



Influence of non-metal dopants (O, S, N) and dimension of carbon nano materials on the fluorescence and photocatalytic degradation of organic pollutants

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The usage of sanitizers and disinfectants results in the dumping of toxic organic residues in water. There is a global need for effective agents which can adsorb and degrade hazardous chemicals effectively and convert into much safer constituents. In this study, the influence of non-metal dopants (O, S, N) and dimensionality on the catalytic ability of carbon nanomaterials (CNs) such as 0-D (Nitrogen-doped Carbon quantum dots (N-CQDs) synthesized from the seed kernel of *Caesalpinia bonducella*) and 2-D (Graphene oxide (GO), Sulphur doped graphene oxide (S-GO), Nitrogen-doped graphene oxide (N-GO) synthesized from glucose) have been compared and correlated. The microstructure, surface morphology, elemental composition, fluorescence emission and catalytic ability of the 0-D and 2-D materials are determined and compared. The defect density and the sub defect band gap states influenced by different electronegative non-metal dopants and the dimensions are discussed. The Micro strain increases with increases in dimension. The percentage of Nitrogen as dopant in N-GO is relatively less compared with N-CQDs which led to less fluorescence intensity observed in N-GO. On comparison of the results, it is evident that greater electro negativity of the dopants and reduction in dimension will increase the photo catalytic activity. Also, in comparison with 2-D structures, the large surface area and greater quantum confinement of 0-D structure enhance the degradation of organic pollutants. This observation is well correlated with PL emission intensities of the compared CNs. The results provide a better correlation between dimensionality and functionality of CNs and their impact on catalytic (adsorption and photo) applications in experimentally possible ways.

Keywords: Adsorption, Catalyst, Chlorophenols, Organic dyes, Fluorescence, Graphene, Graphene oxide, Hydrothermal, Nitrogen doped Carbon quantum dots, Nitrogen doped graphene oxide, Sulphur doped graphene oxide

The emerging trend of nanotechnology is mainly focused on conservation of nature and natural resources. The luminescent and catalytic properties of the nanomaterials were widely used in the field of sensors, electrochemical and biomedical applications. Limited work has been carried out in the field of catalysis and biomedical application using nonmetal functionalized CBNs. The fluorescence emission property of the nanomaterials depends on the conjugated π -domains, surface defects, chemical state, quantum confinement effects and particle size. The fluorescent property of nanomaterial has been extensively used in bioimaging due to low toxicity, photo stability, and biocompatibility and fluorescence emission tunability.

Industrialization, urbanization and pandemic situation led to dumping of tremendous amounts of hazardous organic pollutants into water resources. The pharmaceutical compounds, disinfectants and textile dyes affect the odour, colour and pH of water. Most of the organic water pollutants are highly polar, less volatile, and non-biodegradable and these pollutants tend to degrade water quality and affect the

water ecosystem. The waste water recyclization can be done with eco-friendly purification techniques such as coagulation, oxidation, membrane separation, biological treatment, adsorption and visible-light-induced degradation. Among all these techniques adsorption is considered to be the most effective, economic and easy method for wastewater treatment.

The transition metal (especially Zn, Ti, Fe and Cu) nanomaterials have been widely explored and well utilized for their efficient catalytic degradation properties and the large surface area required for the removal of dissolved organic pollutants in water. Dispersion of large amounts of transition metal nanoparticles in water tends to increase the hardness and the acidity of the water which make it non-consumable. The adsorption properties of transition metal-doped CNs are gaining attention among environmental scientists due to less usage of transition metals and effective removal of organic pollutants¹.

Among the various non-metal elements, Carbon is versatile due to its ability to form different

chemical bonds (σ and π) with different orientations in the different nano structures. The π electrons in Graphite are delocalized whereas the π electrons in graphene is localized which makes them more efficient. Graphene is a hexagonal net of sp^2 hybridized Carbon atom with a C=C bond length of 1.41 Å which is close to the C=C bond distance in benzene (1.40 Å)².

Based on the quantum confinement and morphology, Carbon nanostructures can be classified into 2D (Graphene (sp^2 hybridization), Oxygen doped graphene (GO) (mostly sp^2 hybridization)) with sheet like structure, 1D (single and multi-walled Carbon nanotubes (SWCNTs and MWCNTs)) with tube like structure, and 0-D (Carbon quantum dots (CQDs)) with spherical or quasi spherical structure. The Carbon atoms arrange themselves differently in different hybridizations³. Here, we have discussed the effect and role played by dimensions and the covalent functionalities of the CBNs the photocatalytic removal of organic pollutants in water.

Upon comparing the structure of CNs, graphene consists of sp^2 hybridized honeycomb Carbon. The formation of hexagonal rings where each Carbon atom is bonded to three other Carbon atoms via strong covalent bonds and the unhybridized p_z orbital does generate weak bonds formed by overlapping of two lobes placed above and below the xy plane. It is impossible to control the proportions of elements that take place in the reaction during the synthesis of CNs. Several synthetic i.e. xylene, toluene and benzene, etc., and biomass materials can serve as a precursor for the synthesis of CNs.

CNTs are one dimensional with perfect hollow cylindrical shape. Rolling one layer of graphene leads to single wall Carbon nanotubes (SWCNTs) while rolling several sheets of graphene leads to the formation of multi-walled Carbon nanotubes (MWCNTs). CNTs form three bonds with Carbon atoms separated by 120°. The high mechanical strength of SWCNTs and MWCNTs is due to strong C=C bonds. The SWCNTs and MWCNTs have Young's modulus value of 320 to 1470 GPa and breaking strengths of 13 to 52 GPa respectively⁴.

Among the CNs, CQDs are gaining attention for their intriguing properties. CQDs are more hydrophilic in comparison with rest of the CNs due to large number of covalent groups on the surface. CQDs exhibit excellent fluorescent properties, photo bleaching resistance, and chemical stability⁵

There are several top-down and bottom-up methods are available for the synthesis of CNs such as microwave, ultrasonication, hydrothermal (HT), Solvothermal, Chemical exfoliation, Chemical Vapour deposition (CVD), Arc discharge, Laser ablation etc. Among these methods, CVD was mainly used for the production of high-quality graphene and results in low yield. Apart from those methods there are several other conventional and economic methods which can be used for synthesis of CNs with large number of functional groups in larger amounts which can be used for enormous application. The HT is one such process which requires low temperature and high-pressure which aids the formation of CNs with enhanced morphology and surface properties. The uncontrolled pressure generated during the HT reaction compensates the lower temperature.

However, Carbon being a perfect insulator becomes semiconductor at atomic level and exhibits luminescence properties upon excitation by 254nm UV lamp which can be visibly seen by naked eye. The electronic excitations of these kinds of materials can emit intense fluorescence during the electron hole recombination process. Photoluminescence is induced by band gap, sub defect band gap states and structural defects. Intrinsic tunable fluorescence property of CNs finds application in electronics, optical, biomedical, signalling, sensing and catalysis. The catalytic activity of the CNs mainly depends on the surface defects, surface elements, luminescent nature, and specific surface area.

The catalytic property of the nonmetal doped CNs can be enhanced upon the better understanding of effect of dimension and size. The factors like specific surface area, surface defects, surface elements, quantum confinement, dangling bonds, increase with decrease in dimension of the CNs. The surface area of graphene and CNTs was found to be 2630 m²/g⁻¹ and 1315 m²/g⁻¹ respectively. The surface area of CQDs was found to be 187m²/g⁻¹(Ref. 6). The reduction in the dimension with an increased surface area of the CNs has a positive effect on the catalytic and luminescent property due to the formation of sub defect band gap states.

Functionalization is the process of adding new functional groups, to a material by altering the surface chemistry of the material by means of chemical reaction. The surface functionalization can be classified into two types (i) Oxidation and end/defects functionalization, (ii) Sidewall covalent functionalization. The oxidation takes place by

reaction with strong oxidants such as HNO_3 , H_2SO_4 , KMnO_4 etc., Upon tailoring the surface functional groups with covalent functional groups induces the change in Carbon hybridization from sp^2 to sp^3 and a simultaneous loss of π -conjugation⁷.

The introduction of heteroatoms on the surface of CNs enhances the physicochemical properties like hydrophilicity, fluorescent intensity, photo stability and biocompatibility. The doping of nonmetal elements on the surface of CNs was proved to be non-cytotoxic⁸. The Oxygen-containing functional groups (hydroxyl, epoxy, carboxyl and Carbonyl) and Nitrogen containing functional groups (pyridinic-N, pyrrolic-N, graphitic-N, oxidized-N groups) and Sulphur Containing functional groups (Sulphonate and Sulphite) were introduced onto the surface of CNs and their respective catalytic behaviour was observed⁹.

Peng *et al.*¹⁰ reported that the Nitrogen-doped CQDs (N-CQDs) synthesized by HT method with microcrystalline cellulose and ethylenediamine as a Carbon source and Nitrogen dopant respectively which was utilized for quenching Fe^{3+} ion. Qingsong *et al.*¹¹ consolidated the latest works on modifying the structures and surfaces of GO to luminescence for a wider range of applications. Velusamy *et al.*¹² reported the synthesis of N-CQDs by a HT carbonization method using the aqueous extract of *Phyllanthus emblica* fruit as a Carbon source and aqueous NH_3 as Nitrogen dopant for the removal of toxic effluents from textile wastewater. Siddiqui *et al.*¹³ reported the surface modification of GO upon the effective doping of Sulphur atom towards hydrogen peroxide detection.

Experimental Section

To compare and analyze the role played by the dimensions (0-D & 2-D) and non-metal hetero atoms (N, O and S) of hydrothermally synthesized CNs. Oxygen doped Graphene (GO) were synthesized at 180 and 220°C, Sulphur doped graphene oxide (S-GO) was synthesized at 180°C as reported by Sudhparimala *et al.*^{15,16}, Nitrogen doped graphene oxide (N-GO) was synthesized at 220°C using glucose as precursor and Nitrogen-doped CQDs (N-CQDs) were synthesized using *Caesalpinia bonducella* seed kernel were found to have tunable fluorescence and screened as a heterogenous catalyst for the removal of Chlorophenols and textile dyes, as reported by Fairlin *et al.*¹⁴.

This present study aims to compare and correlate the fluorescence and catalytic activity of 0-D and 2-D CNs with respect to dimensionality and nature of non-metal dopants on catalytic degradation of organic pollutants.

Results and Discussion

Structural and catalytic property relationship of CNs

The comparison of microstructures, surface morphology and elemental composition in terms of dimensionality and functionality of the synthesized CNs were reported in the previous works of Fairlin *et al.*¹⁴ and Sudhparimala *et al.*^{15,16}.

Bonding characteristics and crystal orientation of the synthesized CNs

The Fourier Transformed Infrared (FT-IR) spectra of CNs [Figs 1(a) and (b)]¹⁴⁻¹⁶ exhibited bands corresponding to Oxygen functional groups such as hydroxyl, carbonyl and epoxy¹⁴⁻¹⁶. The FT-IR spectrum of N-CQDs exhibited band corresponding to amino group at 1448cm^{-1} . The FT-IR spectrum of S-GO exhibited bands corresponding to the C-S group at 651 and 605cm^{-1} and the sample N-GO exhibits bands corresponds to symmetric stretching of C=N at 2225cm^{-1} which indicates the introduction of Sulphur and Nitrogen functionality onto the structure of GO. The intense band corresponding to sp^2 aromatic Carbon was obtained around $\sim 1600\text{cm}^{-1}$ and a very low intense band corresponding to sp^3 Carbon was obtained around $\sim 1200\text{cm}^{-1}$ in functionalized 2-D materials (GO, S-GO and N-GO). The N-CQDs exhibited bands corresponding to both sp^2 and sp^3 Carbon atoms with equal intensities due to introduction of more non-metal functionalities.

Raman spectroscopy was used to determine the crystal orientation, and sp^2 and sp^3 hybridization of the synthesized CNs Figs 1(c) and (d)¹⁴⁻¹⁶. The I_D/I_G , $I_D/I_{D'}$ and I_{2D}/I_G ratios were calculated. The I_D/I_G ratio of GO, S-GO, N-GO and N-CQDs was found to be 0.8285, 0.4640, 6.9469 and 1.0555 respectively^{15,16}. The I_D/I_G ratio of N-CQDs (0-D) is greater than 1, in comparison with 2-D CNs (GO and S-GO) which signifies increased structural defect upon dimensional reduction but in the case of N-GO the larger defect ratio is due to replacement of Carbon by Nitrogen in the honeycomb structure of graphene. The 2D band arises due to overtone of D band. The appearance of a broad 2D band is due to the formation of 2-D CNs with few layers of graphene sheets.

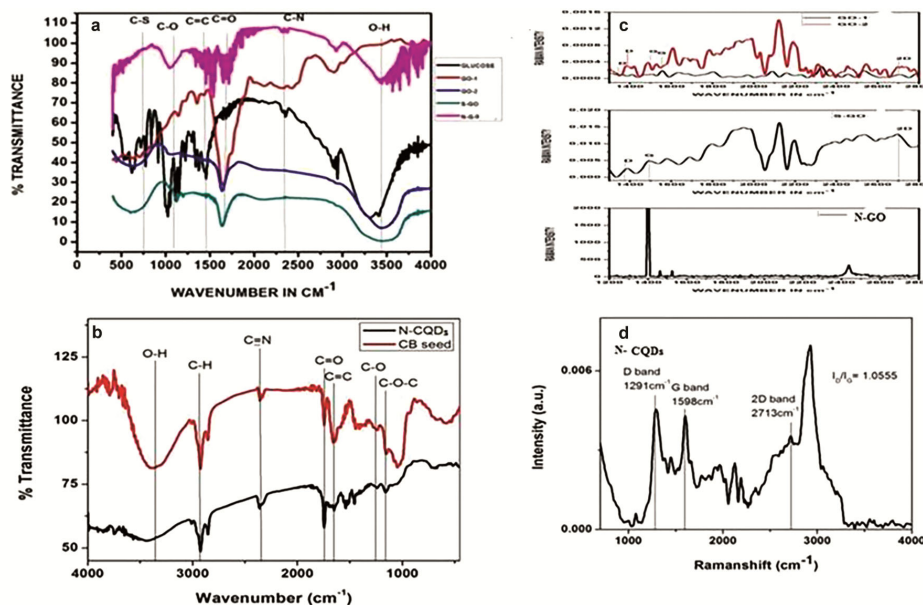


Fig. 1 — (a,b) FT-IR spectra of the synthesized CBNs and (c,d) FT-Raman spectra of the synthesized CBNs¹⁴⁻¹⁶.

The large amounts of heteroatoms on the surface with the twists and folds in the graphene sheets prevent them from restacking which in turn inhibits the conversion of 2-D CNs into graphite. In Raman spectra, the 2D band of GO, S-GO and N-GO were obtained at 2700, 2696 and 2700 cm^{-1} respectively. The I_{2D}/I_G ratio indicates the presence of number of layers in the functionalized 2-D CNs. The I_{2D}/I_G ratios for GO, S-GO and N-GO were calculated to be 0.8285, 2.6300 and 0.4260 respectively. In comparison with GO, the enhanced I_{2D}/I_G ratio by doping with Sulphur indicates the decrease in the number of layers. It clearly indicates that doping with Nitrogen enhances the number of layers in the sample of N-GO. The increase in I_{2D}/I_G ratios and sharpness of the 2D band in Graphene materials further indicate the decrease in agglomeration of graphene layer upon functionalization with the Sulphur atom (few-layer to monolayer) as reported by *Kaushal et al.*¹⁷. The I_D/I_G ratio for GO, S-GO and N-GO was calculated to be 0.5686, 0.6128 and 41.9689 respectively. From the I_D/I_G ratio, it is evident that 2-D CNs have one-dimensional defects in grain boundaries which correlates with the report (*Zhangting et al.*¹⁸.

Microstructures and surface morphology of the synthesized CNs

The microstructure of the synthesized GO, S-GO, N-GO and N-CQDs were studied using X-Ray diffractogram (XRD) analysis [Figs 2(a)

and (b)]¹⁴⁻¹⁶. The d-spacing values of GO, S-GO, N-GO and N-CQDs were calculated to be 0.4339, 0.2878, 0.4061 and 0.4572 nm, respectively. The particle size of N-CQDs was calculated to be 8.2 nm using the Scherrer equation and the specific surface area (SSA) was calculated to be $7317\text{m}^2/\text{g}$ using the formula (specific surface area) $S = 6 \times 10^3/\rho \times D$, where ρ is the density and D is the crystallite size. The high surface to volume ratio indicates the reduction in dimension in N-CQDs. The low d-spacing value of S-GO suggests that Oxygen functional groups are predominantly found in the edges and outermost layer of graphene sheets and not in between the planes of graphene sheets¹⁹. The micro strain of the synthesized CNs was calculated using $\epsilon = \beta/4\text{tan}\theta$, where ϵ represent the micro strain, β and θ corresponds to full width half maximum (FWHM) and diffraction angle respectively. The micro strain of the synthesized samples was found to be 13.748, 50.9276, 60.107 and 39.4783 of N-CQDs, GO, S-GO and N-GO respectively. In Graphene nanomaterials, the number of layers in the synthesized samples has reduced by doping with non-metal dopants in the GO structure which was calculated using $N_L = D/d$, here N_L is the number of layers, D and d represents thickness and interplanar distance respectively. The number of layers of GO, S-GO, and N-GO was calculated to be 0.5747, 0.4752, and 0.7278 respectively. The results were correlated well with FT-Raman analysis.

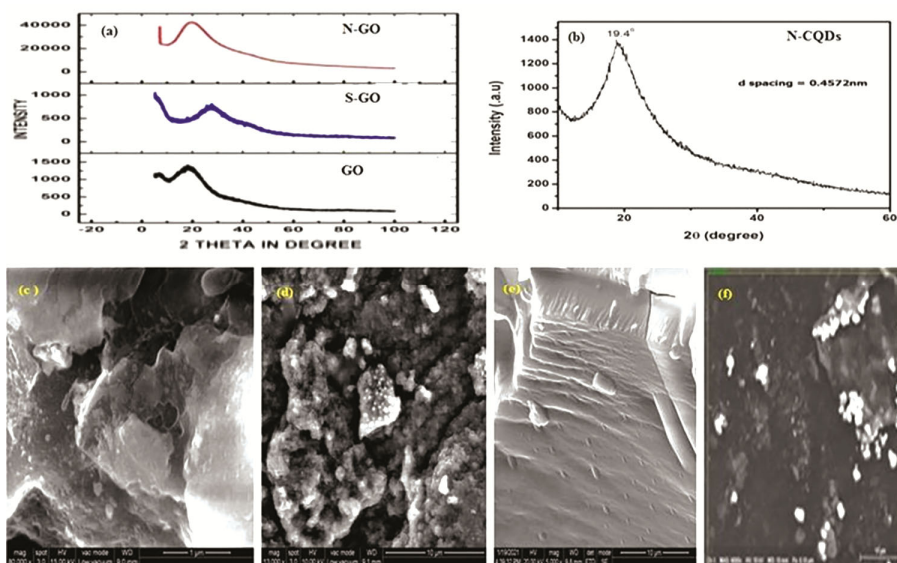


Fig. 2 — (a,b) PXRD spectra of the synthesized Carbon based nanomaterials and (c,d,e,f) FE-SEM images GO, S-GO, N-GO and N-CQDs respectively¹⁴⁻¹⁶

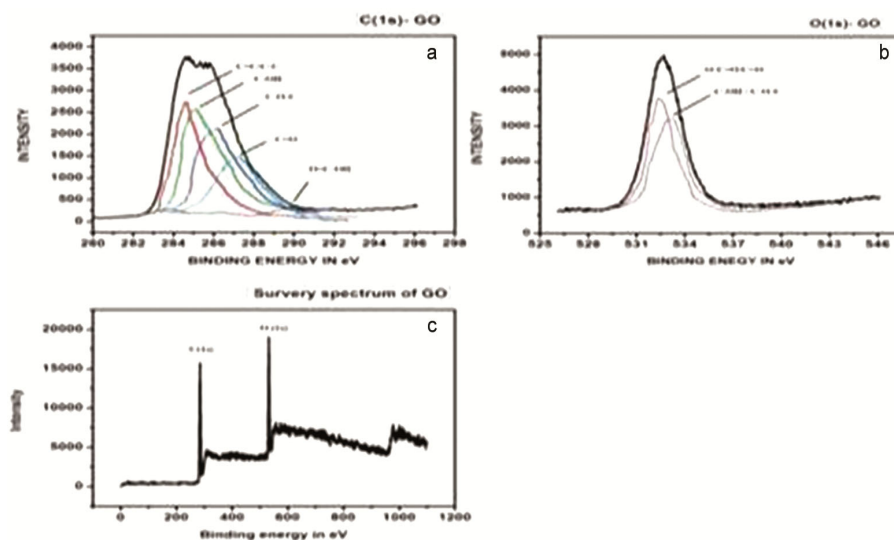


Fig. 3 — Narrow scan X-ray Photoelectron spectra of (a) Carbon (1s); (b) Oxygen (1s) and (c) Wide scan XPS spectrum of graphene oxide (GO).

The morphology of the GO, S-GO, N-GO and N-CQDs were identified with the FE-SEM imaging tool [Figs 2 (c, d, e, f)]¹⁴⁻¹⁶. The layer structures were identified in synthesized GO and S-GO^{15,16}. The FE-SEM image of S-GO shows spherical aggregates of Sulphur on the layer structure and N-GO shows well defined layer morphology. The as prepared N-CQDs show the irregular spherical and quasi-spherical structure with high surface defect due to the presence of heteroatoms (N and O)¹⁴. The surface defects can be increased upon the high level of non-metal dopants.

From the direct band gap value of GO (1.717eV), S-GO (3.57eV)¹⁵, N-GO (4.42eV) and N-CQDs (5.8940eV)¹⁴. it is evident that band gap value of GO increased upon doping²⁰. The dimension reduction and electro negativity of heteroatom (Oxygen, Nitrogen and Sulphur) has increased the band gap value.

Surface elemental composition of the synthesized CNs

The X-ray photoelectron spectroscopy (XPS) analytical tool was used for determining the surface elemental composition and chemical state of the GO, S-GO and N-GO (Figs 3, 4 and 5 respectively).

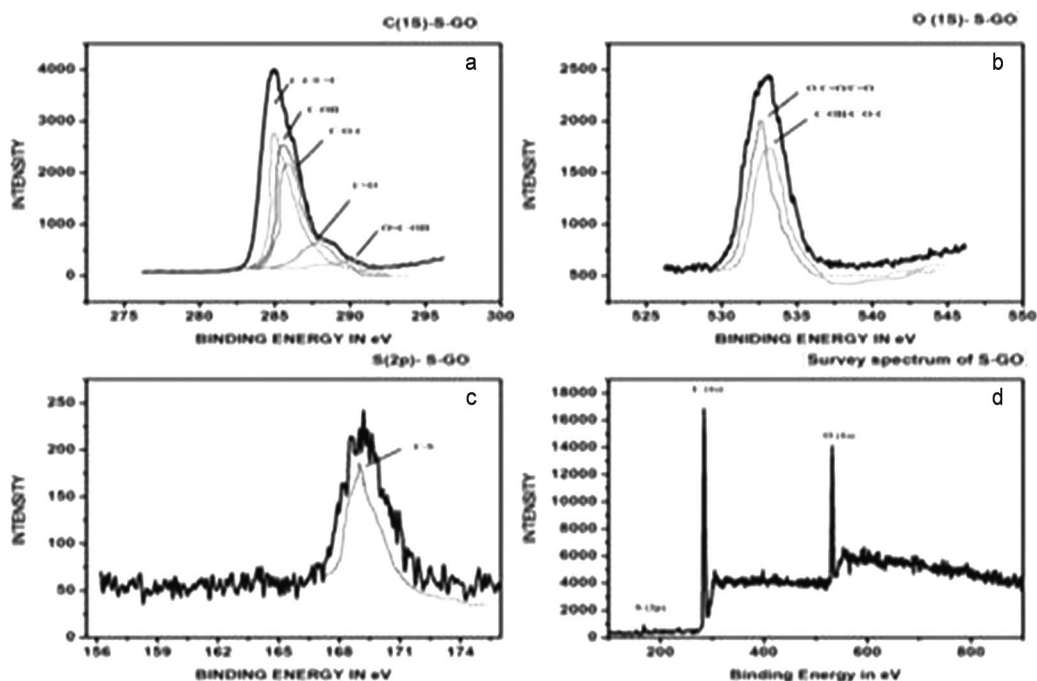


Fig. 4 — Narrow scan X-ray Photoelectron spectra of (a) Carbon (1s); (b) Oxygen (1s); (c) Sulfur (2p) and (d) Wide scan XPS spectrum of Sulfur doped graphene oxide (S-GO).

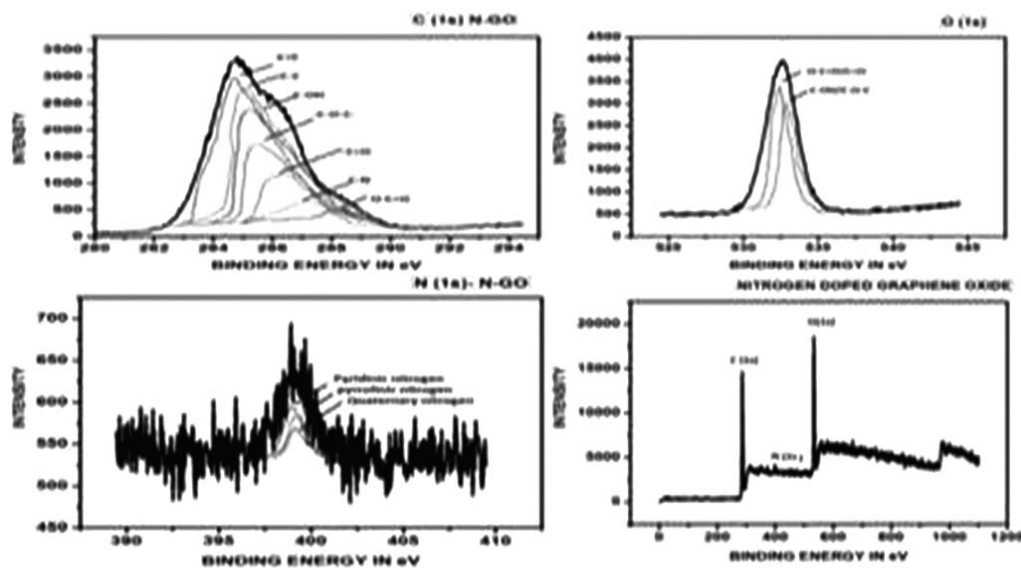


Fig. 5 — Narrow scan X-ray photoelectron spectra of (a) Carbon (1s); (b) Oxygen (1s); (c) Nitrogen (1s) and (d) Wide scan XPS spectrum of Nitrogen doped graphene oxide (N-GO).

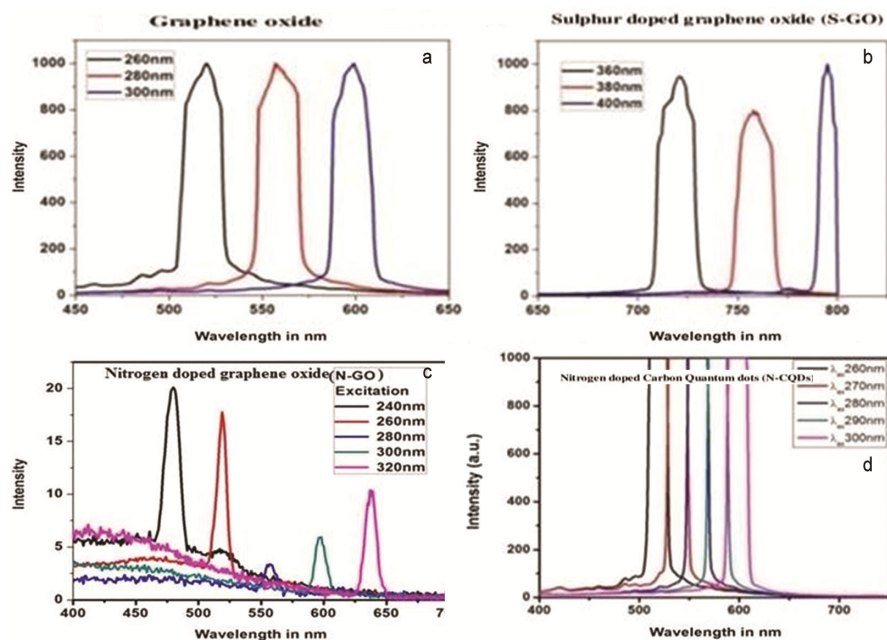
In GO, S-GO and N-GO, the carboxyl functional group was found to be in higher concentration on the surface. The C/O ratio of GO, S-GO and N-GO are 2.8211, 2.4118, 1.8397 respectively²¹. The percentage of epoxy and hydroxyl groups were relatively higher in GO (37%) than S-GO (32%) and N-GO (38%) which implies more structural defect in the sample N-GO than GO and S-GO. The structural defects in

the synthesized graphene nanomaterials from XPS analysis were correlated well with FT-Raman analysis^{22,23}. The comparison of the carbon to oxygen ratio (C/O) of functionalized GO from XPS and EDX analysis was given in Table 1¹⁴⁻¹⁶.

The C/O ratio was calculated from XPS and EDX analysis. The C/O ratio of S-GO was found to be less when compared with GO and N-GO from EDX

Table 1 — Comparison of Carbon to Oxygen ratio of GO, S-GO, N-GO and N-CQDs from XPS and EDX analysis^{14,15,16}

Name of the sample	Name of the element	% of elements from wide scan spectrum of XPS	C/O ratio from wide scan spectra of XPS	% of elements from EDX	C/O ratio from EDX
GO -2	Carbon	73.8	2.8211	58.62	1.40
	Oxygen	26.16		41.72	
S-GO	Carbon	69.34	2.4118	51.16	1.1986
	Oxygen	28.75		42.68	
	Sulphur	1.912		6.17	
N-GO	Carbon	57.97	1.8397	59.79	1.6453
	Oxygen	31.51		36.34	
	Nitrogen	10.51		3.87	
N-CQDs	Carbon	-	-	59	3.1053
	Oxygen	-	-	19	
	Nitrogen	-	-	21	


 Fig. 6 — Tunable luminescence spectra of (a) Go (b) S-GO (c) N-GO (d) N-CQDs¹⁴⁻¹⁶

analysis. The surface elements and the surface defects play a vital role in catalysis and fluorescence property. The as-synthesized N-CQDs have electronegative nitrogen and oxygen atoms on the surface along with increased surface defects. From EDX analysis, the C/O ratio of GO (1.40), S-GO (1.1986), N-GO (1.6453) are comparatively less than the C/O ratio of N-CQDs (3.1052)¹⁴⁻¹⁶. This implies that GO, S-GO and N-GO have high oxygen-containing functional groups than the N-CQDs.

Application of synthesized CNs

Comparison of tunable luminescence property of the synthesized CNs

The excitation dependent emission confirmed the tunable luminescence property of GO, S-GO, N-GO,

N-CQDs (Fig. 6)¹⁴⁻¹⁶ and green fluorescence of the GO, S-GO, N-GO, N-CQDs were confirmed and reported^{14,15}. The oxygen containing functional groups have enhanced the tunable luminescence property of graphene nanostructures in the visible region (red region). The tunable luminescence property of N-CQDs shows green emission due to the synergistic effect of hetero atoms and surface defects on the surface of CQDs. By comparing the tunable luminescent property of synthesized CNs, the sample S-GO have enhanced emission than N-CQDs due to more Oxygen-containing functional groups and grain boundaries observed in XPS and EDX analysis. The intensity of green emission was high in N-CQDs than N-GO due to the presence of large number of Nitrogen atom and reduction in dimension which enhances the band gap of N-CQDs. The tunable

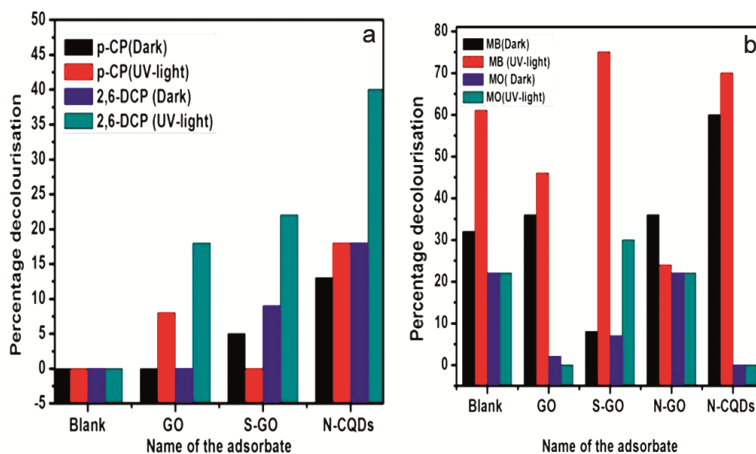


Fig. 7 — Adsorption and photo catalytic (a) Degradation of Chlorophenols (p-CP, 2, 6-DCP) and (b) Decolouration of organic dyes (MB, MO) using synthesized CBNs¹⁴⁻¹⁶.

luminescence property observed in the CNs can be utilized for bioimaging. The study indicated that the green emission safe for bioimaging due to non-cytotoxic nature and does not harm nucleic acid.

Comparison of catalytic property of the synthesized CNs

Few reports are available for adsorption and photocatalytic degradation of Chlorophenols and organic dyes using non-metal-doped CNs as heterogeneous catalyst. *Wonghil Chang et al.*²², *Jun di et al.*²³, *Pérez-Ramírez et al.*²⁵, and *Kalaiselvi Velayutham et al.*²⁶ have synthesized and utilized the transition metal doped graphene nanocomposite as photocatalyst for the removal of toxic organic pollutants.

Adsorption is an effective and economic way to remove pollutants in water and it occurs whenever a solid material with an activated surface i.e., a surface with a large number of defects, pores, atoms with unpaired or lone pair of electrons and large surface area is exposed to a gas or liquid. Adsorbents are used on a large scale as desiccants, catalyst support and also for the separation of gases, purification of liquids and pollution control^{27,28}. The adsorption and photo catalytic property of the GO, S-GO, and N-CQDs for the removal of Chlorophenol were analyzed as reported^{16,14} (Fig. 7a)¹⁴⁻¹⁶. The N-CQDs show good photocatalytic activity for the degradation of Chlorophenols than GO and S-GO. In 2D CNs, S-GO exhibited good photocatalytic removal of Chlorophenol due to introduction of more non-metal dopants which enhanced the band gap and reduction in dimension.

Methylene blue (MB) and Methyl orange (MO) are commonly used dyes in dyeing, printing, cosmetics and leather industries and are found to be toxic and

affects the water ecosystem. Catalytic decolouration of dyes (Methylene blue (MB) and Methyl orange (MO) were carried out in both dark and UV light-medium by using the CNs (GO, S-GO, N-GO and N-CQDs) as catalyst (Fig. 7b)¹⁴⁻¹⁶. The synthesized CNs are good photocatalyst for the decolouration of MB. S-GO has an effective photocatalytic property than GO, N-GO, N-CQDs. N-CQDs are an effective adsorption catalyst than the S-GO for the decolouration of MB due to increased electrostatic attraction between adsorbate and adsorbent. The decolouration efficiency of MO was not effective by using the as-synthesized CNs as a catalyst^{14,16}.

Suggested reaction mechanism of the photocatalytic degradation of chlorophenols

The heterogeneous solid CNs catalyst used in the removal of organic pollutants (Chlorophenols and dyes) were successfully removed from the reaction medium after catalysis by means of filtration. The suggested mechanism for the photocatalytic degradation of Chlorophenols using synthesized CNs (GO, S-GO, N-CQDs) as catalyst was illustrated in Fig. 8.

The heterogeneous photocatalysis is an advanced oxidation process that generates electron-hole pairs under photo-illumination. The functionalized CNs absorb UV radiation and the electrons in the valence band of the photocatalyst are excited to the conduction band. Thus, the photogenerated electron – hole pairs initiate the redox reactions with Chlorophenol. The photo stimulated CNs acts as a dipole, the positive holes induce the oxidation of hydroxyl groups or water molecules by producing hydroxyl free radicals. The degradation of toxic pollutants (Chlorophenols) occurs through the formation of hydroxyl free radical, which

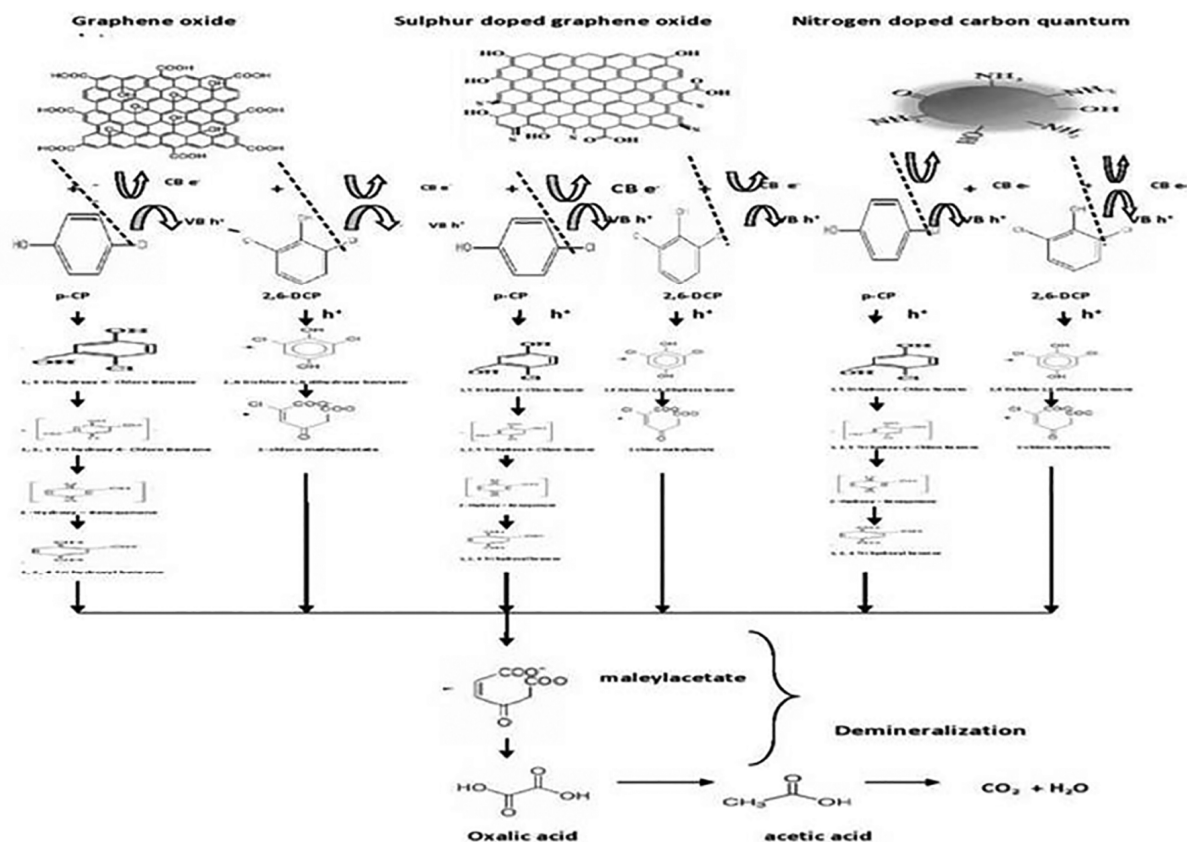


Fig.8 — A Suggested reaction Mechanism of the photocatalytic degradation of Chlorophenols (p-Chlorophenol and 2,6 Dichlorophenol) using as-synthesized CBNs as a catalyst^{29,30}.

has low reaction selectivity²⁵. The photocatalytic activity had been enhanced by the introduction of functional groups with high electronegative value (Oxygen (GO) < Oxygen, Sulphur (S-GO) < Oxygen, Nitrogen (N-CQDs)). The as-synthesized CNs can be employed as heterogenous catalyst for waste water treatment in industries. The electro negativity of hetero atoms increased the band gap value and created sub defect band gap states upon functionalization and reduction in dimension of the CNs.

Conclusion

The increase in electronegativity of non-metal dopants, increase the surface defects and decrease in dimension would efficiently replace the usage of noble metal and transition metal dopants. These kinds of non-metal dopants are comparatively less hazardous, economic, abundant and environmentally friendly. The effect on microstructure and morphology by the dimensionality and functionality of the as-synthesized CNs (GO, S-GO, N-GO N-CQDs) were analyzed. Thus, the size and the dimension of the nanomaterial

play a significant role in luminescence, adsorption and photocatalysis. In 2-D CN material, the presence of adjacent groups tends to affect the catalytic site. The surface area in 0-D material is largely due to quasi-spherical nanostructure which makes the catalytic sites less hindered and more available in comparison with 2-D nanosheets. The synthesized GO, S-GO, N-GO, and N-CQDs were successfully screened as catalyst for the removal of Chlorophenols and textile dyes. The introduction of functional groups and reduction in dimensionality has increased the degradation efficiency. The study provides key points on the role of functionality and dimensionality of CNs in enhancing the photo catalytic activity for the degradation of Chlorophenols and textile dyes. It further suggested a suitable emission mechanism for bioimaging of normal and Cancer cell diagnosis application.

Conflicts of interest

The author(s) declare that there is no conflict of interests regarding the publication of this article

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References

- Nasir Salisu, Hussein Mohd Zobir, Zainal Zulkarnain & Yosof Nor Azah, *Materials*, 11 (2018) 295.
- Serp Philippe & Machado Bruno, *RSC Catal Ser*, 1 (2015) 1.
- Kumar Narendra & Kumbhat Sunita, *Essentials in Nanoscience and Nanotechnology*, 1st edn, (John Wiley & Sons Inc) 2016.
- Anzar Nigar, Hasan Rahil, Tyagi Manshi, Yadav Neelam & Narang Jagriti, *Sens Int*, 1 (2020) 1.
- Lim S Y, Shen W & Gao Z, *Chem Soc Rev*, 44 (2015) 362.
- Nan Wang, *Functionalization and Characterization of Carbon Based Nanomaterials for Electronics Composite and Biomedical Application* (Chalmers University of Technology Göteborg, Sweden), (2017).
- Giorgio Speranza, *Nanomaterials*, 11 (2021) 1.
- Liu Wei & Speranza Giorgio, *J Carbon Res*, 5 (2019) 1.
- Zhenga Peng & Wu Nianqiang, *Chem Asian J*, 12 (2017) 2343.
- Wu Peng, Li Wei, Wu Qiong, Liu Yushan & Liu Shouxin, *RSC Adv*, 7 (2017) 44144.
- Qingsong Mei, Bianhua Liu, Guangmei Han, Renyong Liu, Ming-Yong Han & Zhongping Zhang, *Adv Sci*, 6 (2019) 1.
- Velusamy Arul & Mathur Gopalakrishnan Sethuraman, *ACS Omega*, 4 (2019) 3449.
- Siddiqui Ayesha Saleem, Hayat Akhtar, Nawaz Mian Hasnain, Ahmad Muhammad Ashfaq & Nasir Muhammad, *Appl Surf Sci*, 19 (2019) 1.
- Fairlin Jenitha R & Sudhparimala S, *Indian J Appl Res*, 10 (2020) 1.
- Sudhparimala S & Usha R, *J Phys Conf Ser*, 1706 (2020) 1.
- Sudhparimala S & Usha R, *Mater Sci Forum*, 1019 (2021) 194.
- Kaushal Ashish, Dhawan S K, Singh Vishal, *AIP Conf Proc*, 2115 (2019) 1.
- Wu Zhangting & Ni Zhenhua, *Nanophotonics*, 6 (2017) 1219.
- Hongmei Yang, Jiu-Sheng Li & Xiangqiong Zeng, *ACS Appl Nano Mater*, 7 (2018) 1.
- Velasco-Soto M A, Pe´rez-Garci´a S A, Alvarez-Quintana J, Cao Y, Nyborg L & Licea-Jime´nez L, *Carbon*, 93 (2015) 967.
- Al-Gaashania R, NajjarA, Zakaria Y, Mansoura S & Atieha M A, *Ceram Int*, 45 (2019) 14439.
- Wonghil Chang, Hojun Kim, Ga Young Lee & Byoung Joon Ahn, *Springer Res Chem Intermed*, 8 (2015) 1.
- Jun Di, Jiexiang Xia, Bin Wang, Xiaowei Li, Qi Zhang, Zhigang Chen & Huaming Li, *ACS Sust Chem Environ*, 4 (2016) 136.
- Karina Bustos-Ramírez, Carlos Eduardo Barrera-Díaz, Miguel De Icaza-Herrera, Ana Laura Martínez-Hernández, Reyna Natividad-Rangel, Carlos Velasco-Santos & Bustos-Ramírez, *J Environ Health Sci Eng*, 13 (2015) 1.
- Pérez-Ramírez Eduardo E, Luz-Asunción Miguel de la, Martínez-Hernández Ana L & Velasco-Santos Carlos, *Mech Appl*, 18 (2018) 492.
- Anand Kalaiselvi Velayutham, Anand Sandy Subala, Sripathi Sumathi K & Stanish Antony Lucia Merin, *Europ J Adv Chem Res*, 1 (2020) 1.
- Rouquerol F, Rouquerol J & Sing K, *Adsorption by Powders Porous Solids*, 2nd Edn (Academic press), (2013) 1.
- Dongli Wei, Chaofeng Zhao, Ayub Khan, Lu Sun, Yongfei Ji, Yuejie Ai & Xiangke Wang, *Chem Eng J*, 375 (2019) 1.
- Kumar Brajesh, *Intech Open Chapter*, 1 (2020) 1.
- Huajuan Wang, Zhiyong Song, Jiangjiang Gu, Shuojun Li, Yang Wu & Heyou Han, *ACS Biomater Sci Eng*, 5 (2019) 4739.