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Research Article

Photo-Ni-Dual-Catalytic $C(sp^2)-C(sp^3)$ Cross-Coupling Reactions with Mesoporous Graphitic Carbon Nitride as a Heterogeneous Organic Semiconductor Photocatalyst

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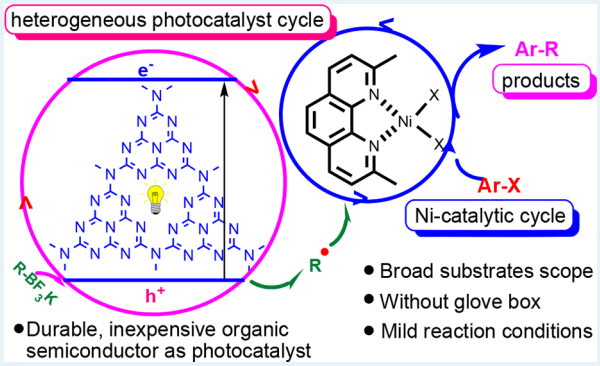
ABSTRACT: The synergistic combination of a heterogeneous organic semiconductor mesoporous graphitic carbon nitride (mpg-CN) and a homogeneous nickel catalyst with visible-light irradiation at room temperature affords the $C(sp^2)-C(sp^3)$ cross-coupling of aryl halides and potassium alkyl trifluoroborates by single electron transmetallation. Like the homogeneously catalyzed protocol, the reaction is compatible with a variety of functional groups including electron-donating and electron-withdrawing aryl and heteroaryl moieties. Moreover, this protocol allows the installation of allyl groups onto (hetero)arenes, enlarging the scope of the method. The heterogeneous mpg-CN photocatalyst is easily recovered from the reaction mixture and reused several times, paving the way for larger-scale industrial applications of this type of photocatalytic bond-forming reactions.



KEYWORDS: *$C(sp^2)-C(sp^3)$ cross-coupling, heterogeneous photocatalyst, nickel catalysis, dual catalysis, single-electron transmetallation*

INTRODUCTION

Metal-catalyzed cross-coupling reactions are standard synthetic methods in academia and industry.[1] The classic cross-coupling protocol is useful for $C(sp^2)-C(sp^2)$ bond-forming reactions but less applicable for the formation of $C(sp^2)-C(sp^3)$ bonds due to slower rates of oxidative addition and transmetallation and a facile β-hydride elimination.[2] While the β-hydride elimination can be suppressed by different metal−ligand combinations,[3] the rate-limiting two-electron transmetallation was a challenge before the pioneering work of Molander and MacMillan introducing single electron transmetallation to organoboron cross-coupling by photoredox-nickel dual catalysis.[4,5] The core of the concept is the oxidative generation of stable radicals from their respective precursors, which are trapped by an in situ generated nickel complex. Reductive elimination from the Ni(III) species generates the desired cross-coupling product. Molander demonstrated that such carbon-centered radicals are easily generated from the respective trifluoroborate salts, while MacMillan used α-heteroatom-containing carboxylic acids for the generation of carbon-centered radicals by oxidative decarboxylation. The one-electron transmetallation overcomes the problem of slow rates for $C(sp^3)$ coupling partners and avoids more harsh reaction conditions required in conventional cross-coupling conditions. *o*-Benzyl xanthates[6] or ammonium alkyl silicates[7] are alternative precursors yielding the respective nucleophilic alkyl radicals under visible-light photoredox conditions and the application of dual photo-nickel cross-coupling has been demonstrated in synthesis.[8] To improve the efficiency of this technology further, we now have replaced the homogeneous iridium photocatalyst of the original reports by a heterogeneous organic semiconductor.

We recently reported that mesoporous graphitic carbon nitride (mpg-CN), an organic semiconductor material, is a versatile photocatalyst capable of performing many organic transformations under diverse reaction conditions.[9] mpg-CN can easily be synthesized using inexpensive starting materials, and the polymeric material is stable toward reactive radicals or nucleophiles. mpg-CN possesses a suitable band gap between valence band maxima (VBM) and conduction band minima (CBM),[10] which allows the use of photoexcited mpg-CN for controlled oxidation and reduction of many substrates. Pieber and Seeberger reported the application of carbon nitrides in photoredox-nickel dual cross-coupling reactions using oxygen-centered nucleophiles.[11] Recently, carbon nitride-based heterogeneous photocatalysts have also been utilized for several other synthetic transformations.[12] We report here organoboron cross-coupling reactions using mpg-CN as a photocatalyst.

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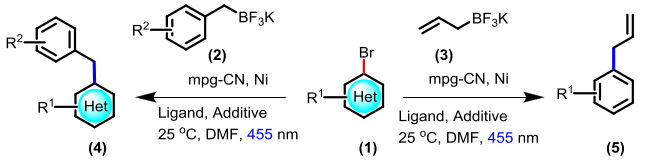
We decided to explore mpg-CN photo Ni-dual catalysis for $C(sp^2)-C(sp^3)$ cross-coupling reactions yielding diarylmethanes, as the structure is present in many bioactive molecules, organic materials, and drug candidates.[13] Diarylmethanes are also frequently used as a motif in catenanes, macrocycles, and rotaxanes.[14] Diarylmethanes **4** and arylvinylmethanes **5** are accessible starting from the respective aryl halide (**1**) and potassium alkyltrifluoro borate (**2** or **3**) as shown in Scheme 1.

Scheme 1. $C(sp^2)-C(sp^3)$ Cross-Coupling Using mpg-CN/Ni Dual Photoredox Catalysis



RESULTS AND DISCUSSION

We began our investigation with ethyl 4-bromobenzoate (**1a**) and potassium benzyl trifluoro borate (**2a**) as model substrates using $Ni(cod)_2$ as a catalyst, 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbbpy) as a ligand, and mpg-CN as a heterogeneous photocatalyst. When the reaction mixture in dimethylformamide (DMF) was irradiated using a 455 nm ((455 (±15) nm), I_{max} = 1000 mA, 1.12 W) blue light-emitting diode (LED) for 20 h under nitrogen, the desired product **4a** was obtained in 81% gas chromatography (GC) yield (Table 1, entry 1). The use of 2,6-lutidine as an additive increased the product yield to 93% (entry 2). Control reactions, which are either performed in the absence of light, Ni catalyst, or mpg-CN confirmed the role of every reaction component in the photocatalytic cross-coupling reaction (entries 3−5). The use of $NiBr_2$·glyme or $NiCl_2$·glyme instead of $Ni(cod)_2$ decreased the yield slightly and prolonged the time to complete the reaction (entry 6−7). However, with increased catalyst loading, the reaction became faster (entry 8). It is to be noted that although the reaction conditions using both Ni sources work equally well in providing the desired product in excellent yield, the use of $NiBr_2$·glyme as a bench-stable solid is advantageous and avoids the use of a glovebox or Schlenk techniques.[2] The reaction becomes very sluggish when performed in the presence of air and shuts down completely when performed under oxygen (entries 9 and 10). Further optimizations revealed that the combination of 2.5 mol % $NiBr_2$·glyme and neocuproine as a ligand provided the best result and the desired product was isolated in 96% yield (entry 12 in Table 1, GC yield 97%). Other commonly used solvents such as dimethyl sulfoxide (DMSO) and acetonitrile (ACN) gave the desired product in lower yield (entries 13 and 14) compared to DMF. The reaction proceeds in the absence of neocuproine or 2,6-lutidine providing the product in 15 and 70% yield, respectively (entries 17 and 18). Finally, the use of recovered mpg-CN without the renewed addition of Ni catalyst (entry 19) did not yield the desired product, indicating any stable nickel precipitation on the heterogeneous photocatalyst surface.[11] The use of other modified carbon nitrides such as Na-PHI,[15a] CN-ATZ-NaK,[15c] and K-PHI[15d] did not increase the product yield, and the use K-PHI,[15b] Mn-PHI,[15e] and H-PHI[15e] gave the desired products in very similar yields (entries 20−25).

With the optimized reaction condition, which requires mixing of reagents under air and illumination of the reaction mixture under nitrogen using a blue LED, we explored the scope of this reaction using different aryl and heteroaryl halides as substrates. Potassium benzyl trifluoroborate (**2a**) was used as the coupling partner. A range of aryl bromide substrates possessing both electron-withdrawing and -donating groups, such as ester, cyano, aldehyde, ketone, trifluomethyl, $-SO_2Me$,

Table 1. Optimization of Reaction Conditions and Control Reactions[a]

entry	Ni catalyst	ligand (mol %)	time	yield[b]
1	$Ni(cod)_2$ (10 mol %)	dtbbpy (10 mol %)	20 h	81%
2	$Ni(cod)_2$ (10 mol %)	dtbbpy (10 mol %)	22 h	93%[c]
3	$Ni(cod)_2$ (10 mol %)	dtbbpy (10 mol %)	22 h	0% (in dark)
4	$Ni(cod)_2$ (10 mol %)	dtbbpy (10 mol %)	22 h	0% (without mpg-CN)
5		dtbbpy (10 mol %)	20 h	0%
6	$NiBr_2$·glyme (5 mol %)	dtbbpy (6 mol %)	45 h	87%
7	$NiCl_2$·glyme (5 mol %)	dtbbpy (6 mol %)	45 h	85%
8	$NiBr_2$·glyme (10 mol %)	dtbbpy (10 mol %)	20 h	70%
9	$NiBr_2$·glyme (5 mol %)	dtbbpy (6 mol %)	45 h	19% (under air)
10	$NiBr_2$·glyme (5 mol %)	dtbbpy (6 mol %)	45 h	0% (under O_2)
11	$NiBr_2$·glyme (5 mol %)	neocuproine (5 mol %)	22 h	97%
12	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	97% (96%)
13	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	55%[d]
14	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	89%[e]
15	$NiBr_2$·glyme (1 mol %)	neocuproine (5 mol %)	24 h	61%
16	$NiBr_2$·glyme (2.5 mol %)	neocuproine (5 mol %)	24 h	85%
17	$NiBr_2$·glyme (2.5 mol %)		24 h	15%
18	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	70%[c]
19		dtbbpy (10 mol %)	22 h	0% (recovered mpg-CN)
20	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	74%[f]
21	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	90%[g]
22	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	72%[h]
23	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	59%[i]
24	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	89%[j]
25	$NiBr_2$·glyme (2.5 mol %)	neocuproine (2.5 mol %)	24 h	87%[k]

[a]The reaction was performed using ethyl 4-bromobenzoate as a model substrate in 0.2 mmol scale, 1 mL of DMF has been used as a solvent. A 1.25 equiv of 2,6-lutidine was used as an additive. [b]GC yields. [c]Without 2,6-lutidine. [d]DMSO was used as a solvent. [e]ACN was used as a solvent. [f]Na-PHI.[15a] [g]K-PHI (prepared from 5-aminotetrazole in LiCl/KCl eutectic mixture using mechanochemical pretreatment of reagents).[15b] [h]CN-ATZ-NaK.[15c] [i]K-PHI (prepared from 5-aminotetrazole in LiCl/KCl eutectic mixture using 0.5 wt. % of K-PHI nanoparticles as nucleation seeds).[15d] [j]Mn-PHI.[15e] [k]H-PHI[15e] was used as a heterogeneous photocatalyst.

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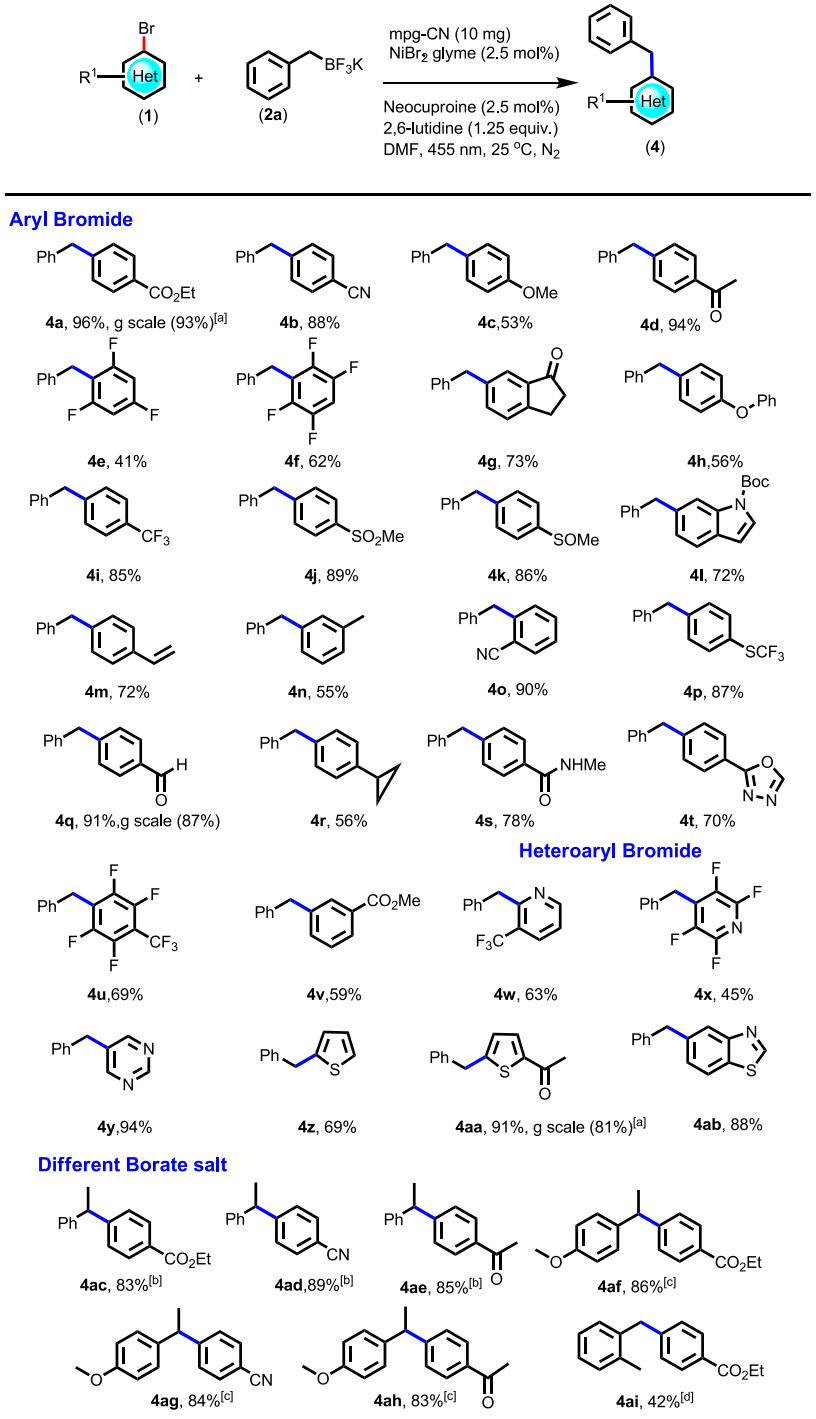
Scheme 2. Examples of C(sp^2)−C(sp^3) Bond-Forming Reactions Using (het)Aryl Halides and Potassium Benzyl Trifluoroborate



[a]Standard conditions: (hetero)aryl bromide (0.2 mmol, 1.0 equiv), 59.4 mg of potassium benzyl trifluoroborate (0.3 mmol, 1.5 equiv), mpg-CN (10.0 mg), 1.5 mg of $NiBr_2$·glyme (0.005 mmol, 2.5 mol %), 1 mg of neocuproine (0.005 mmol, 2.5 mol %), and 29 μL of 2,6-lutidine (0.25 mmol, 1.25 equiv) in DMF (1 mL) under nitrogen atmosphere for 22−24 h. [a]Similar conditions were used for reactions in 5-6 mmol scale; for more details, see the Supporting Information. [b]63.7 mg potassium trifluoro(1-phenylethyl)borate (0.3 mmol, 1.5 equiv) was used instead of potassium benzyltrifluoroborate. [c]72.6 mg potassium trifluoro(1-(4-methoxyphenyl)ethyl)borate (0.3 mmol, 1.5 equiv) was used instead of potassium benzyltrifluoroborate. [d]63.6 mg potassium trifluoro(2-methylbenzyl)borate (0.3 mmol, 1.5 equiv) was used instead of potassium benzyltrifluoroborate.

−SOMe, amide, methyl, −OMe, −OPh, and others, were easily converted to their corresponding C(sp^2)−C(sp^3)-coupled products in good to excellent isolated yields. The presence of the −CN group in ortho-position did not alter the reaction outcome, and the desired products were obtained in a very comparable isolated yield of 90%. Similarly, when 4-bromostyrene, 1-bromo-4-cyclopropylbenzene, or aryl or heteroaryl bromides possessing biologically relevant functional

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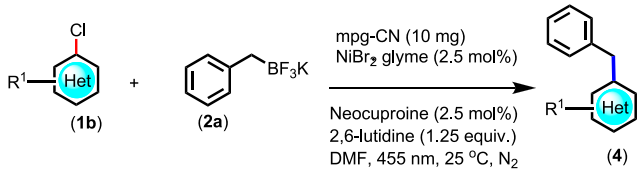
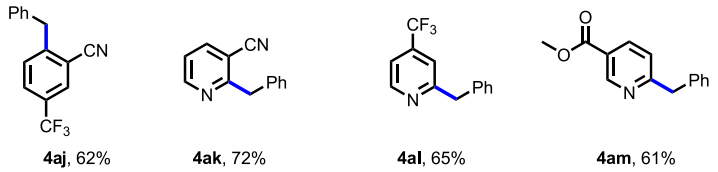
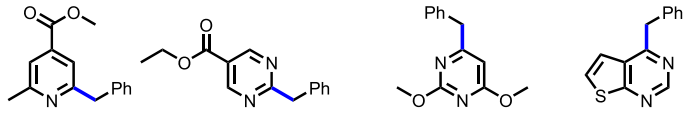
Scheme 3. Scope of (hetero)Aryl Chloride Substrates in C(sp^2)−C(sp^3) Cross-Coupling Reactions

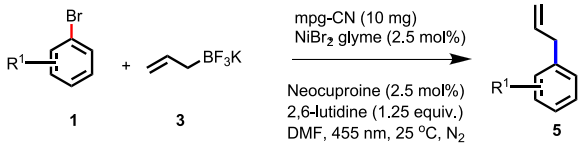


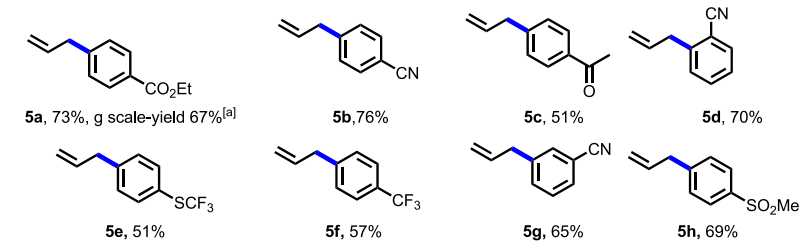




[a]Standard conditions: (hetero)aryl chloride (0.2 mmol, 1.0 equiv), 59.4 mg of potassium benzyl trifluoroborate (0.3 mmol, 1.5 equiv), mpg-CN (10.0 mg), 1.5 mg of $NiBr_2$·glyme (0.005 mmol, 2.5 mol %), 1 mg of neocuproine (0.005 mmol, 2.5 mol %), and 29 μL of 2,6-lutidine (0.25 mmol, 1.25 equiv) in DMF (1 mL), under nitrogen atmosphere for 48 h.

Scheme 4. Scope of the Coupling Reactions Using Allyl Borate Salt and Aryl Halides





[a]Standard conditions: aryl bromide (0.2 mmol, 1.0 equiv), 44.4 mg of potassium allyl trifluoroborate (0.3 mmol, 1.5 equiv), mpg-CN (10.0 mg), 1.5 mg of $NiBr_2$·glyme (0.005 mmol, 2.5 mol %), 1 mg of neocuproine (0.005 mmol, 2.5 mol %), and 29 μL of 2,6-lutidine (0.25 mmol, 1.25 equiv) in DMF (1 mL), under nitrogen atmosphere for 24 h. The second batch of 44.4 mg of potassium allyl trifluoroborate (0.3 mmol, 1.5 equiv) was added after 24 h, and the reaction mixture was further illuminated for an additional 48 h. [a]Similar conditions were used for reactions on 4.5 mmol scale; for more details, please see the Supporting Information.

groups such $-SCF_3$,[16] or polyfluoro aromatic or heteroaromatic bromides were used as substrates, the desired coupling products were isolated, leaving the functional groups intact. When heteroaryl bromides such as pyridines, pyrimidines, thiophenes, and benzothiazoles were used as substrates, the desired products were obtained in good isolated yields. Of note is the mass balance of these reactions. The dehalogenated products were obtained only as byproducts[17] and starting materials could be easily recovered by column chromatography when the product yield is low. All yields were calculated based on the amount of isolated products. Almost similar reactivity and product yields were obtained when the reactions were performed on gram scales (examples **4a** and **4q**). The reactions using heteroaryl bromides proceed effectively on a gram scale, and the desired products were obtained in similar yields as exemplified by the reaction yielding product **4aa**. Different borate salts were effective as a source of the respective C(sp^3) radicals, giving the desired products in very good yields. For example, the borate salts containing a methyl group at the benzyl position also gave the desired products in excellent 83−89% isolated yields. The presence of an electron-donating group at the para position has almost no influence on the yields of the desired product as shown in Scheme 2. An ortho-substituted borate gave product **4ai** in 42% yield. Other borates, such as cyclohexyl-, alfa-alkoxy-, vinyl-, alfa-trifluoromethylbenzyl-, and phenylethyl borate were reacted under standard reaction condition with ethyl 4-bromobenzoate (**1a**) but did not yield the desired product.[18] When 4-MeO_2C-

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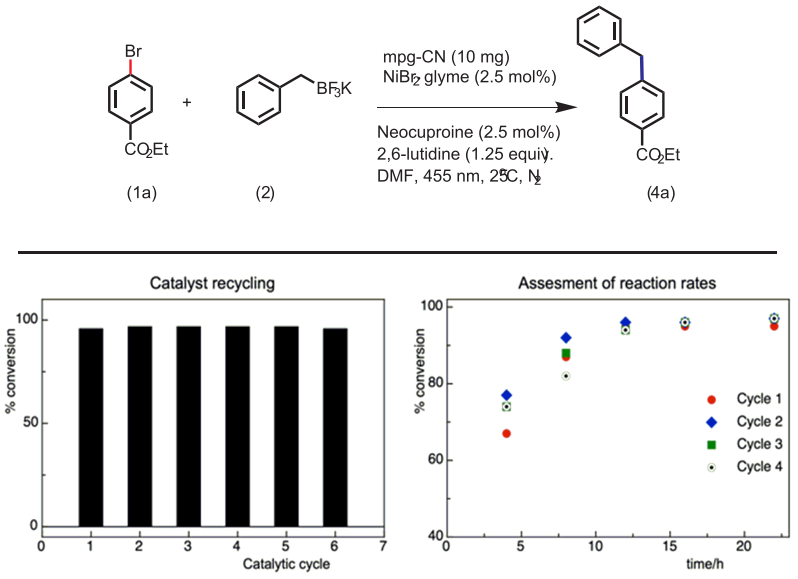

Figure 1. Catalyst recycling (for six catalytic cycles) and assessment of the reaction rates (for four catalytic cycles). Standard conditions: 45.8 mg of ethyl 4-bromobenzoate (0.2 mmol, 1.0 equiv), 59.4 mg of potassium benzyl trifluoroborate (0.3 mmol, 1.5 equiv), mpg-CN (10.0 mg), 1.5 mg of $NiBr_2$·glyme (0.005 mmol, 2.5 mol %), 1 mg of neocuproine (0.005 mmol, 2.5 mol %), and 29 μL of 2,6-lutidine (0.25 mmol, 1.25 equiv) in DMF (1 mL), under nitrogen atmosphere.

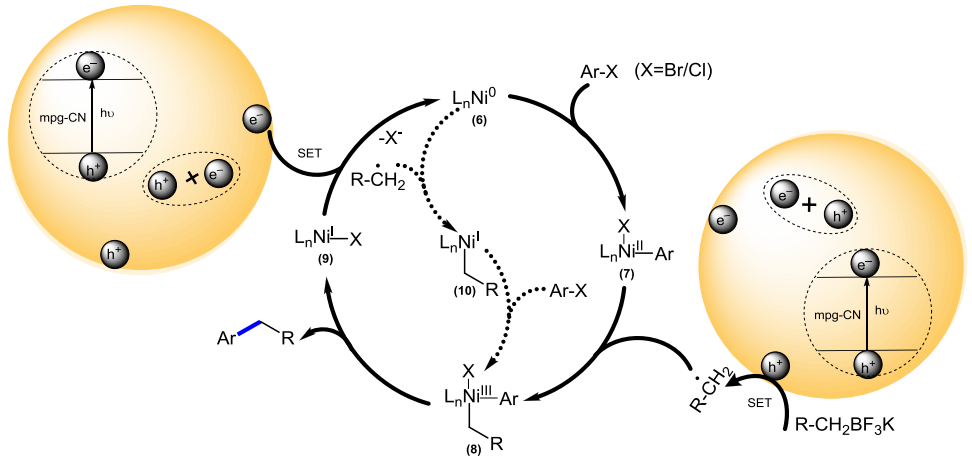

Figure 2. Plausible mechanism of mpg-CN- and Ni-catalyzed $C(sp^2)-C(sp^3)$ cross-coupling reaction.

benzyl borate was reacted under the standard reaction condition, only low substrate conversion was observed. The use of K-PHI,[15b] which possesses a strong oxidation potential (+2.54 V vs RHE),[9b] as a photocatalyst increased the substrate conversion to 10−12% but no preparative useful product yields were obtained.

The $C(sp^2)-C(sp^3)$ cross-coupling protocol is not only effective for heteroaryl bromides but heteroaryl chlorides can also be employed as substrates (see examples in Scheme 3). However, the reaction using 4-chlorobenzonitrile as a substrate requires higher temperatures of 55 °C to complete the reaction and give the desired product **4b** in 56% isolated yield. Chlorinated pyridines, pyrimidines, and thieno[2,3-*d*]-pyrimidine derivatives gave the desired coupling products in good to moderate isolated yields.

We envisioned that the oxidation potential of mpg-CN[10b] might allow the generation of relatively stable allyl radicals from allyltrifluoroborates, eventually offering the installation of functionally important allyl moiety onto arenes. In fact, a reaction mixture containing allyltrifluoroborate and **1a** under our standard photochemical reaction conditions provides the desired product **5a** in a 73% isolated yield. The allylation reaction is also effective for other aryl halide substrates giving the desired products in good to excellent yields (Scheme 4). The −CN group at the −o/−m/−p position yielded the desired products in almost similar amounts (**5b**, **5d**, and **5g**, yields 65−76%).

Unlike molecular photocatalysts that have been used so far for radical-mediated $C(sp^2)-C(sp^3)$ cross-coupling reactions, the use of mpg-CN as a heterogeneous photocatalyst allows easy recovery of the photocatalyst from the reaction mixture, even from gram-scale reactions, via simple filtration or centrifugation (see Figure 1). The heterogeneous nature and the remarkable stability of mpg-CN under the photochemical reaction conditions allow such easy recovery of the photocatalyst from the reaction mixture, and the recovered mpg-CN can be reused several times without the loss of photocatalyst reactivity or yield of the desired product. As shown in Figure 1,

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the photocatalyst can at least be recycled six times, and the rates of the photochemical reactions remain the same.

While the complete mechanistic picture of this transformation remains to be elucidated, we depict a working hypothesis in Figure 2 based on the experimental results and previously published reports using molecular photocatalysts.[4,5,19] Oxidative addition of Ni(0) species **6** to an aryl halide delivers the Ni(II) intermediate **7**. Light absorption by the heterogeneous semiconductor photocatalyst mpg-CN results in charge separation yielding two-dimensional surface redox centers as electron−hole pairs. The photogenerated hole is effective for the oxidative generation of a benzyl radical, which is trapped by the Ni(II) species yielding a Ni(III) organometallic adduct (**8**). Subsequent reductive elimination delivers the desired $C(sp^2)-C(sp^3)$ cross-coupling product. Alternatively, intermediate **8** may be formed from **6** via radical trapping followed by oxidative addition. Finally, the electron at the semiconductor surface is utilized for the reduction of the Ni(I) species to Ni(0) species to complete the Ni catalytic cycle. The formation of bibenzyl via a photoredox radical coupling reaction[8d] was confirmed by GC and GC-mass spectrometry (MS) analysis, supporting the generation of benzyl radicals from potassium benzyl trifluoroborate under the photoredox reaction conditions.

CONCLUSIONS

We have demonstrated the application of a heterogeneous semiconductor mpg-CN in $C(sp^2)-C(sp^3)$ cross-coupling reactions using commercially available (het)aryl halides and potassium alkyl trifluoroborates. A range of aryl and heteroaryl halides, including chlorides, can be used as starting materials and substituted trifluoroborates and allyltrifluoroborates are a suitable source of alkyl and allyl radicals, respectively. The reactions are easily executed using commercially available and bench-stable $NiBr_2$·glyme as the Ni source and mpg-CN as a heterogeneous semiconductor photocatalyst that can be separated from the reaction mixture by filtration or centrifugation. We believe that the reported protocol will facilitate larger-scale applications and make the single electron photoredox transmetallation simpler and more economical.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b05598.

Experimental procedures, characterization of products, and copies of the $^1H/^{13}C/^{11}B/^{19}F$ NMR spectra of the prepared compounds (PDF)

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Notes

The authors declare no competing financial interest.

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