

Photocatalytic oxidation of aromatic amines using $\text{MnO}_2@g\text{-C}_3\text{N}_4$

Sanny Verma and Rajender S. Varma*

Sustainable Technology Division, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, MS 443, Cincinnati, Ohio 45268, USA

*Corresponding author. Tel: 513-487-2701; Fax: 513-569-7677; E-mail: varma.rajender@epa.gov

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Abstract

An efficient and direct oxidation of aromatic amines to aromatic azo-compounds has been achieved using a $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst under visible light as a source of energy at room temperature. Copyright © 2017 VBRI Press.

Keywords: Graphitic carbon nitride, photo-catalyst, manganese dioxide, heterogeneous catalysis, aromatic azo-compounds.

Introduction

Since the discovery of azobenzene derivatives, these compounds have been traditionally employed as organic dyes [1]. Additionally, aromatic azo compounds are important raw materials with industrial applications as food additives, therapeutic agents, radical reaction initiators, drugs, photochemical molecular switches, and liquid crystals [2-4]. Conventional methods for the synthesis of aromatic azo compounds entail coupling of stoichiometric amount of electron rich compounds with diazonium salts [5-6]. However, these protocols generate copious amount of inorganic waste. There are several reports on the synthesis of azo-compounds such as Mills reaction, reduction of azoxybenzene, Wallach reactions, oxidation of amines, triazine rearrangement, thermolysis of azides, metal catalyzed coupling of arylhydrazines [7-10]. These methods are limited in terms of the substrate scope because of their intrinsic reaction mechanism showing the combination of electron rich and electron deficient aromatic amines. Garcia *et al.* reported the synthesis of aromatic azo-compounds from nitroaromatics using gold nanoparticles supported on titanium dioxide (TiO_2) at primarily 9 bar hydrogen and 5 bar oxygen pressure [11]. Recently, Zhang and coworkers synthesized azo compounds *via* aerobic oxidative dehydrogenate coupling of anilines using copper bromide and molecular oxygen as an oxidant [12]. Gu *et al.* reported a worm-like palladium nano-catalyst for the synthesis of aromatic azo compounds from nitro-benzenes under hydrogen pressure [13]. These inspiring methods, however, require expensive catalysts, high temperature and high oxygen pressure. Engaged in the development of benign protocols in organic synthesis [14-18] involving the use of inexpensive, reusable and efficient heterogeneous catalysts for the sustainable chemical advancements, herein, we report a simple and efficient method for the

direct synthesis of aromatic azo-compounds from anilines derivatives using $\text{MnO}_2@g\text{-C}_3\text{N}_4$ under photochemical conditions.

Experimental

Material/ chemicals details

KMnO_4 , Urea, HCl and all aromatic amines were purchased from Sigma-Aldrich (United States of America).

Synthesis of graphitic carbon nitride [19]

Urea (1.0 g) was taken in ceramic crucible and calcinated at 500 °C for 3 hours in furnace at ambient atmosphere. The temperature was brought down to room temperature and graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) was isolated as pale yellow solid.

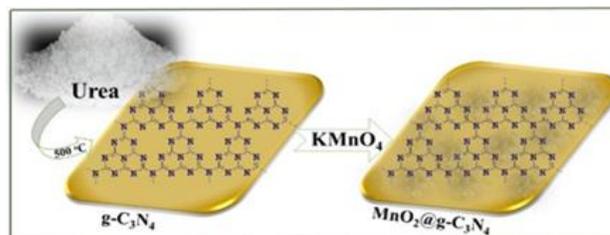


Fig. 1. Synthesis of $\text{MnO}_2@g\text{-C}_3\text{N}_4$.

Synthesis of graphitic carbon nitride supported manganese dioxide ($\text{MnO}_2@g\text{-C}_3\text{N}_4$) [20]

100 mg of $g\text{-C}_3\text{N}_4$ was dissolved in 40 ml water followed by the addition of 31 mg of KMnO_4 and 0.5 ml (1.0 M) HCl. The ensuing mixture was stirred for 10 min at room temperature. The solution was transferred into a Teflon-lined stainless steel autoclave and heated at 100 °C for

4 hours. The product was centrifuged, washed with methanol and dried under vacuum at 50 °C to afford the catalyst, graphitic carbon nitride supported manganese dioxide ($\text{MnO}_2@g\text{-C}_3\text{N}_4$), as an off-white solid (**Fig. 1**).

Synthesis of aromatic azo-compounds

In a 25mL round bottomed flask, aromatic amine (1 mmol), catalyst $\text{MnO}_2@g\text{-C}_3\text{N}_4$ (10 mg), 5 mL of acetonitrile were added and exposed to visible light irradiation using 20 watt domestic bulb. The progress of the reaction was monitored by TLC. After completion of the reaction, the $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst was separated using a centrifuge. The product was extracted using ethyl acetate, dried over sodium sulfate, concentrated and characterized using NMR.

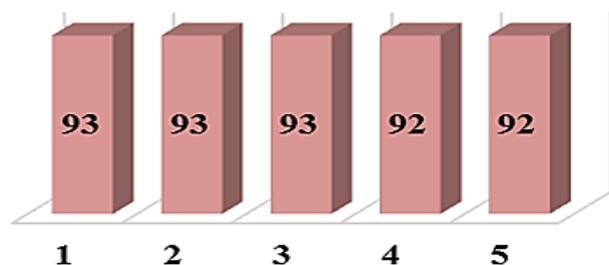


Fig. 2. Recycling of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst.

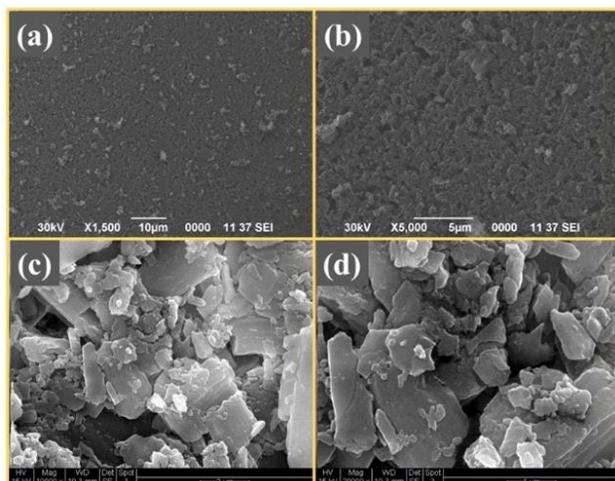


Fig. 3. SEM image of $g\text{-C}_3\text{N}_4$ (a, b) and $\text{MnO}_2@g\text{-C}_3\text{N}_4$ (c, d).

Recycling of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst

To establish the recyclability of the $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst for the oxidation of aromatic amines to aromatic azo-compounds, a set of experiments were performed using aniline as a model substrate. After the completion of each reaction the catalyst was recovered using centrifuge, washed with methanol and reused for the next reaction of aniline as fresh reagent. The $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst could be recycled and reused up to five times without losing its activity (**Fig. 2**). The SEM and XRD pattern of the catalyst before and after the reaction confirmed that there was no significant change in the morphology of the catalyst which also reaffirms the high stability of

$\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst in the course of reaction (**ESI, S1 and S2**).

Results and discussion

The synthesized catalyst, $\text{MnO}_2@g\text{-C}_3\text{N}_4$ was characterized using scanning electron microscope (SEM), X-ray diffraction (XRD). The SEM images (**Fig. 3**) of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ confirmed the immobilization of manganese dioxide on $g\text{-C}_3\text{N}_4$ with the visible difference in their morphology before and after the impregnation; which was further supported by XRD analysis (**Fig. 4**).

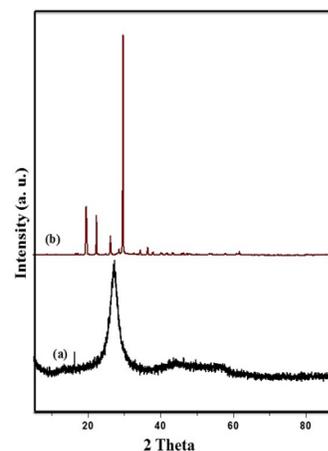
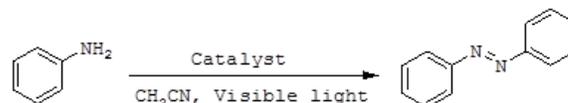


Fig. 4. XRD analysis of a) $g\text{-C}_3\text{N}_4$; b) $\text{MnO}_2@g\text{-C}_3\text{N}_4$.

Table 1. Reaction optimization^a



Entry	Catalyst	Yield ^b
1	$\text{MnO}_2@g\text{-C}_3\text{N}_4$ (2 mg)	33%
2	$\text{MnO}_2@g\text{-C}_3\text{N}_4$ (5 mg)	78%
3	$\text{MnO}_2@g\text{-C}_3\text{N}_4$ (10 mg)	93%
4	$\text{MnO}_2@g\text{-C}_3\text{N}_4$ (15 mg)	93%
5	$g\text{-C}_3\text{N}_4$ (20 mg)	6%
6	MnO_2 (20 mg)	44%
7 ^c	$\text{MnO}_2@g\text{-C}_3\text{N}_4$ (10 mg)	-

Reaction condition: a) Aniline (1 mmol), CH_3CN (5 ml), 20 W domestic bulb, Room Temperature, 12 h; b) Isolated yield; c) Reaction was performed in dark

Implementing the inherent affinity of graphitic carbon nitride towards the visible light, the activity of graphitic carbon nitride supported manganese dioxide was examined in the oxidation of aniline at room temperature. The preliminary outcomes acquired during the reaction optimization are summarized in **Table 1**. The oxidation of aniline into azobenzene was performed using 2 mg, 5 mg, 10 mg and 15 mg of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ in acetonitrile (**Table 1; entries 1-4**). 10 mg of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst was found to be most effective as it offered highest yield of azobenzene (**Table 1, entry 3**). Further increase in wt%

of $\text{MnO}_2@g\text{-C}_3\text{N}_4$ did not show any significant change in yield (**Table 1, entry 4**). The control experiments were performed using $g\text{-C}_3\text{N}_4$ (**Table 1, entry 5**) and MnO_2 (**Table 1, entry 6**); MnO_2 gave only 44% of azobenzene. In the absence of visible light the starting material remained intact as it gave no desired product (**Table 1, entry 7**).

Accordingly, a wide range of substituted aromatic amines were subjected towards the direct oxidation at room temperature using 20 W domestic bulb as a source of visible light (**Table 2, entries 1-5**). The reaction with different substituted amines bearing electron donating (**Table 2; entries 2-3**) and electron withdrawing substituents (**Table 2; entries 4-5**) did not show any significant difference in reactivity and product outcome (**Table 2; entries 2-5**).

Table 2. Synthesis of aromatic azo compounds^a

Entry	Reactant	Product	Yield ^b
1			93%
2			91%
3			91%
4			93%
5			92%

Reaction condition: a) Aromatic amine (1 mmol), CH_3CN (5 ml), 20 W domestic bulb, Room temperature, 12 h; b) Isolated Yield

Conclusion

The present work represents a simple and highly efficient method for the synthesis of aromatic azo-compounds using photoactive $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst at room temperature. The prominent aspect of this reaction is the use of visible light, which was trapped by $\text{MnO}_2@g\text{-C}_3\text{N}_4$ and used in the direct oxidation of aromatic amines.

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Author's contributions

Conceived the plan: SV, RSV; Performed the experiments: SV; Data analysis: SV; Guided the Research: RSV; Wrote the paper: SV, RSV. Authors have no competing financial interests.

Supporting information

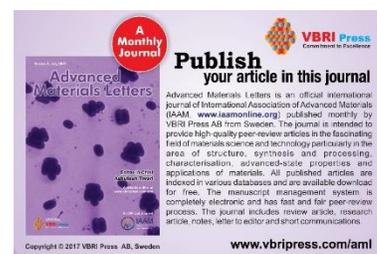
SEM of recycled $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst, XRD of recycled $\text{MnO}_2@g\text{-C}_3\text{N}_4$ catalyst, ^1H NMR and ^{13}C NMR of the product. Supporting informations are available from VBRI Press.

Disclaimer

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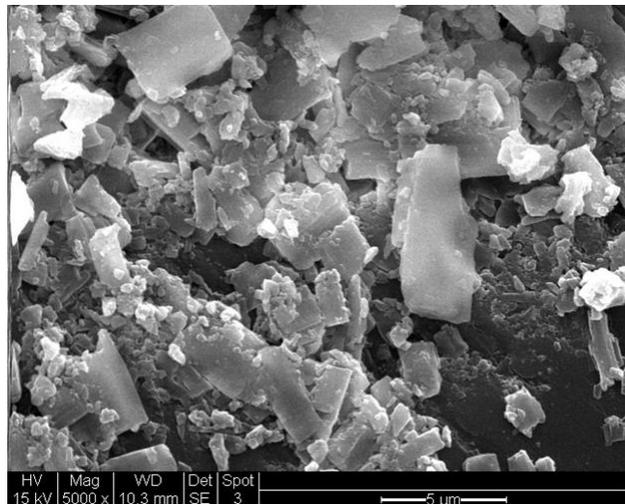
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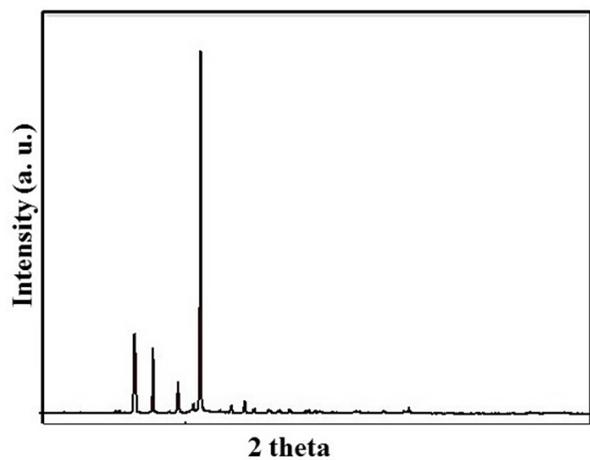
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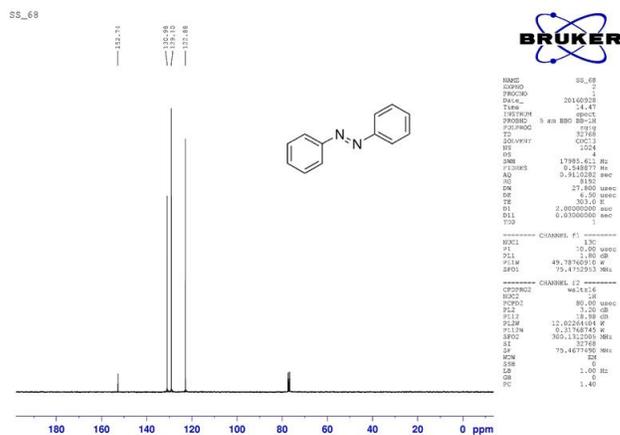
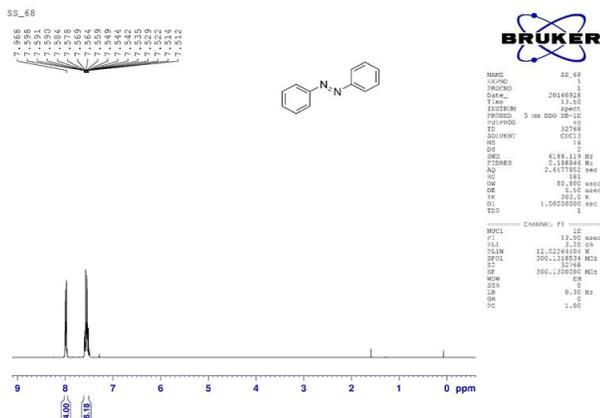
Supporting Information



S1. SEM of recycled MnO₂@g-C₃N₄ catalyst.



S2. XRD of recycled MnO₂@g-C₃N₄ catalyst.



S3. ¹H and ¹³C NMR of Azobenzene.