

Nano science, Nanotechnology, Graphene & 2D material: Photocatalytic activity of the N-rich graphitic carbon nitride- T V M Sreekanth and G R Dillip -Yeungnam University, South Korea

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Abstract

Graphitic carbon nitride (g-C₃N₄) is a novel metal-free polymer semiconductor that has received a great deal of interest for a wide range of applications due to its ease of synthesis, modification, environmental friendliness, suitable bandgap, higher light harvesting, unique electronic properties, and physicochemical properties. Because of these properties, g-C₃N₄ has been considered as a promising photocatalyst for organic pollutant degradation and water splitting. Nitrogen-rich graphitic carbon nitride (Ng-C₃N₄) with improved photocatalytic activity was engineered using a facile post-annealing treatment of pristine g-C₃N₄ in N₂ atmosphere. The thermal annealing did not modify the crystal structure, vibrational modes, or morphology of the N-rich g-C₃N₄ (Ng-C₃N₄). However, it decreased the crystallinity by broadening the dominant X-ray diffraction (XRD) peak and increased the surface area and mesoporous nature because of the formation of carbon vacancies. Diffuse reflectance spectroscopy indicated that the bandgap of the annealed g-C₃N₄ decreased from 2.82 to 2.77 eV compared to pristine g-C₃N₄. The increase of nitrogen content in the annealed Ng-C₃N₄ was quantified by X-ray photoelectron spectroscopy (XPS), which was also used to examine the formation of carbon vacancies. Photocurrent and electrochemical impedance spectroscopy measurements showed that the annealed N g-C₃N₄ had higher light absorption capacity than the pristine g-C₃N₄. The photocatalytic performance of the samples was investigated for the degradation of crystal violet (CV) under ultra-violet light irradiation. The annealed Ng-C₃N₄ sample exhibited superior photodegradation of CV over pristine g-C₃N₄.

Global environmental pollution is becoming a core issue for the modern society, which is directly threatening the terrestrial and aquatic life. Water pollution is considered as one of the foremost challenges. Colored pigments including organic dyes and aromatic nitro compounds are commonly used in various industries including clothing, paper, fiber, pharmaceutical, food, printing, and leather. These industries release a massive amount of effluent with some amount of hazardous compounds such as organic dyes and aromatic nitro

compounds. These effluents with hazardous compounds contaminate water bodies such as river and ponds and so forth because of inadequate treatments before disposal from the industries. Many of these aromatic nitro compounds and organic dyes have been reported to be carcinogenic, used as skin sensitizers, and are capable of causing methemoglobinemia. The hazardous effluent from various industries could cause a serious problem for aquatic as well as for terrestrial life, and their proper treatment before their disposal is the need of hour.

The scientific community for environmental remediation is constantly developing new protocols. Various industrial effluent management strategies have been utilized, including bacterial treatment, coagulation, chemical oxidation, adsorption, photocatalytic degradation, and many more. Several procedures are being employed to reduce the environmental pollution, and a wide range of strategies could be applied to accomplish this purpose.¹² In the recent years, nanotechnology has attracted significant interest because of its applications in different areas of scientific research having a direct impact on improving human life.

Nanostructured inorganic solid support materials are considered as highly efficient materials for various applications such as catalysis, sensing, energy production, and so forth.^{13,14} Because of properties such as high surface area, high thermal stability, and possibility to functionalize with active groups, inorganic solid support materials have been widely used in different fields of scientific research, including biomedical applications, chemical sensing, adsorption, and heterogeneous catalysis. An inorganic solid support material when employed in catalysis has the advantage of further functionalization with a variety of different catalytic moieties and could also be recycled and reused in multiple catalytic cycles.¹⁵ Heterogeneous materials furnish large surface area for the adsorption of reactant molecules on their surface that could result in an increased reaction rate. Heterogeneous catalysis based on the use of inorganic solid support materials has drawn massive interest as an enticing method for environmental remediation. Recently, several reports have been published, involving the use of heterogeneous nanocatalysts being extensively employed for the reduction and degradation of various organic pollutants and for the

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generation of green energy.

Because of diverse applications, nanocarbons such as graphene, carbon nitride, and boron carbon nitride have aroused enormous attention. These materials have a wide range of applications in numerous research fields including energy storage, environmental remediation, biomedicine, and heterogeneous catalysis. Carbon nitride is a family of polymeric structures mainly composed of carbon and nitrogen. Because of its simplistic preparation approach, the minimal cost of production, and controllable electronic properties, graphitic carbon nitride (g-C₃N₄) has drawn enormous attention in recent years. In addition, its remarkable thermal stability (up to 600 °C in air) and stability in neutral, basic, and acidic medium make it a potent material for various applications including solid support materials for heterogeneous catalysis. These g-C₃N₄ materials can be easily prepared from carbon-containing sources, replacing some carbon atoms with nitrogen atoms. g-C₃N₄ is not only the strong carbon nitride allotrope in the natural medium, but it also has diverse surface features that are appealing for catalytic applications. Because of the presence of hydrogen and nitrogen sites on its surface, g-C₃N₄ could be easily functionalized with different catalytic active groups including metal and bimetallic nanoparticles. g-C₃N₄ has been reported as an efficient catalyst for a variety of reactions including oxygen reduction, hydrogen evolution, dye degradation, and various other chemical transformations.,

In the present study, nitrogen-rich g-C₃N₄ was synthesized by a simple direct thermal polymerization procedure, followed by the immobilization of Pd nanoparticles on its surface. Here, g-C₃N₄ has been utilized as a support material to synthesize a heterogeneous catalyst. The catalytic efficiency of palladium-supported g-C₃N₄ was determined for the degradation of organic dyes and the reduction of aromatic nitro compounds. The synthesized catalyst exhibited excellent catalytic efficiency and could be reused for multiple catalytic cycles without any appreciable loss in its activity.

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