

Metal doping in g-C₃N₄ and tuning of band-gap for dye degradation using visible light

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Graphitic carbon nitride (g-C₃N₄), as a fascinating conjugated polymer, has been the hotspot in science as a metal-free and visible-light-responsive photocatalyst. Pure g-C₃N₄ suffers from insufficient sunlight absorption, low surface area and the fast recombination of photo-induced electron-hole pairs, resulting in low photocatalytic activity. Utilizing the thermal polymerization process, metal-doped g-C₃N₄ has been formed and the formed catalysts employed for the degradation of methyl orange under visible light. The produced catalysts have been examined using a variety of characterisation techniques and by experimental means. The lowering of band gap and improved photocatalytic activity of the as-prepared catalyst is resulted by metal doping.

Keywords: Carbon materials, Doped g-C₃N₄, Photocatalysis, Solar energy materials

Rapid industrialization in developing countries leads to the use of huge amount of chemicals¹. Most of these industrial effluents ultimately reach water bodies² and harm the aquatic environment which leads to a negative effect on all the living world. Hereof, measures have been required to control the pollutants, causing aquatic pollution, like chemicals, heavy metals and dyes. Moreover, these chemicals, dyes and heavy metals might have a latent risk to the environment to spread severe diseases to all the flora and fauna^{3,4}. There are a few common approaches to reduce or minimise the waste^{5,6}. The few commonly known strategies are Advanced oxidation processes (AOP)^{7,8} and photochemical water splitting⁹⁻¹¹. In practice, it is worth using metal-free or having a very small quantity of metal as a catalyst.

In the previous few years, graphitic carbon nitride (g-C₃N₄) having carbon and nitrogen with a very small quantity of hydrogen has been widely used as a photocatalyst using visible light¹²⁻¹⁷. This organic catalyst provides new ways to harness the visible light portion of solar light with higher stability and low cost^{18,19} however high recombination rate makes it less useful²⁰.

The addition of a cocatalyst leads to a reduction in charge recombination and provides sites for elementary reactions. Results showed that doping of Fe, enhanced the photocatalytic activity of g-C₃N₄ for the degradation of Rhodamine B under visible light.²¹ Literature show that doping g-C₃N₄ with metal

enhance the photocatalytic activity of g-C₃N₄ (Ref. 22-24) The reported results are summarized in Table 1.

Methyl orange (MO) is used in titration and is regarded as one of the highly-polluting substance having azo groups. Here in this article, metal (Ni, Cu, and Fe) doped g-C₃N₄ was used for degradation of MO dye in presence of visible light.

Experimental Section

Materials

Melamine (C₃H₆N₆) and MO (C₁₄H₁₄N₃NaO₃S), were purchased from SDFCL, and Thermo Fisher Scientific, Mumbai, respectively. Distilled water was used at every step. Each step was performed in ambient conditions unless mentioned.

Methods

g-C₃N₄ nanoparticle synthesis

Melamine was directly heated at 600°C for 6 h in a closed crucible placed in a muffle furnace to form g-C₃N₄ nanoparticles. To preserve the ambient air, the lid of the crucible was shut during the reaction.

Synthesis of metal-doped g-C₃N₄ nanoparticles

The metal compound (250 mg of metal salts) was mixed with melamine (5 mg) and a small quantity of water (5 mL) to form a slurry, which on thermal polymerization resulted in the photocatalyst of Ni, Cu and Fe doped g-C₃N₄ (denoted as g-C₃N₄/X).

Table 1 — g-C₃N₄ doped with metal, their bandgap and photocatalytic application

Doping element	Precursor	Synthesis	E _g (eV)	Application	Reference
Fe	Fe(NO ₃) ₃ ·9H ₂ O (Fe) Melamine (CN)	Thermal condensation	2.64	RhB degradation	21
Cu	CuCl ₂ (Cu) Melamine (CN)	Thermal condensation	2.25	MO degradation	22
Ce	Ce(SO ₄) ₂ ·4H ₂ O(Ce) Melamine (CN)	Annealing	2.57	RhB degradation	23
Co	CoPc (Co) Melamine (CN)	Thermal condensation	2.62	H ₂ evolution	24

Characterization of the synthesized samples

The characterizations of the pure and doped g-C₃N₄ were performed using X-ray diffraction (XRD), UV visible spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) techniques. The XRD data were collected to examine the structure of the synthesized catalyst using the equipment from RIGAKU. UV-visible spectroscopy data was used to determine the band gap using CARY, 100 bio, UV-vis spectrophotometer. SEM and EDX characterization was done with Quanta 450, EDAX to know the morphology of the particles and types of element present in the catalysts, respectively.

Photocatalytic studies on g-C₃N₄/X

The photocatalytic activity was investigated using a reactor with a catalyst (5 mg) under visible light containing hazardous pollutant solution MO dye. The dye solution was incubated for 30 min without light before the experiment to achieve adsorption-desorption equilibrium. A known amount of prepared catalyst was added to 100 mL of MO dye solution. During the initial 10 min, solution kept under dark to attain adsorption-desorption equilibrium. Then the solution was kept under direct sunlight for photocatalytic reaction. After the intervals of 10 minute a certain volume was taken and change in absorbance is recorded using UV-visible spectrophotometer.

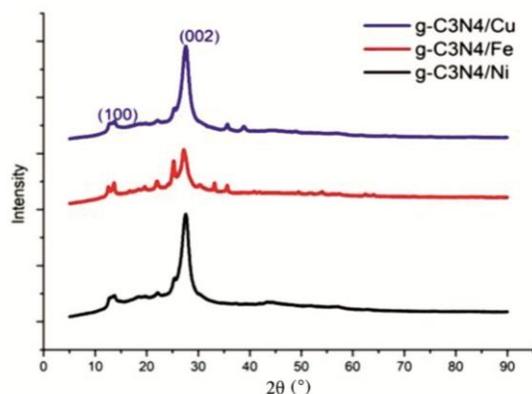
Result and Discussion

Formulation and mechanism of catalysis

Under fixed temperature conditions, melamine undergoes polyaddition and polycondensation processes that result in the synthesis of g-C₃N₄ and doped g-C₃N₄. In the beginning, melamine was heated to a high temperature, which eliminated ammonia²⁰. Additionally, the polymeric network of g-C₃N₄ might have developed at 600°C as a result of the polycondensation of heptazine units¹⁹.

Characterization of g-C₃N₄/X

The XRD plots of pure and doped g-C₃N₄ are shown in Fig. 1. It shows the presence of carbon and a hexagonal phase. The major peaks at 12.78° and 27.38°

Fig. 1 — XRD plots of Ni, Fe and Cu doped g-C₃N₄

corresponding to the (100) and (002) reflection of the plane, respectively, indicate the formation of g-C₃N₄ apart from smaller peaks showing the presence of oxides and sulfates of corresponding metal.

The intensity of the peak at 27.38° is too high as compared to others which show the high crystalline nature of the catalyst. In the case of doped by copper, a very small peak at 48.88° shows the small formation of copper sulfide. Peaks at 35.62° and 38.80° confirmed the presence of oxides of copper (CuO and Cu₂O), respectively. In nickel, a small peak at 44.25° was obtained which shows the presence of oxide of nickel.

The photographs of the synthesized catalysts are as own in Fig. 2a. Absorption spectra were measured in the reflectance mode and corresponding Tauc plots are shown in Fig. 2b. A minute reduction in band gap is noticed in the doped catalysts as compared to the pure one. The bandgaps are calculated to be 2.46, 2.47 and 2.54 eV for g-C₃N₄/Cu, g-C₃N₄/Ni and g-C₃N₄/Fe, respectively.

SEM results confirmed the presence of metal in g C₃N₄. There observed in some change in the morphology of the catalyst g-C₃N₄ (Fig 3a) upon doping with different metals (Fig. 3b-d). EDX analysis confirmed the presence of respective metals in the doped samples.

Photocatalytic activity of g-C₃N₄/X

The percent changes in dye solution irradiated under direct sunlight with ambient temperature using

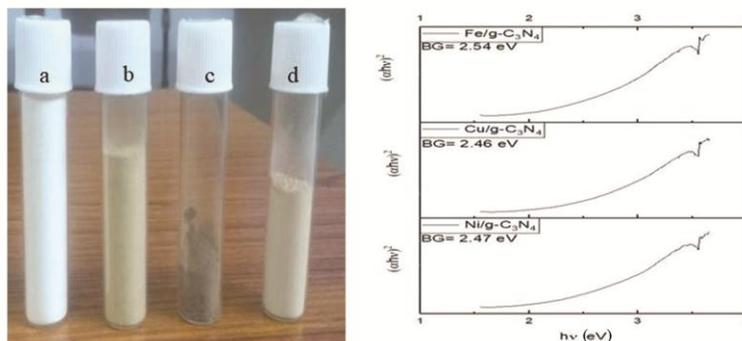


Fig 2 (a) — Photographs of synthesized catalysts A [(a) g-C₃N₄, (b) g-C₃N₄/Cu, (c) g-C₃N₄/Ni and (d) g-C₃N₄/Fe] and (b) Tauc plots

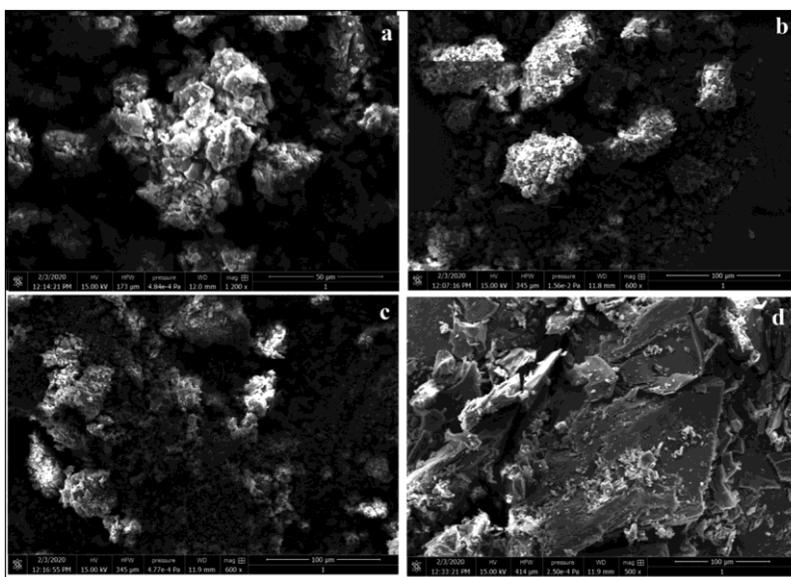


Fig. 3 — SEM images of different catalysts, g-C₃N₄ doped with metal a) Nickel b) Iron and c) Copper, and d) undoped g-C₃N₄

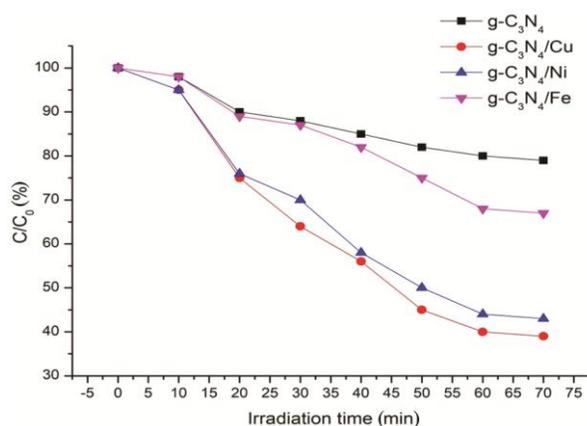


Fig. 4 — % Degradation curves for MO removal by using different catalysts

different synthesized photocatalysts are shown in Fig. 4. The absorbances of the solutions were recorded for 70 min, when there were no changes in the absorption noticed. The percentage degradation in 1 h after exposed to the sunlight was approximately

15% for undoped g-C₃N₄ photocatalyst, whereas the value enhanced to 30% for g-C₃N₄/Fe, 54% for g-C₃N₄/Ni and 62% for g-C₃N₄/Cu. The electron-hole recombination rate in the photocatalyst was the main contributor to its photocatalytic activity.

Conclusion

The fabrication of g-C₃N₄ was done successfully by thermal polymerization technique and the same process was used to form metal-doped g-C₃N₄. The doping resulted a change in the bandgap of the catalyst. The effect of bandgap reduction is reflected in the enhanced %degradation of MO dye after exposure of 1 h under sunlight.

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