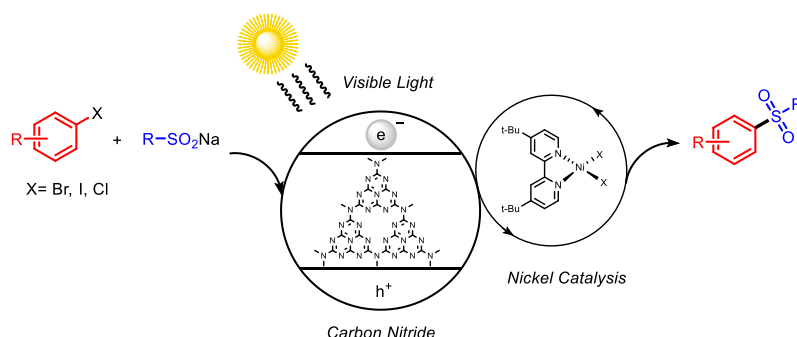


Ni/Photoredox Dual Catalysis Sulfone Compounds Synthesised with Carbon Nitride as the Semiheterogeneous Photocatalyst

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[Supporting Information](#)



ABSTRACT: An easily available heterogeneous semiconductor material, g-CN, proved to be feasible when combined with homogeneous nickel catalysts for light-mediated C(sp²)-SO₂Ar bond formation of aryl bromides with aryl sulfonates under mild conditions and base-free, unlocking a variety of cross-couplings. The metal-free heterogeneous semiconductor is totally recyclable from reaction system, and experimental results demonstrated a series of differently substituted substrates including electron donating groups and electron withdrawing groups can be tolerated with a satisfactory result. The method could even produce the classic drug Dapsone in large scale, showing strong practical application potential.

Visible light driven photoredox catalyzed has gained numerous attentions as a powerful and energy-efficient method for chemical synthesis.¹ The central of concept is rely on oxidation addition with specific radicals from precursors and trapped by transition metal complex such as nickel,² palladium,³ cooper⁴ and so on.⁵ After elimination by reduction, the desired cross-coupling product is generated and the metal complex is reduced through photocatalytic cycle for next process. However, the whole process is highly depended on homogeneous photore-sponse catalysts, such as ruthenium,⁶ iridium⁷ or organic dyes⁸ in numerous reports. It is a pity that these homogeneous photocatalysts are also accompanied by weakness such as the expensive expenses, separation from products, unable to recycle which limits the actual industrialized application to a certain extent.

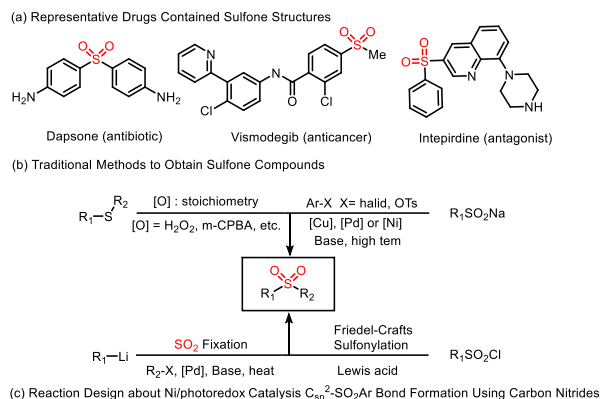
Based on the actual background and requirement, in recent years, some representative heterogeneous catalyst such as g-CN,⁹ TiO₂,¹⁰ CdS¹¹ involved in photoredox process has been gradually developed. König' groups^{9a} reported ligand-free mpg-CN/Ni dual photoredox catalytic protocols for C-N bond formation, and explored mpg-CN/Ni-dual catalysis for C(sp²)-C(sp³) cross-coupling reactions yielding diarylmethanes analogously.^{9b} Pieber and Seeberger reported mpg-CN in combination with nickel catalysis can induce selective C-O cross-couplings of carboxylic acids with aryl halides.^{9c} Meanwhile, they

also reported g-CN/Ni with light-mediated cross-couplings of aryl bromides with alcohols via C-O bond formation.^{9d}

Inspired by previous investigation,¹² we hence developed mpg-CN/Ni dual catalysis sulfone compounds synthesised which are widely found in a number of drug-active molecules such as Dapsone, Vismodegib and Intepirdine (**Scheme 1a**) via C(sp²)-SO₂Ar bond formation. Compared with the traditional method (**Scheme 1b**),¹³ this kind of heterogeneous photocatalyst invovled in photoredox have the potential for industrial and large-scale development due to its advantages including mild conditions, visible light driven, base-free, high-yield outcomes and reutilization.

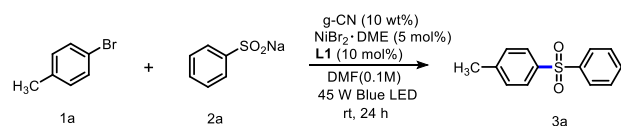
In our consideration of this approach and previous report,¹⁴ we envisioned that aryl sulnate salts have low redox potentials ($E_{1/2} = -0.37$ V vs. SCE in CH₃CN)¹⁵ and could undergo single electron transfer oxidation by photogenerated hole form excited g-CN which is effective to generate sulfonyl radicals. Oxidative addition of Ni(0) species to an aryl halide delivers the Ni(II) intermediate¹⁴ which is tend to trap the sulfonyl radicals yielding a Ni(III) organometallic adduct. Subsequent reductive elimination produces the targeted C(sp²)-SO₂Ar cross-coupling product. Finally, the electron form semiconductor surface is utilized for the reduction of the Ni(I) species to Ni(0) species through another single electron transfer to complete the whole Ni catalytic cycle (**Scheme 1c**).

Scheme 1. Significant of Sulfones and Experimental Design



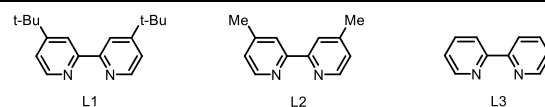
With this design in mind, we began to investigate the possibility and figure out the best conditions primarily. According to the **Table 1**, 4-bromotoluene **1a** and sodium benzenesulfinate **2a** was chosen to be the model substrate separately. To our delight, the product 1-methyl-4-(phenylsulfonyl) benzene **3a** was obtained with the excellent yield up to 82% under 45W blue led (455 nm) irradiation and 10 wt% of g-CN, (Synthesis method was shown in Support information, SI), 5 mol% NiBr₂•DME and 10 mol% **L1** added in DMF as the standard condition (**entry 1**). Then, the reaction could not be happened when the absence of light, g-CN, or nickel catalyst respectively (**entry 2**). We choosed the Ni(COD)₂ as the nickel source but a modest yield was acquired (**entry 3**). Meanwhile, we also investigated the ligand effect to this reaction system. Firstly, when no ligand was involved, the product **3a** did not observed at all (**entry 4**), and we changed similar ligands such as **L2** or **L3**, but an unsatisfactory result (**entry 5, 6**) was shown. MeCN, MeOH or acetone was selected to be solvent respectively, but trace product was detected (**entry 7**). Shortening reaction time to 12h, the yield was decreased to 68% accordingly (**entry 8**). The reaction could not be occurred without degassing (**entry 9**). Under the same conditions, chlorobenzene was introduced but unsatisfactory results were obtained, and we also choosed the iodobenzene as the substrate could also obtain **3a** up to 78% yield (**entry 10**).

Table 1. Screening Data for the Optimization of the Reaction Conditions towards phosphine oxide **3a.**^a



Entry	Deviation from initial conditions	Yield of 3a ^b (%)
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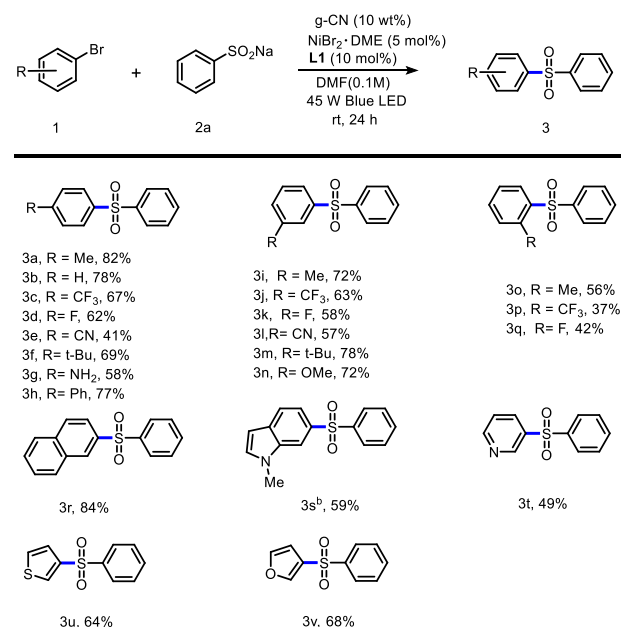
1	none	82
2	no light, no mpg-CN, no nickel catalyst	N.D.
3	Ni(COD) ₂ instead of NiBr ₂ •DME	37
4	no ligand	N.D.
5	L2 instead of L1	21
6	L3 instead of L1	< 5
7	MeCN, MeOH or acetone instead of DMF	trace
8	12 h instead of 24 h	68
9	no degas	N.D.
10	chlorobenzene or iodobenzene as the substrate	32, 78



^a Reaction conditions: **1a** (0.10 mmol, 1.0 eq), **2a** (0.15 mmol, 1.5 eq), g-CN (10 wt%), NiBr₂•DME (5 mol%), L1 (10 mol%), DMF (1 mL, 0.1 M), 45W blue LED, rt, 24 h, N₂. ^b Determined by crude ¹H-NMR with toluene as the internal standard. N.D. = not detected. DMF = N, N'-dimethylformamide.

We then used the optimized reaction conditions to explore the scope of the reaction with respect to the variation of different substituted bromobenzene. As shown in **Scheme 2**, various aryl bromides substituted with electron donating group including methyl **3a**, **3i**, **3o**, methoxy group **3n**, tert-butyl **3f**, or phenyl **3h**, Naphthalene **3r** or strong electron withdrawing group including trifluoromethyl **3c**, **3j**, **3p**, fluorine atom **3d**, **3k**, **3q**, cyan **3e**, **3l** at different positions (o, m, p) were reacted very well, generating the corresponding products with moderate to high yields. In addition, 1-methyl-5-(phenylsulfonyl)-1H-indole **3s** also could be obtained and some heterocyclic compounds like pyridine **3t**, thiazole **3u** and furan **3v** were also tolerated successfully via this method with bromide alternatives as the reagent.

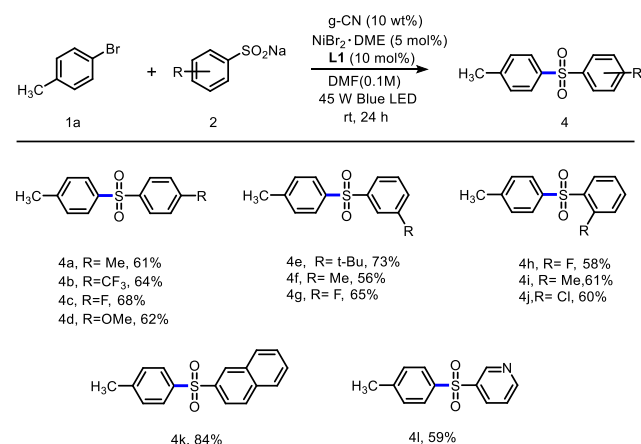
Scheme 2. Substrate Scope of Aryl Halide^a



^a Reactions were performed under the standard conditions (Table 1, Entry 1) and isolated yields were reported. ^b Aryl iodide and 3.0 eq of sulfinate salt were used as the substrate.

In order to further investigate the comprehensive scope of the reaction method, various sodium benzenesulfonates were selected to participate in model reaction condition, and the corresponding good results were obtained similarly. As shown in **Scheme 3**, some of the common substituent groups like methyl **4a**, **4f**, **4i**, methoxy group **4d**, tert-butyl **4e**, Naphthalene **4k** or trifluoromethyl **4b**, fluorine atom **4c**, **4g**, **4h**, chlorine **4j** were proved to be compatible with suitable yield. In addition, pyridine compound **4l** was suitable for this condition.

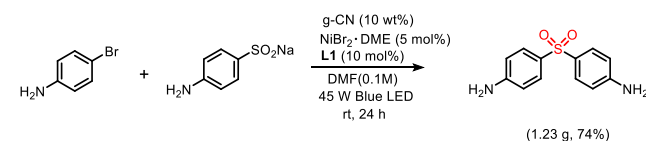
Scheme 3. Substrate Scope of Sulfinate salt^a



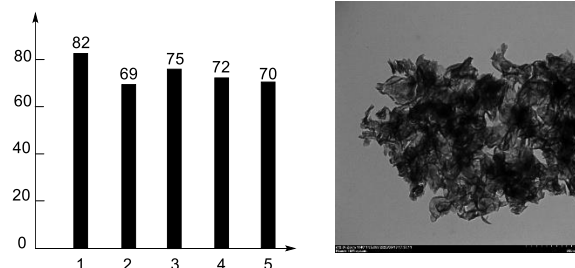
^a Reactions were performed under the standard conditions (Table 1, Entry 1) and isolated yields were reported. ^b Aryl iodide was used for the reaction partner.

Figure 3. Actual catalytic performance testing used in industrial manufacture

(a) Synthesis of drugs dapsone on a gram scale



(b) Crude ¹H-NMR yield of 3a in five consecutive runs with recovered g-CN (TEM attached)



In view of dapsone is a famous bio-active molecule with the corresponding structure, we used the corresponding raw materials, through the standard explored conditions, to achieve the synthesis of this drug in large scale up to 74% yield successfully (**Figure 1a**). What's more, considering that the numbers of cycles from stabilization were the key to measure the practical application towards heterogeneous catalysts, we have studied the

effect of g-CN though repeated to use. As shown in the **Figure 1b**, after each single reaction cycle, excellent conversion rate was obtained in spite of 5 times under the same conditions and recovered g-CN still represent a thin layer appearance with TEM image attached.

In summary, a dual Ni/photocatalytic C(sp²)-SO₂Ar coupling was developed using a carbon nitride semiconductor as recyclable photocatalyst with low toxicity. The semi-heterogeneous nickel/carbon nitride catalysis is an inexpensive, sustainable alternative to homogeneous protocols. The method selectively couples a broad range of aryl bromides with sodium benzenesulfonate in good to excellent isolated yields. Dapsone synthesis was also demonstrated on a gram scale and cyclic experiments also demonstrated the great potential of g-CN in such reactions.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, materials characterization and copies of relevant NMR spectra for all new products, this material is available free.

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Notes

The author declares no competing financial interest.

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