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Visible Light-Catalytic Hydroxylation of Aryl Halides with Water to Phenols by Carbon Nitride and Nickel Complex Cooperative Catalysis

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The efficient conversion of aryl halides to phenols under mild reaction conditions remains a grand challenge. Here we demonstrate that a facile and efficient hydroxylation reaction of aryl halides with water could be accomplished through a merger of a heterogeneous organic semiconductor graphitic carbon nitride (g-C₃N₄) photocatalyst and a homogeneous nickel(II) bipyridine organometallic catalyst under visible-light irradiation at room temperature. The protocol is tolerant to a wide range of substituted aryl halides, resulting in various phenol products with excellent conversion and selectivity. Noted that the OH group of the resulting phenols originated from water increased the environmental friendliness of the reaction. Noted that, among all the previously reported catalysts (even including thermal catalysts with harsh reaction conditions), our Nidabpy/g-C₃N₄ dual catalysis system demonstrated the highest reported catalytic activity in the shortest reaction time. This remarkable catalytic performance was attributed to the strong interaction between Nidabpy complex and g-C₃N₄, which decreased the transfer distance of photo-generated electrons transferring to Ni(II), accelerating the catalytic cycle. Furthermore, g-C₃N₄ was easily recovered from the reaction mixture and reused five times, showing the good potential for larger-scale industrial application of green hydroxylation reactions.

Introduction

Phenols, as a common compound in natural products and minerals, are widely used in pesticide production, drug synthesis and industrial materials over the world¹⁻². Moreover, as an important intermediate, the demand for phenolic compounds in the industry has increased year by year, and its production currently exceeds 7.2 megatons per year³. Direct oxidation of benzene through three-step cumene process is a currently used method for the production of phenols in worldwide industrial practice, where benzene are used as starting materials. But, the cumene process suffers from various drawbacks, including high energy-consuming, significant amounts of byproducts and wastes.⁴ Compared with the above methods, hydroxylation of aryl halides is considered to be one of the most promising methods due to the abundance of various low-toxicity haloarenes.⁵ Recently, A series of copper, iron and palladium catalysts has been successfully developed to prepare phenols from unactivated aryl halides (Scheme 1A)⁶⁻¹⁰. However, these transformation methods usually require high temperature, strong base, resulting in a limited range of substrate applications. Furthermore, high energy consumption and strong corrosion inevitably generate considerable amounts of pollutant and waste. Also, these homogenous metal and organo-metal catalysts are hard to reuse and recycle, which is not suitable for continuous production process.¹¹⁻¹²

Despite these achievements, the hydroxylation of aryl halides with green nucleophiles by using base metals is believed to be a more promising strategy for the synthesis of phenols. Recently, MacMillan and Xue reported a photocatalytic redox and transition metal Ni(II) dual-catalytic systems for the hydroxylation of aryl halides with water as a nucleophile, which was considered to be a major advancement progress in this field (Scheme 1B)¹³⁻ ¹⁴. However, homogeneous iridium, and ruthenium based photosensitizers are expensive and toxic. Organic dyes, such as eosin Y, acridinium salts, perylene and boron-dipyrromethene derivatives (BODIPY) as photosensitizers usually complicated synthesis steps and are easily decomposed, which bring the potential environmental risks.¹⁵ Accordingly, the catalytic conversion of aryl halides to phenols by heterogeneous photocatalytic strategy with minimum waste production is of high significance from an academic as well as industrial point of view.

Heterogeneous semiconductors as a class of recyclable photocatalysts have been extensively applied to hydrogen generation, water oxidation, organic pollutants degradation,

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organic synthesis, and carbon dioxide reduction. Recently, heterogeneous semiconductor photocatalysts/Ni(II) dualcatalytic systems has recently attracted widespread attention owing to its excellent photocatalytic activity. Wu and co-workers developed nickel/CdSe quantum dots for dehydrogenative oxidation.¹⁶ Xiao group used nickel/CdS for C-N and C-O coupling reactions of aryl halides.¹⁷ Scaiano demonstrated that nickel/TiO₂ can be utilized as an efficient heterogeneous photoredox catalyst in the decarboxylative cross-coupling of carboxylic acids with aryl iodides.¹⁸ However, Cadmium-based semiconductors are unstable and easily decompose into highly toxic Cd ions. TiO₂ can only be used under ultraviolet light due to its wide band gap about 3.2 eV. Compared with the semiconductors above, graphitic carbon nitride (g-C₃N₄) is a low toxicity, recyclable, metal-free and cheap heterogeneous visible light photocatalyst with excellent electron-transfer ability and high thermal stability.¹⁹⁻²¹ Recently, Seeberger's group reported that g-C₃N₄/nickel can induce selective C-O cross-couplings of carboxylic acids with aryl halides.²² Pieber and co-workers developed a similar catalyst system Ni/g-C₃N₄ for C-O coupling.²³ König's group found mesoporous g-C₃N₄ and a homogeneous nickel catalyst can activate organoboron cross-coupling reactions.²⁴ However, to our knowledge, the synergistic combination of g-C₃N₄ and Ni(II) complex for hydroxylation reaction of aryl halides with water have not been reported so far. Herein, for the first time, we developed a synergistic combination of $g-C_3N_4$ and nickel(II) bipyridine to efficiently prepare phenols from unactivated aryl halides by using water as the sole nucleophile (Scheme 1C). This excellent photocatalytic activity is attributed to the Nidabpy is easily attached to the surface of g-C₃N₄ by electrostatic action, which promotes effective interface transfer and spatial separation of photo-generated electron-hole pairs. Meanwhile, the results confirmed the cooperative effect of Nidabpy and g-C₃N₄, in which the Ni domains demonstrated the high ability to activate aryl halides to phenols and g-C₃N₄ is excited by visible light to produce photo-generated electron-hole pairs. Furthermore, the nanosheet structure of g-C₃N₄ reduced the diffusion limitation of the reactants. Moreover, $g\text{-}C_3N_4$ is easily recovered from the reaction mixture and reused.

A. Thermal catalysis

h+ b+ h+, h+, 🦓



Scheme 1 Synthesis of phenols from aryl halides by different catalytic strategies.

Experimental section

Synthesis of graphitic carbon nitride $(g-C_3N_4)$. In a typical preparation, 20 g urea was put into a sealed crucible, and treated to 550°C at a heating rate of 5.0°C/min for 4.0 h to get a pale yellow solid. The solid was washed with water. Subsequently, the sample was dried under vacuum at 100°C overnight to remove the solvents.

Characterization.

Powder X-ray diffraction (PXRD) data was obtained on a Rigaku D/maxr B diffractometer using Cu K α radiation. UV-Vis spectra were measured on a Shimadzu UV 2600 spectrometer. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet Magna 550 spectrometer. The surface electronic states of nickel and nitrogen were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA using Al K α as the excitation source with a base pressure of 10⁻⁹ Torr). All the binding energy values were calibrated by using C1s = 284.6 eV as a reference. Morphology was observed by field scanning electron microscopy (FESEM, HITACHI, S-4800). The electrochemical tests (photocurrent and EIS) were done on an electrochemical analyzer (CHI660D Instruments) in a standard three electrode system.

Activity Test.

In a typical run, an oven dried quartz vial (20 × 100 mm) equipped with a stir bar was charged with the 4-bromobenzonitrile (91.1 mg, 0.5 mmol, 1.0 equiv.), NiBr2·glyme (2.0 mol%), 2,2'bipyridine-5,5'-diamine (dabpy 2.0 mol%) and $g-C_3N_4$ (50 mg). Then, DMF/CH₃CN (1:1, 3.0 mL), H₂O (360 μL, 20 equiv.) and Et₃N (0.75 mmol, 1.5 equiv.) were added and the vial was sealed with a rubber plug. The reaction mixture was sonicated and stirred for 20 min. Thereafter, the mixture was degassed by bubbling nitrogen for 10 min. The reaction mixture was irradiated in the 300 W xenon lamp (>420 nm) at 25°C with rapid stirring. After that, the reaction mixture was filtered. The obtained organic phase was diluted with chromatographic grade methanol and the volume was fixed in a 1.0 mL analysis bottle. The sample was analysed by an Agilent 6410 Series Triple Quad high performance liquid chromatography with Agilent C18 reverse phase chromatographic column. The conversion of aromatic halides and the yield of phenol products were determined by using trimethylbenzene as internal standard sample. All the data was repeated at least twice, and the data error was guaranteed within ±5 %.

Recyclability Test

In order to determine the stability of g-C₃N₄, it was allowed to settle down after each run of the reactions and then the clear supernatant liquid was decanted slowly. The residual solid catalyst was washed and reused with fresh charge with fresh charge of solvent and the reactants for subsequent reaction under the same conditions.

Results and discussion

To evaluate the suitability of Nidabpy $/g-C_3N_4$ as photoredox catalyst for the hydroxylation reaction of aryl halides with water, we used a model reaction with 4-bromobenzonitrile (1a) as the

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substrate. In particular, Table S1 shows the results of the exploratory experiments of the hydroxylation reaction by using different materials as the photocatalysts. Commercial cuprous oxide (Cu₂O), iron oxide (α -Fe₂O₃) and tungsten oxide (WO₃) did not promote the reaction at all (Table S1 entry 1-3), cadmium sulphide (CdS) only afforded the desired product of phenol in low yields (4.2%, Table S1 entry 4). Interestingly, graphitic carbon nitride (g-C₃N₄) displayed the good conversion (67.1%) and excellent yield (66.5%) at 25 °C after 6.0 h irradiation with xenon lamp (>420 nm) under nitrogen conditions (Table S1 entry 5). The inferior catalytic performances of entry 2-3 were probably attributed to its low conduction band position despite having the ability to absorb both visible and ultraviolet light (Figure S2). We further extended the reaction time to 12 h, and excellent conversion of 4-bromobenzonitrile (99.9 %) and phenol yield (99.9 %) were obtained (Table S2).

Table 1 Optimization of reaction conditions.^a



Entry	Conditions	Conversion (%)	Yield (%) ^b	
1	standard conditions	99.9	99.9	
2	blank	trace	trace	
3	no photocatalyst	10.1	9.10	
4	no Ni catalyst, no base	trace	trace	
5	no Ni catalyst	trace	trace	
6	no base	trace	trace	
7	no dabpy	31.1	30.7	
8	air instead of nitrogen	34.8	34.0	
9	no H ₂ O	trace	trace	

^aReaction conditions: 4-bromobenzonitrile (1a) (91.1 mg, 0.5 mmol, 1.0 equiv), NiBr₂·glyme (2.0 mol%), dabpy (2.0 mol%), g- C_3N_4 (50 mg), DMF/CH_3CN (1:1, 3.0 mL), H_2O (360 $\mu L,$ 20 equiv), Et₃N (0.75 mmol, 1.5 equiv), N₂, xenon lamp (>420 nm), 12 h. ^bDetermined by HPLC anlysis against an internal standard.

Next, the control test revealed that the blank experiment without Nidabpy $/g-C_3N_4$ catalyst didn't gives any products. Furthermore, light, g-C₃N₄, NiBr₂glyme, 5,5'-diamino-2,2'-bipyridine (dabpy), triethylamine (Et₃N) and anaerobic conditions were proved to be necessary conditions for successful hydroxylation reaction of aryl halides with water. The OH group of the resulting phenols originates from water was demonstrated by the absence of the desired product when it was omitted. Then, we found that the type of base had a critical influence on the reactivity. Compared with thermally catalyzed hydroxylation reaction that needs to be performed in a strongly alkaline environment, the

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h of reaction, respectively. When dimethylphenylamine, DABCO							
and 2,6-lutidineare were selected as bases, none of the desired							
phenol products are obtained. Furthermore, inorganic bases							
cannot effectively promote the hydroxylation reaction, which							
may be attributed to the fact that inorganic bases cannot capture							
holes, resulting in photo-generated electrons and holes cannot							
be effectively separated and easily recombined, greatly reducing							
electron transfer efficiency. Next, the effects of nickel salts on							
hydroxylation reactivity were tested. As shown in Table S4, the							
use of NiBr ₂ or NiCl ₂ of without glyme ligand instead of							
NiBr ₂ ·glyme decreased the yield obviously. These resulted were							
probably attributed to the fact that the absence of glyme ligands							
which reduces the stability of the valence state of Ni(II) and was							
not conducive to the redox cycle of Ni(II). Furthermore, the effect							
of the reaction parameters including solvent types, the amount							
of solvent, the loading of photocatalyst and light intensity were							
investigated (Table S5-S9). Increasing the amount of							
photocatalyst and light intensity can greatly improve the reaction							
rate, which was due to the increase in the number of							
photogenerated carriers. Satisfactorily, Nidabpy $/g-C_3N_4$ catalyst							
achieved excellent conversion (99 %) and selectivity (99 %) by							
using triethylamine (Et ₃ N) as the base after 12.0 h irradiation with							
300 W xenon lamp (>420 nm) in DMF/acetonitrile mixed solvent.							
Among all the reported active catalysts (even including thermal							
systems with harsh reaction conditions), our Nidabov /g-C ₂ N ₄							
dual catalysis system demonstrates the highest reported catalytic							
activity in the shortest time (Figure 1). Encouraged by the above							
results, we extended the scope of this hydroxylation reaction by							
using different aromatic halides under the optimized reaction							
conditions. As shown in Table 2, various aromatic bromide							
derivatives with methoxy, nitro, ethanoyl, trifluoromethyl and							
methyl can smoothly react with water and gave good to excellent							
vields of the corresponding products. Moreover, consistent with							
the expected results, a series of arvl iodine substituents with							
methyl, cyano, ethanoyl, and ester groups also showed verv good							
yields. pyridine heterocyclic bromoaromatic also can be							
efficiently transferred to the corresponding product. However,							
aromatic chlorides displayed inferior activities, which were							
attributed to the higher dissociation energy of C-Cl bond							
compared with C-Br bond ²⁹ .							
Pof							
Cul/L: 1.0 mmol substrate, CsOH, Ar, 110°C, 15h (6)							
Cul: 1.0 mmol substrate, CsOH, n-BuNOH, 80°C, 48h							
Cu(OAc) ₂ /D-glucose: 1.0 mmol substrate, KOH, Ar, 120°C, 28h (8)							
Pd/RockPhos: 1.0 mmol substrate, CsOH, Ar, 80°C, 18h (10)							
Pd(cod)(CH ₂ SiMe ₃) ₂ /L: 1.0 mmol substrate, CsOH, RT, 24h (25)							
Supervised and a substrate NaOH a Ru NE 120% 24h							

photocatalyzed hydroxylation of aryl halides can obtain excellent

activity in a mildly base environment. As showo in Table \$30 when 67A

using DIPEA and TEOA as bases, the efficiency of the reaction only

34.0% and 1.95% of the desired phenol product obtained after 12



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Figure 1. Performance comparison with the reported catalysts for synthesis of phenol including photocatalytic and thermal catalytic systems.

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Table 2 Reaction scope of Nidabpy/g-C_3N_4 dual catalyzed hydroxylation of aromatic halides. $^{\rm a}$



Entry	Substrate	Temp. (°C)	Conv. (%)	Yield (%) ^c	TON ^d
1	⟨Br	25	99.9	99.9	50.0
2	O-Br	25	99.9	99.9	50.0
3	O ₂ N-	25	99.9	99.9	50.0
4	°	25	90.1	89.7	44.9
5	F ₃ C-	25	57.9	57.1	28.6
6		25	99.9	99.9	50.0
7		25	99.9	99.9	50.0
8		25	98.7	98.1	49.1
9		25	97.9	97.9	49.0
10	№-√_у-сі	25	99.9	99.9	50.0
11 ^b		25	31.4	27.1	13.5
12 ^b	°	25	29.9	22.3	11.0

^aReaction conditions: aromatic halide (2a) (0.5 mmol, 1.0 equiv), NiBr₂·glyme (2.0 mol%), dabpy (2.0 mol%), g-C₃N₄ (50 mg), DMF/CH₃CN (1:1, 3.0 mL), H₂O (360 μ L, 20 equiv), Et₃N (0.75 mmol, 1.5 equiv), N₂, xenon lamp (>420 nm), 12 h.^bNiBr₂·glyme (5.0 mol%) and dabpy (5.0 mol%) were added, ^cDetermined by HPLC anlysis against an internal standard. ^dTON = n_{prod}/n_{cat}, which is defined as the total moles of product formed (n_{prod}.) divided by the total moles of catalyst employed in the reaction (n_{cat}.).

To gain insight into the reaction mechanism of Nidabpy $/g-C_3N_4$ catalyst, the trapping experiments were firstly performed by using 4-bromobenzonitrile (1) as the substrate. As shown in Figure 2, isopropanol, p-benzoquinone, AgNO₃ and Na₂S/Na₂SO₃

were used as the scavenger of hydroxyl radical (\cdot OH), superaxidentine radical (\cdot O₂⁻), electron (e⁻), hole (h⁺), D@espectively GCTM#67A photocatalytic activity decreased dramatically with the addition of AgNO₃. But, after adding isopropanol, p-benzoquinone or Na₂S/Na₂SO₃, no reduction of catalytic efficiency was observed. These results confirmed that electron played a dominant role in this photocatalytic hydroxylation reaction with water.



Figure 2 Control experiments with different additives in the Nidabpy /g-C_3N_4 catalyzed visible-light-driven hydroxylation reaction.



Figure 3 Powder X-ray diffraction patterns (a), FTIR spectra of g-C₃N₄ and Nidabpy /g-C₃N₄ samples.

Firstly, the phase identification of pristine $g-C_3N_4$ and Nidabpy /g-C₃N₄ catalyst were first characterized by X-ray diffraction (XRD) patterns. As shown in Figure 3a, XRD pattern of Nidabpy /g-C₃N₄ was very similar to that of pristine $g-C_3N_4$, confirming that the structure of g-C₃N₄ was preserved with NiBr₂·glyme and dabpy addition. XRD pattern of g-C₃N₄ (Figure 4a, top line) showed two distinct characteristic peaks at 13.0° and 27.4°, which are reflections from (100) and (002) crystal planes, representing inplane packing and interfacial stacking of g-C₃N₄ sheets, respectively. However, the lateral peak shifted slightly to a lower 20 value by about 0.1°, indicating a progressively larger stacking distance between nanosheets. This result indicated that there existed the strong interaction between Nidabpy complexes and g-C₃N₄. FT-IR spectrum of g-C₃N₄ (Figure 3b) displayed the strong absorption peaks around 810 cm⁻¹, which was due to the out-ofplane bending vibration of heptazine rings skeleton. The multiple

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bands between 900 and 1800 cm⁻¹ corresponded to the stretching vibration absorption peak of the "melon" framework while the multiple broad peaks in the 3000-3500 cm⁻¹ region were attributed to the stretching vibration modes of the -NH group and -OH group of the adsorbed H₂O from air.³⁰ But, for the Nidabpy /g-C₃N₄, a distinct change can be observed with a weak absorption peak located at 600 cm⁻¹, which was attributed to Ni-N bands. It confirmed that NiBr₂·glyme/dabpy complexes was successfully deposition onto g-C₃N₄.



Figure 4 N 1S (a) and Ni 2P (b) XPS spectra of Nidabpy $/g-C_3N_4$, Nidabpy and $g-C_3N_4$ samples, the schematic picture of the interaction between Nidabpy and $g-C_3N_4$ (c).

To further demonstrate the existed interaction, we first analysed high-resolution XPS spectra of N 1s and Ni 2p regions for both Nidabpy /g-C₃N₄, g-C₃N₄ and Nidabpy complexes (Figures 4a and 4b). Evidently, N 1s region of g-C₃N₄ sample can be deconvoluted into three peaks at around 398.2, 399.8 and 400.8 eV, assigning to sp²-hybridized nitrogen (pyridine-N) in triazine rings (C-N=C), nitrogen bonded to carbon atoms (amino-N) in the form of C-N-H and pyrrolic-N in the form of N-C₃, respectively. For the N 1s spectrum of Nidabpy complexes, only two peaks can be resolved at around 398.7 and 399.9 eV, assigning to pyridine-N (C=N-Ni) and amino-N. But, N 1s region of Nidabpy $/g-C_3N_4$ can be deconvoluted into four peaks at around 398.3, 399.8, 400.8, and 401.7 eV, assigning to pyridine-N in triazine rings (C-N=C), nitrogen bonded to carbon atoms (amino-N) in the form of C-N-H and pyrrolic-N in the form of N-C₃, graphitic-N in the form of C-N-C, respectively³¹. The content of amino-N was slightly higher than pyridine-N, which was attributed to the deposition of NiBr₂·glyme/dabpy complexes on the surface of g-C₃N₄. Moreover, the slight changes of pyridine-N binding energies can also be attributed to the interaction between NiBr₂·glyme, dabpy and $g-C_3N_4$. As for Ni 2p spectrum of Nidabpy / $g-C_3N_4$ sample in Figure 3b, two obvious peaks at 874.1 and 856.4 eV, as well two broad satellite peaks assigning to the Ni $2p_{1/2}$ and Ni $2p_{3/2}$, respectively. This result was attributed to the presence of Ni (II)³². Compared to pure Nidabpy complexes, two peaks of $N_{i2}p_{4Ai}aBd_{nline}$ Ni $2p_{3/2}$ in Nidabpy /g-C₃N₄ sample were slightly shifted to the strong interaction between Nidabpy and g-C₃N₄, possibly *via* the axial coordination of nitrogen atoms in g-C₃N₄ with the central Ni(II) metal in Nidabpy and π -conjugated between Nidabpy and g-C₃N₄ (Figure 4c). These results confirmed NiBr₂·glyme will first coordinated with dabpy to form Nidabpy. The formed Nidabpy was easily attached to the surface of g-C₃N₄ by electrostatic interaction.

The optical absorption properties of g-C₃N₄ and Nidabpy /g-C₃N₄ were characterized using UV-vis absorption spectra. It can be seen from Figure 5a that, compared with $g-C_3N_4$, the incorporation of NiBr2·glyme/dabpy complexes can effectively improve the light absorption in both the UV and visible regions. Moreover, Nidabpy /g-C₃N₄ displayed intensified and red-shifted light absorption. This result was may be attributed to the extended electron delocalization in the 2D networks of g-C₃N₄ because of the incorporation of NiBr₂·glyme/dabpy complexes, and the activation of π to π^* electron transition due to the strong interaction between NiBr₂·glyme/dabpy complexes and g-C₃N₄ networks³³. The band gap was also estimated from the transformed Kubelka-Munk function (Figure 5b). The Eg value decreased from 2.78 eV of g-C₃N₄ to 2.76 eV of Nidabpy /g-C₃N₄, the electronic structure changed, implying that an obvious interaction between NiBr₂·glyme, dabpy and g-C₃N₄.



Figure 5 UV-Vis spectra (a), and plots of transformed Kubelka-Munk function versus photon energy (b) of $g-C_3N_4$ and Nidabpy /g-C₃N₄ samples.

The strong interaction between NiBr₂·glyme/dabpy complexes and g-C₃N₄ is also confirmed by comparison of the Photoluminescence (PL) spectra of g-C₃N₄ and Nidabpy /g-C₃N₄ (Figure S1). g-C₃N₄ exhibited a strong emission in the range of 400~600 nm, which corresponded to the carrier recombination. But, the PL emission intensity of Nidabpy /g-C₃N₄ decreased markedly, which suggested that the photoinduced charge could be efficiently separated when the biphase interfaces were formed between Nidabpy and g-C₃N₄. It implied that there existed a strong electron interaction between Nidabpy and g-C₃N₄, which involved the empty d orbital of Ni(II) with free electrons from the π -conjugated molecule or the lone-pair electrons of the nitrogen atoms in g-C₃N₄.³³

To further elucidate charge generation and charge transfer behaviors of $g-C_3N_4$ and Nidabpy $/g-C_3N_4$ materials, we investigated their photoelectronic properties. As shown in Figure 6a, the transient photocurrent-time (i-t) curves of $g-C_3N_4$ and Nidabpy /g-C₃N₄ were recorded by several on-off cycles of intermittent irradiation under xenon lamp (>420 nm). As expected, the highest transient photocurrent response for Nidabpy $/g-C_3N_4$ was obtained compared with $g-C_3N_4$, indicating a notable promotion of generation and separation of photogenerated electrons-holes. Next, the electrochemical impedance spectroscopy (EIS) Nyquist plots about g-C₃N₄ and Nidabpy /g-C₃N₄ were used to further characterize the resistance during interfacial charge transfer. As shown in Figure 6b, the arc radius of Nidabpy $/g-C_3N_4$ on the EIS Nyquist plot was smaller than that of g-C₃N₄, indicating the smaller resistance of charge transfer of Nidabpy $/g-C_3N_4$ than that of $g-C_3N_4$.³⁴ Thus, we can safely concluded that this excellent charge transfer property was responsive for the excellent photocatalytic performance of our Nidabpy /g-C₃N₄ catalyst.

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Figure 6 Photocurrent responses (a and electrochemical impedance spectra (EIS) (b) of $g-C_3N_4$ and Nidabpy $/g-C_3N_4$ samples under visible-light irradiation ($\lambda > 420$ nm).

Unlike homogeneous molecular photocatalysts, a major advantage of $g-C_3N_4$ catalyst was its easy recycle and reuse. As shown in Figure 7, no significant reduction was found in the yields after being used repetitively five times, the morphology of $g-C_3N_4$ showed irregular size lamellar stacking texture that was not altered during the catalytic transformation (Figure S3), demonstrating that $g-C_3N_4$ had high photocatalytic stability in the hydroxylation reaction with water. To emphasize the practicability of our heterogeneous catalysis system, a scale-up reaction by using 10 mmol 4-bromobenzonitrile (1.82 g) was performed. As expected, the hydroxylation reaction product of 4-Cyanophenol can be achieved in 98.4% yield (1.79 g) with 250 mg $g-C_3N_4$, 1.0% NiBr₂·glyme and 1.0% dabpy in 12 h (Scheme 2).

Finally, the reaction mechanism was proposed based on the experimental results and the previously published reports, as shown in Scheme 3. In our Nidabpy $/g-C_3N_4$ dual catalytic system, $g-C_3N_4$ was a photocatalyst, Et₃N provided the electron. After visible light illumination, $g-C_3N_4$ was excited to produce an effective separation of the photogenerated electron-hole pairs. The photogenerated hole can effect the oxidation of Et₃N to form

cationic radical. Then, Et₃N radical was through a hydrogen atom_{nine} transfer process with water to generated hydroxyPradical_PAtter_Atter_ stage, concurrent oxidative addition of aromatic halides to Ni(0) species should deliver the Ni(II) species, which would be trapped by the hydroxyl radical to form Ni(III) organometallic adduct. Thereafter, reductive elimination would deliver the desired phenols product and Ni(I) species. Finally, the photogenerated electron by semiconductor excitation was utilized for the reduction of the Ni(I) species to Ni(0) species via a single electron transfer. Then, concurrent oxidative addition of aromatic halides to Ni(0) species should deliver the Ni(II) species to complete the Ni catalytic cycle.¹³



Scheme 2 Nidabpy/g- C_3N_4 catalyzed gram-scale synthesis of the representative 4-Cyanophenol.



Figure 7 Recycling test of $g-C_3N_4$ catalyst in hydroxylation of 4bromobenzonitrile with water. Reaction conditions were in Table 1.



Scheme 3 Proposed mechanism of Nidabpy $/g-C_3N_4$ catalyzed visible-light-driven hydroxylation of aromatic halides with water.

Conclusions

In summary, we have developed a novel Nidabpy /g-C₃N₄ cooperative catalytic system for hydroxylation reaction with water by using less-activated aromatic halides. This semiheterogeneous Nidabpy /g-C₃N₄ catalyst exhibited excellent catalytic activity and selectivity. Importantly, g-C₃N₄ as a metalfree heterogeneous semiconductor can be recyclable at least five times without significant reduced activity. Therefore, this protocol provides a green and sustainable pathway for the synthesis of phenols. We believe that the discovery will find wide applications in some fields.

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Conflict of interest The authors declare that they have no conflict of interest.

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