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## ARTICLE



# Quaternary ammonium hydroxide-functionalized $g-C_3N_4$ catalyst for aerobic hydroxylation of arylboronic acids to phenols

# Ibrahim Muhammad<sup>1</sup> 💿

Subramaniyan Mannathan<sup>2</sup> | Manickam Sasidharan<sup>1</sup>

<sup>1</sup>SRM Research Institute and Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur, Tamilnadu, India

<sup>2</sup>Department of Chemistry, SRM University-AP, Amaravati, Andhra Pradesh, India

#### Correspondence

Manickam Sasidharan, SRM Research Institute and Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur, Tamilnadu, India. Email: sasidham@srmist.edu.in Subramaniyan Mannathan, Department of Chemistry, SRM University-AP, Amaravati, Andhra Pradesh, India. Email: mannathan.s@srmap.edu.in

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# Abstract

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A new and efficient metal-free approach toward the synthesis of phenols via an aerobic hydroxylation of arylboronic acids by using a novel quaternary ammonium hydroxide g-C<sub>3</sub>N<sub>4</sub> catalyst has been described. The functionalized quaternary ammonium hydroxide (g-C<sub>3</sub>N<sub>4</sub>-OH) has been prepared from graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) scaffold by converting the residual  $-NH_2$  and -NH groups to quaternary methyl ammonium iodide by performing a methylation reaction with methyl iodide followed by ion-exchange with 0.1 N KOH or anion exchange resin Amberlyst A26 (OH- form) by post-synthetic modification. The resultant g-C<sub>3</sub>N<sub>4</sub>-OH was characterized by XRD, FTIR, field-emission scanning electron microscope (FESEM), high-resolution transmission electron microscope (HRTEM), N<sub>2</sub> adsorption/desorption isotherms, and acid-base titration. Tested as solid-base catalysts, the g-C<sub>3</sub>N<sub>4</sub>-OH showed excellent catalytic activity in the aerobic hydroxylation reaction by converting a variety of arylboronic acids to the corresponding phenols in high yields. More importantly, the g-C<sub>3</sub>N<sub>4</sub>-OH solid-base has been successfully reused four times with the minor loss of initial catalytic activity (10.5%).

#### K E Y W O R D S

aerobic hydroxylation, functionalization of g- $C_3N_4$ , heterogeneous catalyst, phenols, quaternary ammonium hydroxide

# **1** | INTRODUCTION

In recent years, metal-free organic polymeric materials have received great attention as heterogeneous catalysts owing to their abundance, nontoxicity, chemical/thermal stability, and readily tailorable surface chemistry.<sup>[1–3]</sup> Carbon as heterogeneous catalysts allows controlling their surface chemistry and designing catalytic sites for a specific application. In this perspective, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has received great attention because of its photocatalytic and other diverse applications.<sup>[1–3]</sup> In the last decade, g-C<sub>3</sub>N<sub>4</sub> has been extensively investigated in the field of photo-catalysis because of its interesting electronic and optical properties, photo-electrochemical water splitting,<sup>[4,5]</sup> CO<sub>2</sub> reduction,<sup>[6,7]</sup> and photocatalytic degradation of pollutants.<sup>[8–11]</sup> Later on, g-C<sub>3</sub>N<sub>4</sub> was also widely studied as versatile support for noble metals to accomplish photocatalytic hydroxylation of benzene, oxidation and hydrogenation reactions, Suzuki and Sonogashira couplings, and Knoevenagel reaction.<sup>[12–16]</sup> In the context of metal-free catalysis, g-C<sub>3</sub>N<sub>4</sub> has been tethered with several functional groups such as amines, polyethyleneimine (PEI), and hydrazine either by chemical grafting or physical impregnation for CO<sub>2</sub> capture, CO<sub>2</sub> reduction, and water splitting to H<sub>2</sub>.<sup>[17–19]</sup> Later on, boronic

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2

acid and phenyl groups were also chemically functionalized on the surface of g-C<sub>3</sub>N<sub>4</sub> scaffold to enhance the photoluminescence and sensing properties, which helps in the detection of glycoprotein under physiological environments.<sup>[20,21]</sup> However, g-C<sub>3</sub>N<sub>4</sub> has rarely been utilized in non-photocatalytic heterogeneous catalysis for organic transformations. Very recently, -SO<sub>3</sub>H functionality has been anchored onto the g-C<sub>3</sub>N<sub>4</sub> matrix, which served as an efficient solid-acid catalyst in Biginelli three component coupling reactions.<sup>[22]</sup> Mesoporous g-C<sub>3</sub>N<sub>4</sub> has also been scrutinized for thermal reactions involving oxidation, and hydrogenation reactions without any light illumination.<sup>[23,24]</sup> In view of academic and industrial relevance, phenols constitute an essential class of compounds mainly due to its importance in biological, pharmaceuticals, and polymer industries.<sup>[25]</sup> Among the several methods that have been developed for phenol synthesis, oxidative hydroxylation of organoboronic acids represents a simple and elegant approach to obtain phenols and its derivatives in an efficient way. Conventionally, peroxides, oxones, benzoquinones, N-oxides, and hypervalent iodine compounds were employed to accomplish such а transformation.<sup>[26-29]</sup> However, nowadays, the eco-friendly molecular oxygen ( $O_2$  and air) are conveniently used as an effective oxidant, albeit in the presence of transition metal catalysts or under photochemical reaction conditions.<sup>[30,31]</sup> Despite these advances, hydroxylation of organoboronic acids to give phenols with heterogeneous organocatalyst is scarcely studied.<sup>[32]</sup> Particularly, methods involving heterogeneous organo-catalysts under photochemical free conditions remain underdeveloped. Herein we report an aerobic hydroxylation of arylboronic acids by using a novel quaternary ammonium hydroxide g-C<sub>3</sub>N<sub>4</sub> catalyst.<sup>[33]</sup> The functionalized quaternary ammonium hydroxide (g-C<sub>3</sub>N<sub>4</sub>-OH) was prepared from graphitic carbon nitride  $(g-C_3N_4)$ scaffold by converting the residual -NH<sub>2</sub> and -NH groups to quaternary methyl ammonium iodide by performing a methylation reaction with methyl iodide followed by ionexchange with 0.1 N KOH or anion exchange resin (Amberlyst-A26) by post-synthetic modification (Scheme 1). The resultant solid base was thoroughly characterized by XRD, FTIR, FESEM, HRTEM, and acid-base titration.

#### 2 | RESULTS AND DISCUSSION

The crystallinity of pristine g-C<sub>3</sub>N<sub>4</sub>, quaternary ammonium salt (g-C<sub>3</sub>N<sub>4</sub>-I), and quaternary ammonium hydroxides (g-C<sub>3</sub>N<sub>4</sub>-OH) were assessed with powder X-ray diffraction as shown in Figure 1. The pristine g-C<sub>3</sub>N<sub>4</sub> exhibits an intense peak at  $27.4^{\circ}$  corresponding to (002) reflection, which is ascribed to graphite-like interlayerstacking<sup>[16]</sup>; whereas other weak (100) reflection at  $13.1^{\circ}$ is attributed to in-plane tris-s-triazine motif structural packing. On treatment with methyl iodide and subsequent conversion to g-C<sub>3</sub>N<sub>4</sub>-OH, the diffraction peak features are well maintained except that the intensity of (100) peak is rather reduced. These observations suggest that possible delamination of g-C<sub>3</sub>N<sub>4</sub> layer and subsequent restacking upon treatment with CH<sub>3</sub>I and KOH (0.1 N KOH). The XRD results indeed confirm the high stability of g-C<sub>3</sub>N<sub>4</sub> toward functional group modification.

The FTIR spectra of pristine and functionalized samples are shown in Figure 2a-c. The broad absorption bands at 2,830-3,450 cm<sup>-1</sup> are assigned to N-H stretching vibration.<sup>[34]</sup> The bands observed between 1,000 and 1,650 cm<sup>-1</sup> corresponds to C=N and C-N heterocyclic aromatic ring units, which are characteristic peaks of tris-s-triazine as observed in the case of XRD.<sup>[35]</sup> Upon treatment with methyl iodide, the intensity of N-H rocking vibration at 703 and 782 cm<sup>-1</sup> decreased significantly, and the appearance of a new band at  $802 \text{ cm}^{-1}$ (O-H out of plane bending vibration) confirms the formation of g-C<sub>3</sub>N<sub>4</sub>-OH. However, due to overlapping of – NH and -OH stretching vibrational frequencies, functional group information could not be drawn in the highfrequency region between 3,000–3,600 cm<sup>-1</sup>. We further investigated the morphological features with electron microscope (FESEM and HRTEM). Scanning electron microscope of pristine g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>-I, and g-C<sub>3</sub>N<sub>4</sub>-OH materials showed rod-like morphology (Figure 3a-c); the particle size of pristine material was found to be  $\sim$ 2–7 µm in length with thickness of about 200-300 nm, whereas the post-synthetically modified g-C<sub>3</sub>N<sub>4</sub>-I, and g-C<sub>3</sub>N<sub>4</sub>-OH materials were found to be in the range of 1-3 µm in length. The rod-like morphology was further observed



**SCHEME 1** Schematic representation of the formation of  $g-C_3N_4$ -OH(c) from  $g-C_3N_4(a)$ 

with high-resolution TEM, which revealed nano-rods of size approximately ~1–2  $\mu$ m in length as shown in Figure 3d–f. The textural features were evaluated with N<sub>2</sub> sorption at liquid nitrogen temperature, 77 K (Figure 4a–c). Both pristine g-C<sub>3</sub>N<sub>4</sub> as well as modified g-C<sub>3</sub>N<sub>4</sub>-I, and g-C<sub>3</sub>N<sub>4</sub>-OH samples showed irregular large mesopores of size ranging 2–12 nm. The large pores could have originated from restacking and refolding of inter-layers and rod-like particles. The BET surface of all the materials was found to be between 38–87 m<sup>2</sup>/g<sup>-1</sup>, while the pore volume was



**FIGURE 1** Powder X-ray diffraction pattern of  $g-C_3N_4$ ,  $g-C_3N_4$ -I and  $g-C_3N_4$ -OH

found to be 161 and 208 ml/g<sup>-1</sup> for  $g-C_3N_4$  and  $g-C_3N_4$ -I, respectively. However, pore volume of  $g-C_3N_4$ -OH was found to be lower ~61 ml/g<sup>-1</sup>, possibly due to restacking of inter-layers after treatment with KOH during anion exchange. The concentration of OH<sup>-</sup> estimated by acidbase titration was found to be 1.6 mmol/g of  $g-C_3N_4$ -OH.

After characterizing g-C<sub>3</sub>N<sub>4</sub>-OH, the efficacy of the solid base for the hydroxylation of phenylboronic acid (1a) to phenol (2a) was investigated (Table 1). Preliminary studies on solvent screening indicated that the reactions with water, acetonitrile, t-butanol, toluene, DMF, and dichloroethane as solvents are totally ineffective at  $100^{\circ}$ C with g-C<sub>3</sub>N<sub>4</sub>-OH (20 wt%). However, changing the solvent to THF, and 1,4-dioxane gave 2a in 61 and 82% yields, respectively (Table 1, entries 1-2). Notably, binary solvent system comprising THF as cosolvent, significantly improved the desired product yield. Among them, solvent systems such as H<sub>2</sub>O/THF, acetonitrile/THF, and t-butanol/THF, and toluene/THF in the ratio of 4:1 (2 ml) provided 2a in 96, 92, and 95% yields, respectively (entries 3-5). As shown in Table 1, lowering the reaction temperature, catalyst loading, and reaction duration led to an incomplete conversion (entries 7–13). The g- $C_3N_4$  serves as functional support for anchoring quaternary ammonium hydroxide ( $\equiv N^+$ OH<sup>-</sup>) and moreover, no reaction was observed in the absence of catalyst (entry 14) and also in the presence of either pristine  $g-C_3N_4$  or quaternary ammonium salt (g- $C_3N_4$ -I). Similarly, no hydroxylation was realized for the reaction carried out in an inert atmosphere, which



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FIGURE 4  $N_2$  adsorption/ desorption isotherms of g- $C_3N_4$ (a); g- $C_3N_4$ -I (b); and g- $C_3N_4$ -OH (c)

indeed signifies the importance of oxygen in aerobic hydroxylation (entry 15). Thus, the 20 wt% catalyst and  $H_2O/THF$  solvent system (4:1, 2 ml) at 100°C for 12 hr was chosen as the final optimized conditions (Table 1) for further investigation.

With the above standard reaction conditions, we investigated the scope of the reaction using different kinds of substituted phenylboronic acids (Table 2). All substituted arylboronic acids proceeded smoothly and afforded the corresponding phenolic compounds in good to excellent yields (66–96%). Both electron-donating and electron-withdrawing substituents like methyl, methoxy, fluoro, chloro, bromo, trifluoromethyl, cyano, carbonyl, and nitro containing aryl boronic acids were progressed

well and gave the corresponding phenolic compounds in good to high yields. The nature of substituents on the phenyl ring at *para-*, or *ortho* positions on phenylboronic acids has no major effect on the yield (Table 2). In order to investigate the reusability of solid base, we recovered the catalyst by centrifugation, washed thoroughly with ethanol and water, and vacuum dried for overnight. Then the reaction was performed under identical conditions and the catalyst furnished 86% yield after four successive recycles with loss of 10.5% initial activity.

Based on the literature reports,  $^{[36-39]}$  a plausible mechanism is proposed as shown in Scheme 2. The reaction may be initiated by forming superoxide radical ion I via single electron transfer from OH<sup>-</sup> ion to O<sub>2</sub>. The, superoxide



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**TABLE 1**Optimization ofreaction conditions for aerobichydroxylation of phenylboronic acida

Solvent, T°C				
<b>1a</b> 12 h <b>2a</b>				
Entry	Solvents	Temp. (°C)	Cat. loading (Wt%)	Yield (%) <sup>b</sup>
1	THF	100	20	61
2	1,4-dioxane	100	20	82
3	H <sub>2</sub> O/THF	100	20	96
4	CH <sub>3</sub> CN/THF	100	20	92
5	<i>t</i> -butanol/THF	100	20	95
6	Toluene/THF	100	20	56
7	H <sub>2</sub> O/THF	90	20	74
8	H <sub>2</sub> O/THF	80	20	31
9	H <sub>2</sub> O/THF	100	5	18
10	H <sub>2</sub> O/THF	100	10	43
11	H <sub>2</sub> O/THF	100	15	74
12 <sup>c</sup>	H <sub>2</sub> O/THF	100	20	79
13 <sup>d</sup>	$H_2O/THF$	100	20	63
14	H <sub>2</sub> O/THF	100	No catalyst	_
$15^{\rm e}$	$H_2O/THF$	100	20	

g-C<sub>3</sub>N<sub>4</sub>-OH

<sup>a</sup>All the reactions were carried out using phenylboronic acid **1a** (1.0 mmol), H<sub>2</sub>O/THF (4:1 ratio, 2 ml), g-C<sub>3</sub>N<sub>4</sub>-OH (20 wt%) at 100°C for 12 hr.

<sup>b</sup>Isolated yields.

<sup>c</sup>Reaction time 10 hr.

<sup>d</sup>Reaction time 8 hr.

<sup>e</sup>Reaction was carried out in an inert atmosphere.

radical anion reacts with **1a** to give the intermediate **II** and further protonation gives **III**. The hydroxyl ion was obtained back during 1, 2-aryl shift of the intermediate **III** and the final phenol products **2a** was obtained after the hydrolysis of **IV**. To have an insight on the mechanism of the reaction, we carried out control reactions using a radical scavenger (TEMPO). Thus, the reaction of **1a** with 1.0 equivalent of TEMPO yielded 18% of **2a**. The reduction in the yield of **2a** is ascribed to the scavenging of radical intermediate during the course of reaction. Notably, with 2.5 equivalent of TEMPO, no hydroxylation reaction was observed which in turn confirms that the reaction may proceed via a radical pathway mechanism.

# 3 | EXPERIMENTAL

## 3.1 | Synthesis of g-C<sub>3</sub>N<sub>4</sub>

Nanosilica (0.5 g) (10 nm) and 4.0 g melamine was dispersed by stirring in 5 ml ethanol in a round bottom flask (50 ml). Then the content was refluxed at 70°C for 6 hr with continuous stirring. Then, the solvent was removed

under vacuum using a rotary evaporator and the resultant white solid was dried in an oven at 80°C for 24 hr under air. The dried white solid was transferred to a crucible and heated in a tubular furnace under nitrogen at 500°C for 4 hr with heating rate of 3°C/min. The resultant pale yellow material with yield of 2.30 g was collected and ground well using mortar and pestle. Finally, the pore forming nanosilica template was removed by stirring with 15.0 ml of 5% dil. HF per gram of material for 24 hr at room temperature. Then, the sample was thoroughly washed with water until the filtrate attains a neutral pH. The final material was dried in an oven at 80°C for overnight and the yield of the final product was found to be 1.7 g.

# 3.2 | Conversion of $g-C_3N_4$ to $g-C_3N_4$ -I and $g-C_3N_4$ -OH

In a typical reaction, 0.5 g of  $g-C_3N_4$  was suspended in a mixture of 4.0 ml methanol and 1.8 ml methyl iodide in a 50 ml round bottom flask and covered with a septum to avoid vaporization of solvent as well as the methyl iodide. The content was then stirred for 24 hr at 25°C and then



<sup>a</sup>All the reactions were carried out with **1a-o** (1.0 mmol),  $g-C_3N_4$ -OH (20 wt%) in H<sub>2</sub>O/THF (4:1; 2.0 ml) at 100°C for 12 hr unless otherwise mentioned.

washed with ethanol thoroughly to remove the excess methyl iodide to get g-C<sub>3</sub>N<sub>4</sub>-I. The material was dried in an oven at 40°C for 24 hr. To obtain g-C<sub>3</sub>N<sub>4</sub>-OH, 1 g of g-C<sub>3</sub>N<sub>4</sub>-I was treated with either 10 ml KOH (0.1 M) or Amberlyst-A26 anion exchange resin at room temperature for 2 hr. Then the resultant solid was washed with copious water and then dried under vacuum at 40°C for overnight and stored in a desiccator.

#### 3.3 | Acid-base titration of g-C<sub>3</sub>N<sub>4</sub>-OH

Back titration procedure has been used to estimate the concentration of OH<sup>-</sup> liberated by the g-C<sub>3</sub>N<sub>4</sub>-OH in 20 ml distilled water. In a typical experiment, 0.5 g of g-C<sub>3</sub>N<sub>4</sub>-OH was suspended in a mixture containing 20 ml distilled water, 0.5 g NaCl, and 10 ml of HCl (0.1 M) and stirred at room temperature for 24 hr for completion of neutralization of [OH<sup>-</sup>], which was released from the catalyst (g-C<sub>3</sub>N<sub>4</sub>-OH).<sup>[22,40]</sup> Then, two drops of phenolphthalein indicator were added to the aqueous solution and the excess [H<sup>+</sup>] was titrated with 0.1 M NaOH until the appearance of pink color.



**SCHEME 2** A plausible mechanism for the aerobic hydroxylation of arylboronic acid to phenol

# 3.4 | Hydroxylation of phenylboronic acids

In typical hydroxylation of phenylboronic acid to phenol, phenylboronic acid (1.0 mmol) and mixture of H<sub>2</sub>O/THF (2 ml, 4:1 ratio) were added to a 50 ml round bottom (RB) flask. The RB flask fitted with a condenser was placed in a preheated oil bath and stirred at 100°C for 12 hr. The reaction progress was monitored by thin layer chromatography (TLC) and after completion; the reaction mixture was allowed to cool down to ambiance temperature. The reaction mixture was extracted with ethyl acetate (3 ml × 3), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. Column chromatography was used to isolate the product from the concentrated crude reaction mixture.

#### 4 | CONCLUSIONS

In summary, we have demonstrated a new and efficient protocol for the hydroxylation of arylboronic acids to phenols by using quaternary ammonium hydroxide functionalized graphitic carbon nitride ( $g-C_3N_4$ ). The catalyst was prepared through modification of -NH and – NH<sub>2</sub> groups in the carbon nitride (g-C<sub>3</sub>N<sub>4</sub>). The XRD data showed high crystallinity of functionalized materials similar to pristine g-C<sub>3</sub>N<sub>4</sub>. FTIR spectral data confirmed the –NH<sub>2</sub> functional group transformation and formation of g-C<sub>3</sub>N<sub>4</sub>-OH. The concentration of OH<sup>-</sup> ions was found to be 1.6 mmol per gram of g-C<sub>3</sub>N<sub>4</sub>-OH. The present solid-base catalysts will be highly useful for scientists who are working in the areas of catalysis and organic synthesis.

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#### ORCID

Ibrahim Muhammad D https://orcid.org/0000-0002-7254-6446

Subramaniyan Mannathan https://orcid.org/0000-0002-3114-8265

Manickam Sasidharan <sup>10</sup> https://orcid.org/0000-0002-0795-7062

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7

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