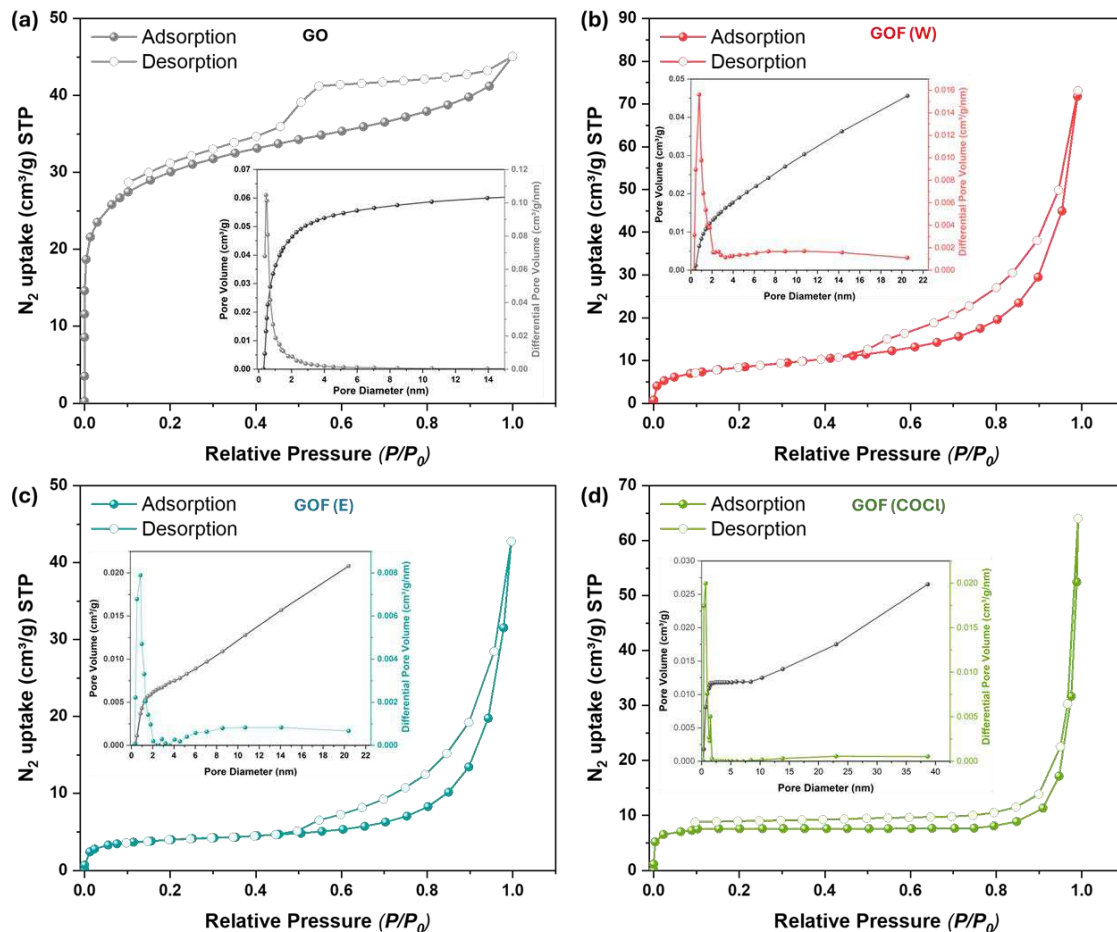


Figure 4: BET of synthesized (a) GO, (b) GOF (W), (c) GOF (E), and (d) GOF (COCl). (inset) pore size distribution of every material.

Morphological Characterization (TEM and SEM)

The morphological characteristics of graphene oxide (GO) and its functionalized derivatives were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in **Figure 5**, providing direct visual evidence of the structural changes induced by polyethyleneimine (PEI). The SEM image of pristine GO (**Figure 5a**) reveals a typical layered and wrinkled sheet-like morphology with significant agglomeration, which is attributed to strong van der Waals interactions between adjacent GO sheets. In contrast, GOF (W) (**Figure 5b**) exhibits a more fragmented and loosely

packed morphology with reduced stacking and increased structural disorder, suggesting effective exfoliation of GO sheets. Similarly, GOF (E) and GOF (COCl) (**Figure 5c and 5d**) shows a less compact structure compared to pristine GO but remains more aggregated than GOF (W), indicating a lower degree of exfoliation. The TEM images (**Figure 5e–h**) provide further insight into the nanoscale structure of these materials. Pristine GO (**Figure 5e**) displays thin, transparent, and relatively smooth sheets, confirming the formation of few-layer graphene oxide with a well-defined layered structure. In contrast, GOF (W) and GOF (E) (**Figure 5f and 5g**) shows more wrinkled, folded, and thicker sheet-like structures with reduced transparency, indicating the presence of PEI coating and strong interaction with GO sheets. This increased roughness and thickness further confirm successful functionalization and are consistent with FTIR and XPS results demonstrating the formation of amide bonds and high nitrogen content. For GOF (COCl) (**Figure 5h**), the TEM image shows partially wrinkled sheets with moderate aggregation and slightly increased thickness compared to pristine GO, suggesting a lower degree of PEI coverage compared to GOF (W) and GOF (E), which agrees with the relatively lower nitrogen content observed in XPS.

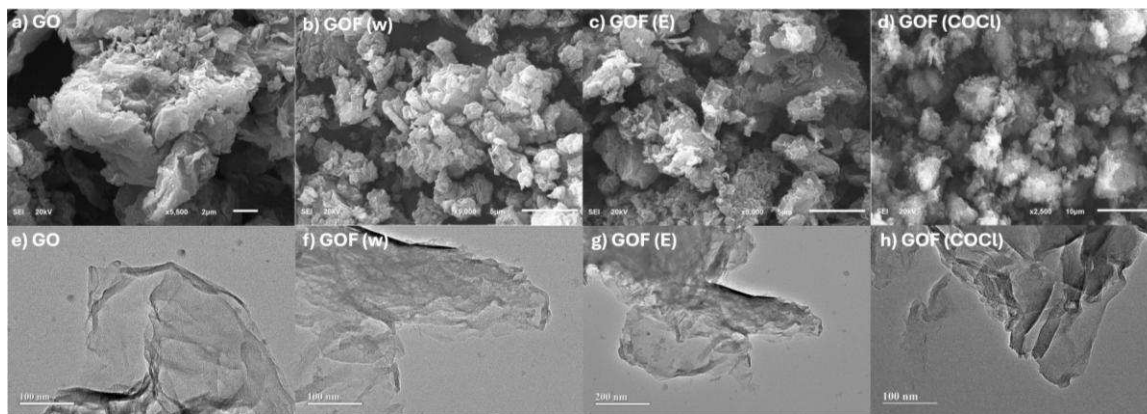


Figure 5: SEM images of GO (a), GOF (W) (b), GOF (E) (c), and GOF (COCl) (d). TEM images of GO (e), GOF (f) (e), GOF (E) (g), and GOF (COCl) (h).

Figure 6 presents the EDS spectra and elemental mapping of the PEI-functionalized GO samples prepared via different functionalization routes. The EDS spectra confirm the presence of carbon, oxygen, and nitrogen as the major elements, with the detected nitrogen verifying the successful incorporation of PEI onto the GO surface. The corresponding elemental maps show a homogeneous distribution of C, O, and N throughout the GO sheets, indicating uniform surface functionalization without noticeable PEI aggregation. Quantitative EDS analysis (**Table S3**) reveals that the nitrogen content decreases from 9.8 wt% to 7.3 wt% and then to 4.5 wt%. This trend suggests that the functionalization route significantly influences the PEI grafting efficiency, with the aqueous method achieving the highest nitrogen incorporation, followed by the ethanol- and acyl chloride-mediated methods. The lower nitrogen content observed for the acyl chloride-treated sample is consistent with the XPS results, indicating that the chlorination process reduces the number of oxygen-containing functional groups available for PEI attachment.

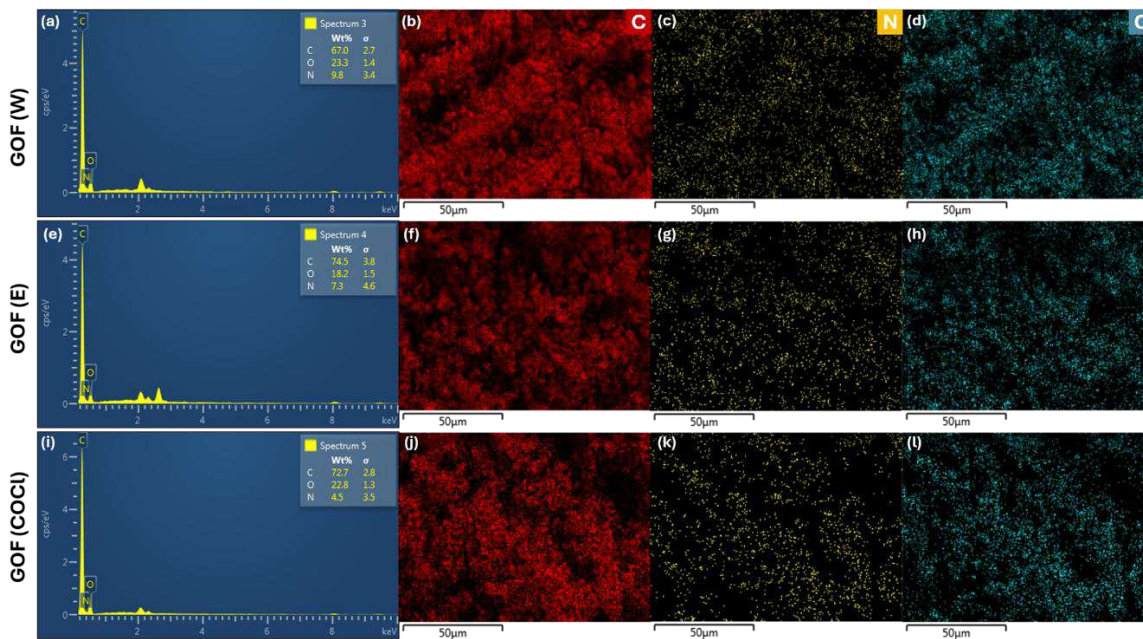


Figure 6. EDS spectra and elemental mapping of GOF (W) (a–d), GOF (E) (e–h), and GOF (COCl) (i–l). (a, e, i) EDS spectra; (b, f, j) carbon (C) mapping; (c, g, k) nitrogen (N) mapping; and (d, h, l) oxygen (O) mapping.

CO₂ Capture Performance and Selectivity

The CO₂ adsorption capacity, N₂ uptake behavior, and corresponding CO₂/N₂ selectivity of graphene oxide (GO) and its functionalized derivatives are shown in **Figures 6a–f, S4a–b, S5, and S6**. These data provide direct evidence of how structural, chemical, and textural modifications govern gas capture performance. Specifically, the optimization of synthesis parameters of GOF (W), highlights the critical roles of reaction temperature and polyethyleneimine (PEI) concentration (**Figure S4**). As shown in **Figure S4a**, increasing the synthesis temperature from 50 °C to 100 °C significantly enhanced CO₂ uptake from 7.3 to 23 cc g⁻¹. This improvement indicates that elevated temperatures promote stronger interfacial interactions between GO and PEI, thereby enhancing the dispersion and accessibility of amine functionalities. However, further increasing the temperature to 120 °C reduced the adsorption capacity to 13.5 cc g⁻¹. This decline may arise from partial thermal degradation or structural rearrangement of the oxygen-containing functional groups and PEI chains, which ultimately diminished the number of accessible adsorption sites. Similarly, PEI concentration strongly influenced adsorption performance (**Figure S4b**). The optimized W-80 sample (80 mg of PEI) achieved the highest CO₂ uptake of 35 cc g⁻¹. In contrast, lower PEI loadings of 30 and 55 mg (W-30 and W-55) may provide insufficient amine density, while an excessive concentration of 100 mg (W-100) may induced pore blockage and diffusion limitations. The superior performance of W-80 confirms that a balance between PEI incorporation and structural porosity is essential to maximize CO₂ capture efficiency. The pure-gas adsorption isotherms further emphasize

the impact of the synthesis pathway and interfacial chemistry on gas capture (**Figure 6a**). GOF (W) exhibited the highest CO₂ uptake (35 cc g⁻¹), followed by GOF (E) (22.5 cc g⁻¹), GOF (COCl) (12.6 cc g⁻¹), and pristine GO (5.8 cc g⁻¹). Notably, N₂ adsorption remained negligible for all PEI-functionalized samples. Direct comparison between GOF (W) and pristine GO (**Figure 6b**) clearly demonstrates that PEI functionalization transforms GO from a weak physisorbent into a highly selective chemisorbent. The pronounced increase in CO₂ uptake, combined with negligible N₂ co-adsorption, confirms that the introduced nitrogen-containing groups serve as highly selective sites that interact with acidic CO₂ molecules via reversible acid–base chemistry, while nonpolar N₂ molecules exhibit only weak, non-specific interactions with the surface.

To evaluate performance under mixed-gas conditions, Ideal Adsorbed Solution Theory (IAST) modeling was conducted (**Figures 6c-f**). For pristine GO (**Figure 6c**), an isotropic (intersection) point between the CO₂ and N₂ adsorption curves occurred at a gas fraction of approximately CO₂/N₂ = 0.3. This indicates that pristine GO cannot effectively discriminate between the two gases at low CO₂ concentrations, requiring significant CO₂ enrichment before selective adsorption becomes dominant, a direct consequence of non-specific physisorption and a lack of nitrogen functionalities. Conversely, GOF (W), GOF (E), and GOF (COCl) displayed no isotropic points across the investigated composition range (**Figures 6d-f**), maintaining consistently higher CO₂ uptakes even at ultra-low CO₂ fractions. This absence of an isotropic point underscores the intrinsically favorable CO₂ selectivity induced by PEI functionalization. Among the modified materials, GOF (W) demonstrated the highest CO₂ affinity and near-zero N₂ uptake across the entire composition range. The IAST selectivity results shown in **Figure S5** confirm the

outstanding separation performance of GOF (W). While pristine GO exhibited a low, nearly constant selectivity across the pressure range, GOF (W) displayed an exponential increase in CO₂/N₂ selectivity with pressure, approaching 3×10^6 near 1 bar. Furthermore, the inset in **Figure S5** highlights that GOF (W) maintains significantly higher selectivity than pristine GO even at low pressures, reinforcing that PEI functionalization fundamentally alters the thermodynamics of gas capture from weak physisorption to highly selective, efficiency-driven physisorption. **Figure S6** illustrates the cyclic CO₂ adsorption–desorption performance of the adsorbent over seven consecutive cycles. The CO₂ uptake decreases only slightly from approximately 35.2 to 32.8 cc g⁻¹, indicating excellent adsorption stability and minimal loss of capacity during repeated operation. Similarly, the regeneration efficiency remains high throughout the cycling test, decreasing marginally from about 100% in the first cycle to 94% after the seventh cycle. The small decline in adsorption capacity and regeneration efficiency may be attributed to the incomplete desorption of strongly adsorbed CO₂. Nevertheless, the adsorbent retains more than 93% of its initial CO₂ uptake after seven cycles, demonstrating good structural stability, efficient regeneration, and excellent reusability. These results highlight the potential of the functionalized GO adsorbent for repeated CO₂ capture with minimal performance degradation.

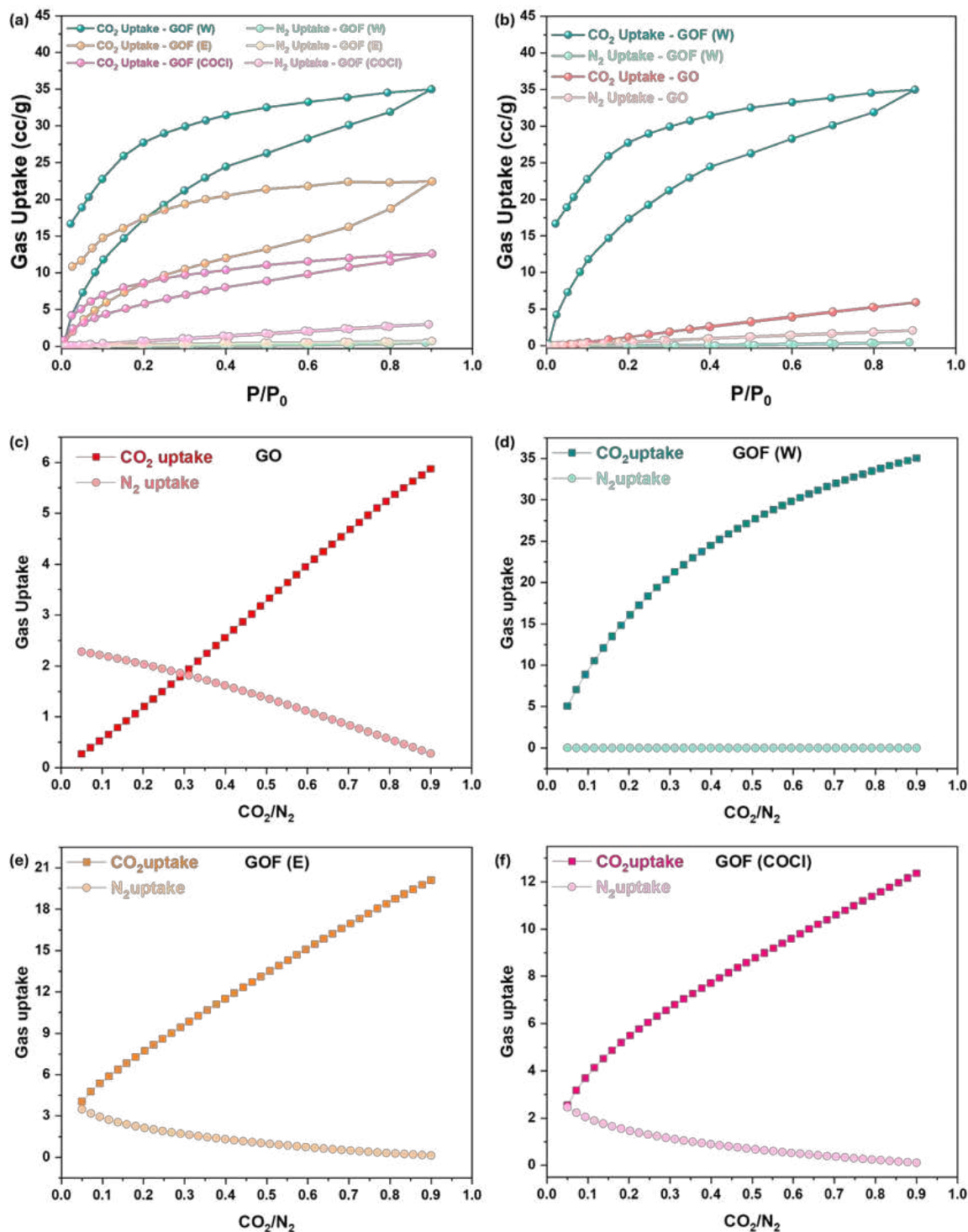


Figure 6: (a) Pure-gas adsorption isotherms of CO_2 and N_2 for GOF (W), GOF (E), and GOF (COCl). (b) Comparative adsorption isotherms of CO_2 and N_2 for pristine GO and GOF (W). (c-e) Ideal Adsorbed Solution Theory (IAST)-based mixed-gas adsorption profiles for GO, GOF (W), GOF (E), and GOF (COCl), respectively.

DFT

To investigate the structural effect observed experimentally during the synthesis of the GO/PEI composite, density functional theory (DFT) geometry optimizations were performed in the gas phase as well as implicitly within three distinct solvent environments of ethanol (EtOH), dimethylformamide (DMF), and aqueous water (H₂O). As illustrated in **Figure 7a**, the medium dielectric properties exert a profound influence on the conformation of the branched PEI chains tethered to the graphene oxide sheet. In the gas phase, the absence of solvent screening forces the highly polar amine branches to collapse down toward the hydrophobic GO basal plane to minimize surface energy. Conversely, as solvent polarity escalates, a stark structural "unfolding" or vertical extension is observed. Crucially, in the aqueous medium of H₂O the PEI branches stretch completely outward away from the GO support, maximizing the exposure of active primary (-NH₂) and secondary (-NH-) amine functional sites. This conformational shifting is further validated by the thermodynamic profiles and electronic trends summarized in **Figure 7b**. The relative stabilization energy (ΔE_{solv}), computed by subtracting the gas-phase energy from the respective solvated configurations, highlights a clear exothermic trend: Gas phase (0.0 eV, control) > EtOH (-1.282 eV) > DMF (-1.528 eV) > H₂O (-1.581 eV). The system achieves its global thermodynamic minimum in water, capturing an extra -1.581 eV ($\sim$ -36.5 kcal/mol), and 0.299 eV ($\sim$ 6.92 kcal/mol) of stabilization energy compared to the vacuum and EtOH configuration, respectively. This energy represents a synergistic mixture of electrostatic stabilization and structural strain relaxation as the polymer unravels. Accordingly, this structural expansion induces a pronounced change in the molecular dipole moment (inset, **Figure bc**). The dipole moment increased from 20.34 Debye in the

collapsed gas phase to a maximal 50.08 Debye in the water-optimized configuration. This large dipole moment arises directly from the spatial separation between the central framework and the extended polar amine end groups. In particular, when the GO/PEI composite is explementary synthesized in water and subsequently dried into a solid matrix, this highly extended, open architecture due to structural optimization. The combination of an open, sterically accessible morphology (high free volume) and strong localized electrostatic field explain the enhanced solid-state CO₂ capture capacity of the water-synthesized sample.

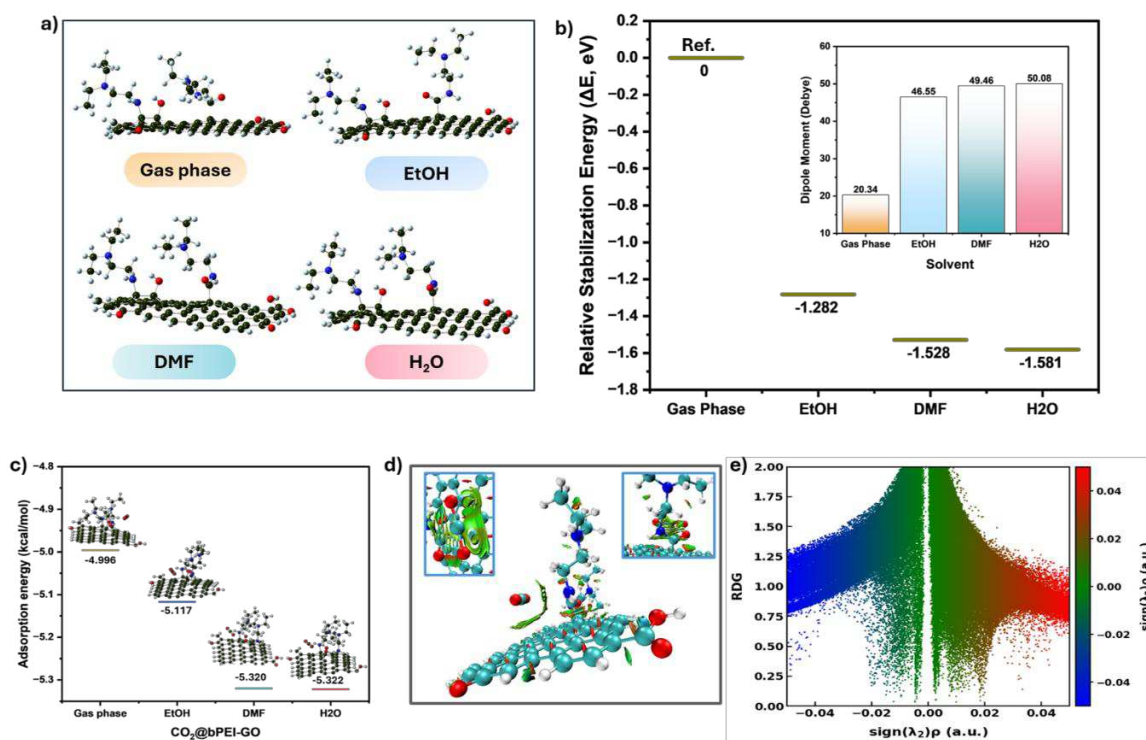


Figure 7. DFT optimization analysis of the GO/PEI composite. (a) Optimized structural configurations and (b) corresponding energy profiles and dipole moments (inset) highlighting the solvent-dependent conformation and electronic stabilization. (C) Calculated adsorption energies of CO₂ on the GO/PEI composite pre-optimized in different environments (Gas phase, EtOH, DMF, and H₂O). (d) Three-dimensional non-covalent interaction (NCI) isosurface analysis of the CO₂@ GO/PEI composite formed via the water-optimized structure. (e) Corresponding 2D scatter plot of the reduced density gradient (RDG), highlighting the nature of the weak intermolecular interactions stabilizing the captured CO₂ molecule.

To confirm the structural effect on gas capture efficiency, a single CO₂ molecule was introduced to the optimized configurations structures by each synthesis environment. As presented in **Figure 7c**, the calculated adsorption energies follow a distinctly favorable downward trend as a function of the preparation medium's polarity: Gas phase (-4.996 kcal/mol) > EtOH (-5.117 kcal/mol) > DMF (-5.320 kcal/mol) > H₂O (-5.322 kcal/mol). Although the GOF (COCl) system in DMF exhibits adsorption energy comparable to that of the water-based system, its CO₂ capture performance is inferior. This reduced performance is attributed to the partial reduction of graphene oxide during the acyl chloride functionalization process, which diminishes the density of oxygen-containing functional groups that serve as anchoring sites for PEI. Consequently, the GOF (COCl) system attains a lower PEI loading than the GOF (W) system, resulting in a decreased CO₂ adsorption capacity. In addition, to deeply understand the nature of the chemical forces trapping the CO₂ molecule within the optimized GO/PEI composite configuration (in H₂O), the non-covalent interactions (NCI) and reduced density gradient (RDG) analysis were performed (**Figures 7 d,e**). The 3D NCI isosurface surrounding the captured CO₂ molecule reveals a broad, green-colored disc of attractive van der Waals (vdW) interactions for the CO₂ molecule and the > NH group (next to > C=O in amid group at GO surface) of the bPEI amine chains, as well as GO network. The large green area confirms that the CO₂ molecule is well-stabilized via cooperative, multi-centered physisorption networks spanning unfolded polymer chains. Further, the 2D RDG scatter plot shown in **Figure 7c**, represents attractive interactions. The spike visible between -0.01 a.u. and -0.02 a.u. mainly corresponds precisely to the green vdW discs surrounding the CO₂ molecule, validating a tight, non-covalent trapping zone.

Inter-correlation of Structure and Performance

The CO₂ adsorption performance of the GOF–PEI composites is strongly dependent on the synthesis route because each solvent and functionalization strategy governs the dispersion of graphene oxide, the grafting mechanism of PEI, and ultimately the accessibility of amine adsorption sites (**Figure 8**). In the aqueous route (GOF(W)), the high polarity of water promotes excellent exfoliation and homogeneous dispersion of graphene oxide sheets. These maximize the probability of amidation during thermal treatment, resulting in the highest nitrogen incorporation and the greatest density of uniformly distributed primary and secondary amine groups. DFT calculations further reveal that PEI adopts a more extended conformation in water, producing the highest molecular dipole moment and exposing a larger fraction of amine functionalities toward the pore environment. Consequently, CO₂ molecules can readily diffuse through the expanded layered structure and react with accessible amines to form carbamate species, leading to the highest CO₂ uptake despite a reduction in BET surface area. Therefore, CO₂ adsorption in GOF(W) is controlled by amine accessibility rather than surface area, demonstrating that chemisorption dominates the adsorption process. In contrast, the ethanol-mediated synthesis (GOF(E)) produces a markedly different interfacial environment. The lower polarity of ethanol weakens GO dispersion, leading to less efficient grafting and a more compact polymer configuration on the graphene surface. DFT calculations indicate a lower dipole moment and less favorable PEI extension compared with GOF(W), suggesting that a significant fraction of amine groups remains buried within the polymer network rather than being exposed to incoming CO₂ molecules. As a result, the balance between gas

diffusion and active-site density shifts toward diffusion, producing only moderate CO₂ adsorption capacity.

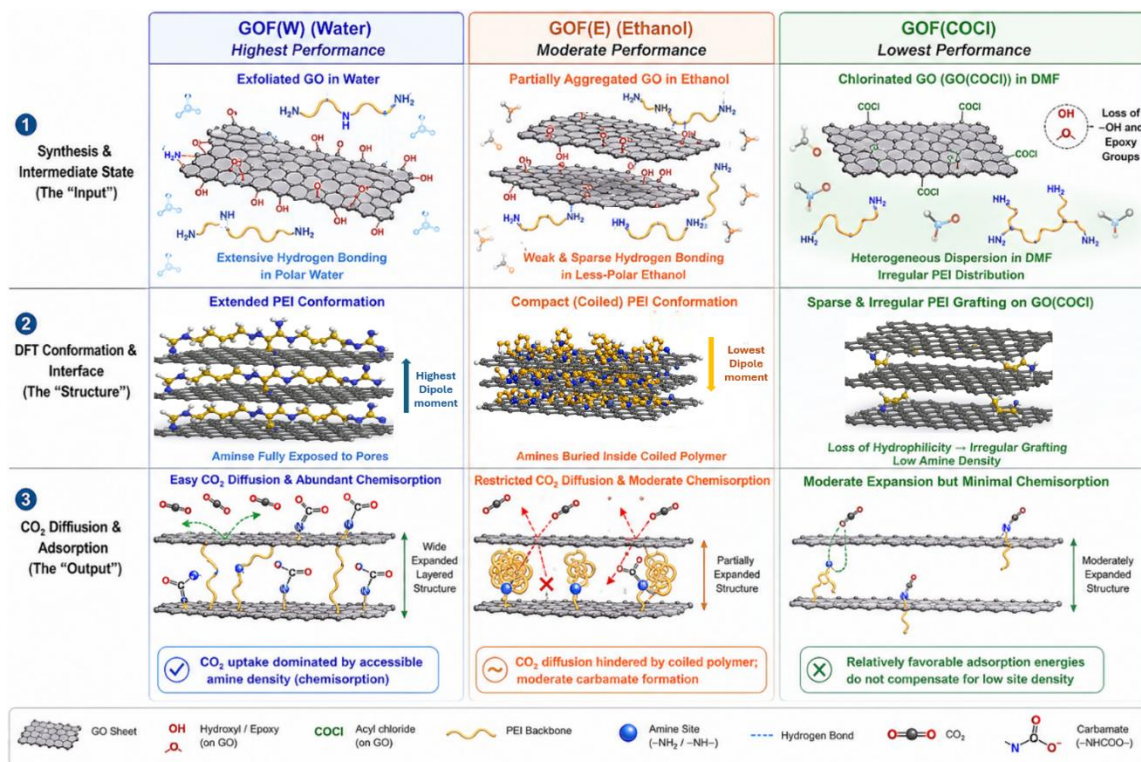


Figure 8. Proposed mechanism of synthesis-dependent CO₂ adsorption in GOF–PEI composites, showing that accessible amine density determines the adsorption performance, following the trend GOF(W) $\gg$ GOF(E) > GOF(COCl).

The GOF(COCl) composite follows an entirely different adsorption mechanism. Conversion of GO into GO(COCl) activates the surface for covalent amide formation with PEI; however, the chlorination process simultaneously consumes a large proportion of the hydroxyl, epoxy, and carboxyl groups that maintain GO hydrophilicity and strong interfacial interactions with PEI. The reduced surface polarity and poorer dispersion of GO(COCl) in DMF lead to heterogeneous PEI distribution and a lower overall nitrogen content. Consequently, fewer chemically accessible adsorption sites are available for carbamate formation, and the moderate interlayer expansion cannot compensate for the

reduced amine density. Although DFT calculations predict relatively favorable adsorption energies for individual CO₂ molecules, the overall adsorption capacity remains the lowest because CO₂ uptake is determined by the number of accessible adsorption sites rather than the binding strength of isolated sites. Overall, the results demonstrate that the synthesis route controls CO₂ capture through a hierarchy of structure–property relationships. Water produces optimal GO exfoliation, homogeneous PEI distribution, expanded interlayer spacing, and maximum exposure of reactive amine groups, resulting in the highest adsorption capacity. Ethanol provides intermediate performance due to reduced PEI accessibility despite relatively open diffusion pathways, whereas the acyl chloride route sacrifices accessible adsorption sites because excessive covalent immobilization and loss of oxygen functionalities hinder effective PEI utilization. Therefore, the observed adsorption trend, GOF(W) > GOF(E) > GOF(COCl), originates from the combined effects of GO dispersion, PEI conformation, interfacial bonding, and accessible amine density, confirming that the efficiency of CO₂ capture is governed primarily by the utilization efficiency of grafted amine groups rather than by PEI loading, surface area, or adsorption energy alone.

Conclusion

This study demonstrates that the CO₂-capture performance of polyethyleneimine-functionalized graphene oxide frameworks is governed primarily by the combined effects of PEI loading, amine accessibility, and interfacial organization. Among the investigated routes, aqueous assembly produced GOF(W) with the highest nitrogen incorporation, expanded interlayer structure, and most accessible amine-rich domains, resulting in the highest CO₂ uptake of 35 cm³(STP) g⁻¹ (1.56 mmol g⁻¹) and negligible N₂ adsorption.

Ethanol-mediated assembly yielded a more compact structure with lower PEI incorporation and an intermediate CO₂ capacity of 22.5 cm³(STP) g⁻¹. Although acyl-chloride functionalization enabled covalent PEI anchoring, the associated depletion of oxygenated groups, consumption and confinement of basic amines, and lower PEI loading limited the capacity of GOF(COCl) to 12.6 cm³(STP) g⁻¹. Experimental characterization and theoretical calculations collectively indicate that the performance hierarchy—GOF(W) > GOF(E) > GOF(COCl)—originates predominantly from differences in accessible amine density rather than intrinsic CO₂-binding strength. These findings establish solvent-regulated interfacial assembly as an effective strategy for balancing active-site density and molecular transport in selective, regenerable CO₂ adsorbents

Data availability

All data needed to evaluate the conclusions in the article and the Supplementary Information. Additional data available from the corresponding authors upon request.

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Competing interests

The authors declare no competing interests

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