Green
Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Wang, J. Shen, S. Yang, W. Liu, Q. Chen and M. He, *Green Chem.*, 2018, DOI: 10.1039/C8GC00012C.

ROYAL SOCIETY
OF CHEMISTRY

rsc.li/green-chem

View Article Online
DOI: 10.1039/C8GC00012C

Journal Name

ARTICLE

C-H arylation reactions through aniline activation catalysed by PANI-g-C_3N_4-TiO_2 composite under visible light in aqueous medium

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Liang Wang,[a*] Jun Shen,[a] Sen Yang,[a] Wenjie Liu,[a] Qun Chen[a] and Mingyang He[a*]

PANI (polyaniline)-g-C_3N_4-TiO_2 composite was prepared and found to be efficient for the radical C-H arylation reactions. The arylation process involved the coupling of in situ generated aryl diazonium salts from aniline with heteroarenes, enol acetates or benzoquinones under visible light in aqueous medium or pure water. A broad scope of substrates survived the reaction conditions to provide the desired products in moderate to good yields. Scale-up (10 mmol) synthesis was also achieved. This semiconductor photocatalyst showed good photocatalytic performance and stability. Recycle studies showed that this composite could be readily recovered and slight decrease in the catalytic activity was observed after ten consecutive runs.

Introduction

Arylated heteroarenes, enol acetates and benzoquinones are ubiquitous structures that have found wide applications in materials science and pharmaceutical chemistry.[1] The most efficient and economical approach for constructing these structures is direct C-H arylation process, in which no preactivation of the substrates is required. Thereby, a series of C-H arylation reactions employing aryl halides, arylboronic acids, diazonium salts as well as other arylating reagents have been developed.[2-4] However, these reported methodologies usually involved the use of transition metal catalysts, unfriendly reagents/solvents, or harsh conditions.

Recently, photoredox reactions under visible light has emerged as an powerful and green synthetic technology for a wide range of reactions.[5] These catalytic systems are environmentally friendly since visible light is abundant and nontoxic, thereby no extra waste is generated. In this context, considerable progress has been made in photocatalyzed C-H arylation reactions.[6] Particularly, diazonium salts, as an ideal source of aryl radicals, have shown widespread applications in photocatalyzed C-H arylations due to their high reactivity and reduction potentials.[7] However, there are still some issues to be addressed from green point of view. Firstly, the high reactivity and hazardous profile of diazonium salts made them unsuitable for safe handling. Despite the two-step, one-pot procedure involving the in situ preparation of diazonium chlorides in HCl solution followed by addition of the substrates could be an alternative approach, the strongly acidic solution and the excess of bases still limited its practical application, especially on a large scale. Secondly, most of the photocatalyzed C-H arylations were conducted in organic solvents. Such reaction in aqueous medium or even in pure water was rare.[7h] Finally, the photocatalysts used in previously reported procedures were either expensive or could not be recovered and reused. Hence, the development of a facile and green approach for photocatalyzed C-H arylation reactions is still highly desirable.

Semiconductor composites have become a rapidly growing class of photocatalysts in recent years. The low-cost, stability and recyclability of such heterogeneous photocatalysts make them more advantageous than the homogeneous ones. Among them, titanium dioxide (TiO_2)-based composites are the most popular since TiO_2 is cheap, stable, and nontoxic.[7k,8] Up to date, many modifications of TiO_2 have been made to overcome its inherent drawbacks including the wide band gap (3.2 eV, anatase) and the high recombination rate of electron−hole pairs.[9-16] However, it should be pointed out that most of these semiconductor composites are used for photo-degradations, their applications in synthetic chemistry have been less reported yet. Recently, we focused on the heterogeneous photocatalysis,[17] and a ternary PANI−g-C_3N_4−TiO_2 composite exhibited good photocatalytic activity, stability as well as reusability for radical addition reaction between aryl diazonium salts and aryl alkynes.[17c]

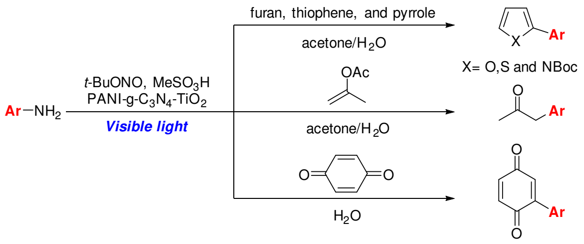
To address the above mentioned issues and in continuation of our interest in photocatalysis and green chemistry, herein, we reported a PANI−g-C_3N_4−TiO_2 composite-catalyzed C-H arylation reactions through in situ aniline activation under visible light in aqueous medium or pure water (Scheme 1).

---

[a] *School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Changzhou University, Gehu Raod 1, Wujin, Changzhou, 213164, P. R. China. E-mail: liangwang@cczu.edu.cn; hemingyangjpu@yahoo.com*

†Electronic Supplementary Information (ESI) available: Experimental procedures, NMR spectra. See DOI:10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C8GC00012C



Scheme 1 PANI-g-C_3N_4-TiO_2 composite catalysed C-H arylations under visible light.

Results and discussion

The detailed preparation of g-C_3N_4, PANI-g-C_3N_4 and PANI–g-C_3N_4–TiO_2 composites as well as the corresponding characterizations by x-ray diffraction (XRD), ultraviolet–visible light (UV-vis), photoluminescence spectroscopy (PL) and transmission electron microscope (TEM) have been reported in our previously published paper (See ESI†).[17c] Briefly, comparison of the XRD patterns clearly indicates that these diffraction peaks are assigned to the PANI, g-C_3N_4 and TiO_2, respectively (Figure S1, ESI†). Meanwhile, no crystal transfer occurs during the composition process and no obvious variation in terms of peak position is observed with different weight percentages of PANI in the PANI–g-C_3N_4–TiO_2 composite. The UV–vis spectra shows that the introduction of PANI and g-C_3N_4 in PANI–g-C_3N_4–TiO_2 composite can significantly enhance its visible-light absorption (Figure 1, a). The PL spectra shows that PANI–g-C_3N_4–TiO_2 composite has the lowest intensity, indicating the photo-induced electron–hole pairs can be effectively separated (Figure 1, b). TEM and HRTEM images of PANI–g-C_3N_4–TiO_2 composite shows that TiO_2 nanoparticles disperse well, and both TiO_2 and PANI are physically supported on g-C_3N_4 (Figure 1, c and d).

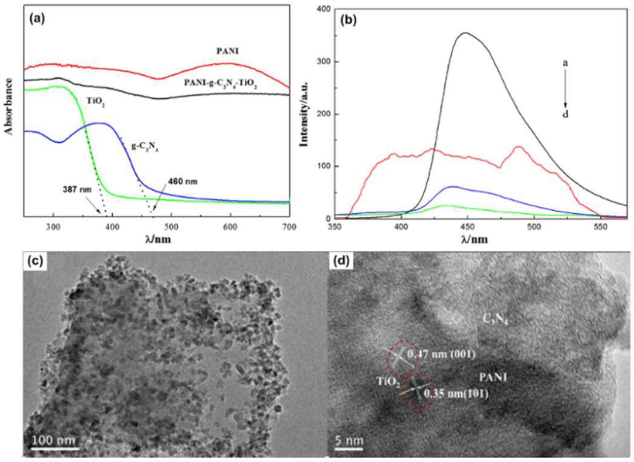
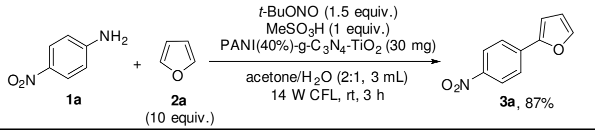


Figure 1. (a) UV–vis DRS of TiO_2, g-C_3N_4, PANI, and PANI-g-C_3N_4-TiO_2 composite; (b) PL spectra of g-C_3N_4 (black), TiO_2 (red), g-C_3N_4-TiO_2 (blue) and PANI-g-C_3N_4-TiO_2 (green); (c) TEM image of PANI-g-C_3N_4-TiO_2; (d) HRTEM image of PANI-g-C_3N_4-TiO_2.

With PANI–g-C_3N_4–TiO_2 composite in hand, we initially explored its photocatalytic activity toward the C-H arylation of heteroarene using *p*-nitroaniline (**1a**) and furan (**2a**) as the substrates (Table 1).

Table 1. Optimization of reaction conditions.[a]



Entry	Variation of the standard conditions	Yield (%)[b]
1	-	87
2	DMF	47
3	DMSO	59
4	MeOH	32
5	CH_3CN	17
6	THF	15
7	H_2O	20
8	Acetone	43
9	DMF/H_2O (2:1)	60
10	DMSO/H_2O (2:1)	69
11	acetone/H_2O (3:1)	77
12	acetone/H_2O (1:1)	72
13	PANI(20%)-g-C_3N_4-TiO_2	45
14	PANI(60%)-g-C_3N_4-TiO_2	71
15	PANI(80%)-g-C_3N_4-TiO_2	65
16	PANI(40%)-g-C_3N_4	39
17	g-C_3N_4-TiO_2	37
18	PANI(40%)-TiO_2	22
19	g-C_3N_4	30
20	TiO_2 (anatase)	NR[c]
21	without photocatalyst	NR[c]
22	without light	NR[c]
23	other visible light sources	74[d], 65[e], 37[f]
24	without $MeSO_3H$	47
25	other acid additives	61[g], 72[h]
26	under N_2	80
27	12 h	85
28	PANI(40%)-g-C_3N_4-TiO_2 (20 mg)	69
29	PANI(40%)-g-C_3N_4-TiO_2 (40 mg)	81
30	**2a** (5 equiv)	73
31	**2a** (15 equiv)	85

[a] Standard reaction conditions: **1a** (0.3 mmol), **2a** (10 equiv.), *t*-BuONO (1.5 equiv.), $MeSO_3H$ (1.0 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), acetone/H_2O (2:1) (3 mL), irradiation with a 14 W CFL at room temperature for 3 h. [b] Isolated yields. [c] No reaction. [d] Irradiation with a blue LED (3W) for 3 h. [e] Irradiation with a green LED (3W) for 3 h. [f] Irradiation with sunlight for 12 h. [g] CF_3SO_3H instead of $MeSO_3H$. [h] TsOH·H_2O instead of $MeSO_3H$.

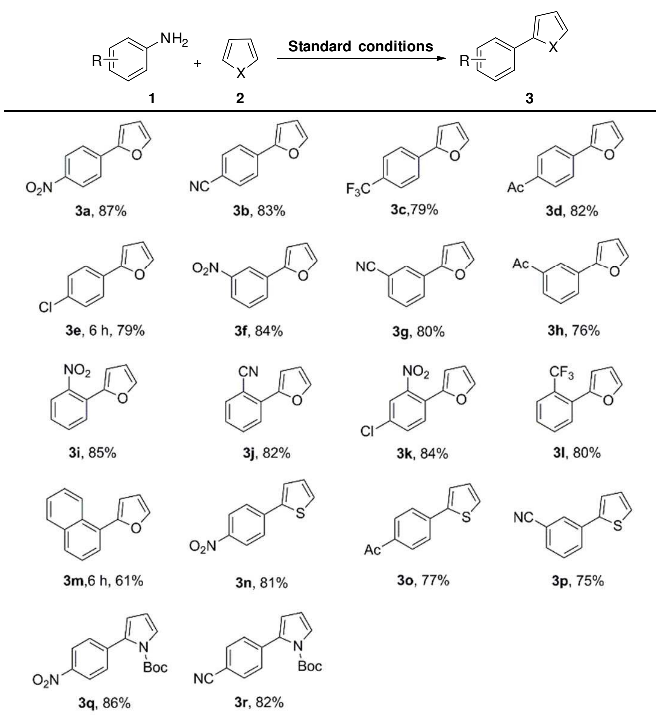
Pleasingly, after investigating various reaction parameters, we found that the reaction could provide the desired product **3a** in 87% yield under the following reaction conditions: **1a** (1 equiv.), **2a** (10 equiv.), *t*-BuONO (1.5 equiv.), $MeSO_3H$ (1 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg) in acetone/H_2O (2:1, 3 mL) under irradiation with a 14 W CFL at room temperature for 3 h (Table 1, entry 1). Control experiments showed that reaction in DMF, DMSO and acetone afforded **3a** in moderate yields, while poor yields were obtained when conducting the reactions in methanol, acetonitrile, tetrafuran and water (entries 4~7). Addition of water to DMF, DMSO and acetone significantly promoted the reaction, and acetone/H_2O (2:1) turned out to be the optimal (entries 9~12). This result might be ascribed to the fact that the addition of water could

View Article Online
DOI: 10.1039/C8GC00012C

enhance the solubility of the in situ generated aryl diazonium salt. The evaluation of a series of PANI-g-C_3N_4-TiO_2 composites showed that the loading of PANI could affected the catalytic activity of PANI–g-C_3N_4–TiO_2 composite (entries 13~15). Although it remained unclear currently, the 40% loading of PANI turned out to be the best choice. The highest surface area (128 m^2 g^{-1}, Table S1, ESI) might be account for the highest catalytic activity among the four PANI–g-C_3N_4–TiO_2 composites. By contrast, using g-C_3N_4-TiO_2, PANI(40%)-TiO_2 and g-C_3N_4 as the photocatalysts gave the product in 37%, 22%, and 30% yields, respectively (entries 17~19). No reaction occurred when TiO_2 (anatase) was employed (entry 20). These results suggested that a synergistic effect may exist in the ternary composite. Expectedly, no reaction was observed in the absence of either visible light or a photocatalyst (entry 21 and 22). The light sources were also checked and reactions irradiated with a blue LED and green LED afforded a relatively lower yields, while the reaction proceeded under sunlight led to a rather poor yield (entry 23). Moreover, the absence of $MeSO_3H$ which was used for the formation of the corresponding diazonium salt gave a much lower yield (47%, entry 24), and 61% and 72% yields were obtained by switching the additive to CF_3SO_3H or TsOH·H_2O (entry 25). No obvious change in the yield was observed under nitrogen atmosphere or by prolonging the reaction time to 12 h (entry 26 and 27). Finally, the survey on the loadings of catalyst and **2a** clearly showed that 30 mg of catalyst and 10 equiv. of **2a** were sufficient (entries 28~31).

The scope of this photocatalyzed C-H arylation reaction with anilines and heteroarenes was then examined using the optimized reaction conditions (Table 2).

Table 2. Photocatalyzed α-arylation of heteroarenes.[a]

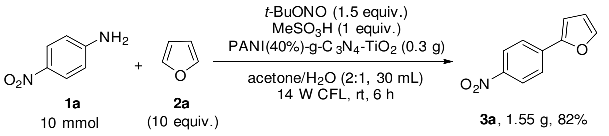


3a, 87%
3b, 83%
3c,79%
3d, 82%
3e, 6 h, 79%
3f, 84%
3g, 80%
3h, 76%
3i, 85%
3j, 82%
3k, 84%
3l, 80%
3m,6 h, 61%
3n, 81%
3o, 77%
3p, 75%
3q, 86%
3r, 82%

[a] Standard conditions: **1** (0.3 mmol), **2** (10 equiv.), *t*-BuONO (1.5 equiv.), $MeSO_3H$ (1.0 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), acetone/H_2O (2:1) (3 mL), irradiation with a 14 W CFL at room temperature for 3 h, isolated yields.

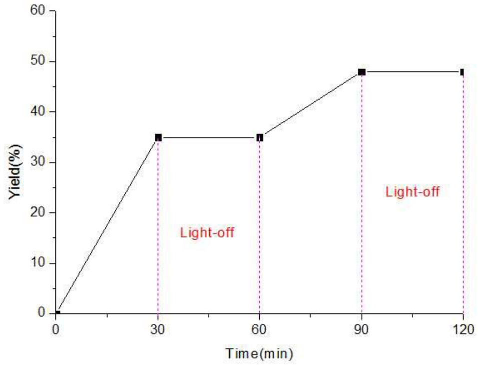
Generally, anilines containing electron-withdrawing groups such as -NO_2, -CN, -CF_3, and -Ac, reacted with furan smoothly to give the desired products in good yields. Notably, the C-Cl bonds in **3e** and **3k** was not affected, enabling the further manipulation of the initial products. The *ortho*-substituted anilines also showed good compatibilities, delivering the corresponding products **3i**~**3l** in 80~85% yields. Although the results were not shown in the table, it should be pointed out that the present reaction conditions were not compatible for the electron-rich anilines, and very low yields were obtained. This result was consistent with previous literature,[7d] which might be attributed to the relatively lower reduction potentials of their aryl diazonium salts compared with those bearing electron-withdrawing groups.[18] By contrast, the 1-naphthylamine could survived the reaction conditions to give product **3m** in 61% yield after 6 h. Other heteroarenes such as thiophene and pyrrole were also checked, and all the reactions proceeded smoothly to provide the corresponding products **3n**~**3r** in good yields.

Furthermore, gram-scale synthesis of **3a** was performed. Fortunately, product **3a** was obtained in 82% yield at 10 mmol scale after 6 h (Scheme 2). This result provides a potential application of this catalytic system in practical scale-up synthesis.



Scheme 2 Gram-scale synthesis of **3a**.

Time profile of photocatalytic reaction toward the synthesis of **3a** was also carried out (Scheme 3). The result showed that the reaction was totally inhibited in the absence of light and continuous irradiation of visible light is essential for this reaction.



Scheme 3 Control experiment.

View Article Online
DOI: 10.1039/C8GC00012C

The stability and reusability of heterogeneous photocatalysts are very important for the advancement of sustainable processes. It was worth noting that the present PANI-g-C_3N_4-TiO_2 catalyst is highly stable. Under the standard reaction conditions for synthesis of **3a**, the catalyst could be recovered by centrifugation. Results showed that slight decrease in the catalytic activity was observed after ten consecutive runs (Figure 2). The recycled catalyst was also subjected to XRD and TEM analyses, and no obvious change in the structure was observed.

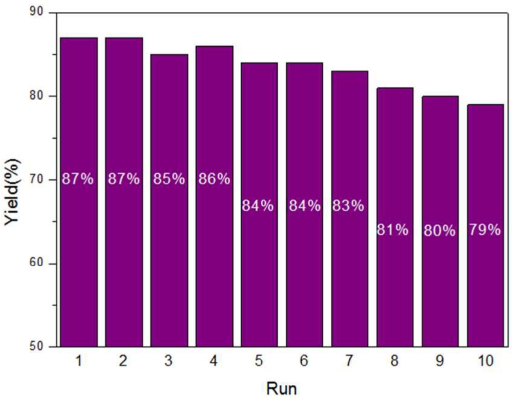
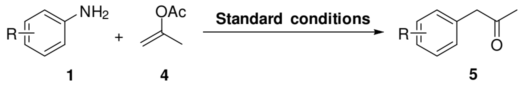
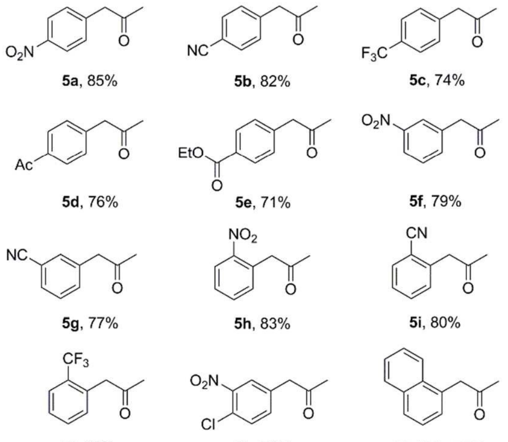


Figure 2 Recyclability of the PANI(40%)-g-C_3N_4-TiO_2 for the synthesis of **3a** under standard reaction conditions.

Then, we envisioned that whether this catalytic system could be extended to other C-H arylation reactions. The α-aryl ketone motifs have also been found wide applications in pharmaceutical chemistry and synthetic chemistry. Generally, this reaction can be achieved via the reaction of diazonium salts with enolacetates under the assistance of a transition metal catalyst,[19] a transition metal photocatalyst,[7c] an organocatalyst[2j] or stoichiometric amounts of bases.[3a] To our literature, photocatalyzed C-H arylation of enolacetates in the presence of a heterogeneous catalyst, especially in aqueous medium, has never been disclosed. Pleasingly, the standard reaction conditions for C-H arylation of heteroarenes were also suitable for the synthesis of α-aryl methyl ketones (Table 3).

Table 3. Photocatalyzed the synthesis of α-aryl methyl ketones.[a]





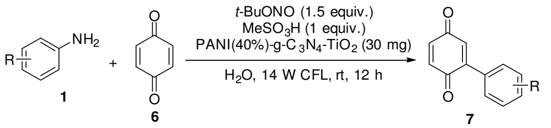
5a, 85% **5b**, 82% **5c**, 74%
5d, 76% **5e**, 71% **5f**, 79%
5g, 77% **5h**, 83% **5i**, 80%
5j, 73% **5k**, 76% **5l**, 12 h, 72%

[a] Reaction conditions: **1** (0.3 mmol), **4** (10 equiv.), *t*-BuONO (1.5 equiv.), $MeSO_3H$ (1.0 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), acetone/H_2O (2:1) (3 mL), irradiation with a 14 W CFL at room temperature for 6 h, isolated yields.

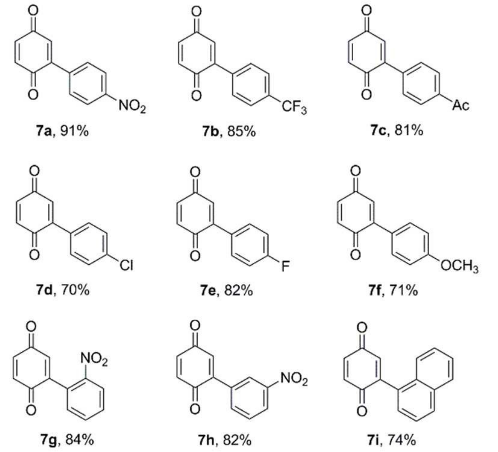
Several functional groups, such as nitro, cyano, trifluoromethyl, acetyl, ester, and halogen were well tolerated, providing the corresponding products **5** in 72~85% yields. Similarly, substrates with strong electron-withdrawing groups gave excellent yields, while those with strong electron-donating groups showed poor reactivity. Notably, no obvious steric hindrance of the substrates was observed (**5h** and **5i**), and the C-Cl bond in **5k** was intact. Moreover, 1-naphthylamine showed good compatibility, delivering the desired product **5l** in 72% yield after 12 h.

We further applied the catalytic system to prepare arylated benzoquinones. Although Lamblin and co-workers[4b] showed that the C-H arylation of benzoquinones could occur in the absence of any acid additive and catalyst in DMSO-water system, their reaction conditions did not suitable for the present protocol since relatively lower yield was obtained and meanwhile the product was not pure enough. We reasoned that the introduction of a photocatalyst could significantly promote the formation of an aryl radical. In order to develop a general C-H arylation process in a more green solvent, we tried the reaction in acetone-water. Encouragingly, the present protocol was well suitable for such reaction, and the reaction could even proceeded in pure water (Table 4). As shown from the results, this protocol tolerated diverse functional groups and good to excellent yields were obtained. Notably, anilines bearing strong electron-donating groups also survived the reaction conditions.

Table 4. Photocatalyzed C-H arylation of benzoquinone.[a]



View Article Online
DOI: 10.1039/C8GC00012C



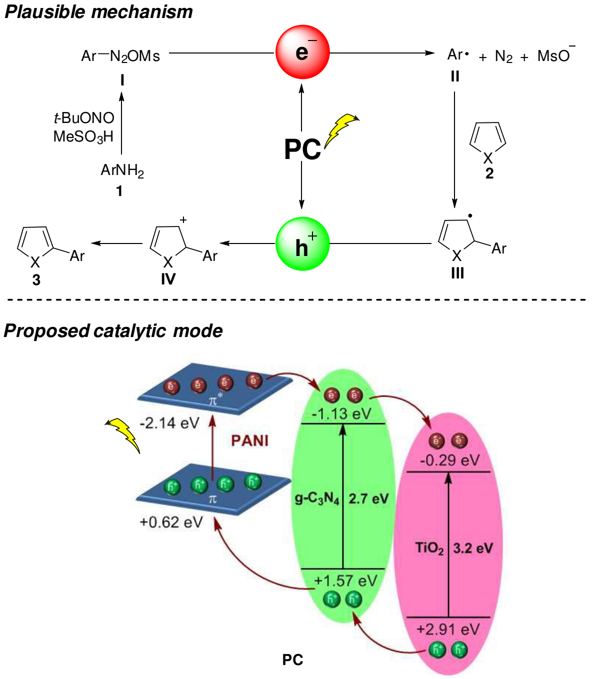
7a, 91% **7b**, 85% **7c**, 81%

7d, 70% **7e**, 82% **7f**, 71%

7g, 84% **7h**, 82% **7i**, 74%

[a]Reaction conditions: **1** (0.3 mmol), **6** (5 equiv.), *t*-BuONO (1.5 equiv.), $MeSO_3H$ (1.0 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), H_2O (3 mL), irradiation with a 14 W CFL at room temperature for 12 h, isolated yields.

Based on above results as well as previous study,[7c,7d,17c] a plausible catalytic mode of this semiconductor photocatalyst (**PC**) was proposed using C-H arylation of heteroarenes as example (Scheme 4). Initially, the composite absorbs photons and excites electron and hole pairs under visible light. Then, homolytic dediazoniation of the *in situ* generated diazonium salt **I** via SET process provides the aryl radical **II**. The addition of radical **II** to heteroarene **2** gives radical **III**, which is further oxidized by the photogenerated holes (H^+) to form carbocation intermediate **IV**. Finally, intermediate **IV** is deprotonated to deliver the desired products. As for the catalytic mode, considering the edge potentials of PANI (π*-orbital: -2.14 eV; π-orbital: +0.62 eV)[20] are more negative than the VB and CB potentials of g-C_3N_4 (-1.13 eV and +1.57 eV, respectively)[21] as well as those of TiO_2 (-0.29 eV and +2.91 eV, respectively), we assume that excited electrons migrate to the CB of TiO_2 while the holes are collected by the π-orbital of PANI. Thereby, the photogenerated electron–hole pairs are efficiently separated, and the recombination process is hindered. This hypothesis is probably account for its good catalytic activity. However, we still cannot determine the exact catalytic site of the photocatalyst at current stage since both g-C_3N_4-TiO_2 and PANI-TiO_2 can promote this reaction (Table 1, entry 17 and 18). The possibility that the oxidation reaction takes place at the VB of g-C_3N_4 and the PANI works as a conductor is still cannot be exclude out.



Scheme 4 Plausible catalytic pathway.

Conclusions

In summary, a PANI-g-C_3N_4-TiO_2 composite has been prepared and found to be efficient for a series of photocatalyzed C-H arylation reactions under visible light. The C-H arylation of heteroarenes and enol acetates could be carried out in acetone/water medium, while the C-H arylation of benzoquinones could even be performed in pure water, thereby avoiding the use of a large amount of organic solvents. The in situ generated aryl diazonium salts from anilines in the presence of *t*-BuONO and $MeSO_3H$ were used as the aryl radicals and a broad scope of substrates survived the reaction conditions. The starting materials are simple and cost-effective, and the catalyst is readily prepared and stable. Scale-up (10 mmol) synthesis of **3a** was also achieved, providing a potential application of this catalytic system in practical synthesis. Recycle studies showed that this composite could be readily recovered and only slight decrease in the catalytic activity was observed after ten consecutive runs. Control experiments showed that a radical pathway might be involved. Notably, although we still could not determine the exact catalytic site of the photocatalyst at current stage, the synergistic effect of the three components in PANI-g-C_3N_4-TiO_2 composite might be account for the enhanced photocatalytic activity as well as the reusability.

Experimental

Preparation and characterization of PANI–g-C_3N_4–TiO_2 composite

The PANI–g-C_3N_4–TiO_2 composites were prepared according to our previous report.[17c] Briefly, g-C_3N_4 was prepared using

DOI: 10.1039/C8GC00012C

melamine as a precursor via calcination at 580 ^{o}C for 4 h. For the preparation of the ternary composite PANI-g-C_3N_4-TiO_2, initially, 15 mL of sodium hydroxide solution (c = 1.5 mol/L) was added slowly to 3 mL of aqueous $TiCl_4$ solution (2.5 mol/L), which was diluted with 80 mL of deionized water. The mixture was stirred and a certain amount of PANI-g-C_3N_4 (n(g-C_3N_4): n(TiO_2) = 1:2) was added to the above mixture. The temperature was then raised slowly to 80 ^{o}C, and the mixture was crystallized for 2 h. Afterwards, aqueous sodium hydroxide solution(c = 2.5mol/L) was added dropwise to maintain the pH at 5~6. The solid was filtrated, washed with deionized water, dried under vacuum, and grinded to afford PANI-g-C_3N_4-TiO_2.

Typical procedure for synthesis of 3a

To a mixture of aniline (0.3 mmol) and $MeSO_3H$ (0.3 mmol) in acetone/H_2O (2:1, 3 mL) at 25 °C was added *t*-BuONO (0.45 mmol). The reaction mixture was stirred for 10 minutes at 25 °C. Then, furan **2a** (10 equiv.) and PANI-g-C_3N_4-TiO_2 (30 mg) were successively added. The mixture was then irradiated with a 14 W CFL and stirred at room temperature for 3 h. The distance of the reaction vial from the light is about 5 centimeters. After reaction, the mixture was diluted with EtOAc (10 mL) and H_2O (5 mL), and the solid catalyst was recovered by centrifugation. The aqueous phase was extracted with EtOAc (5 mL × 3). The collected organic extracts were dried on Na_2SO_4, filtered and evaporated to dryness. The crude was purified by flash chromatography on silica gel to give the pure product **3a** in 87% yield.

2-(4-Nitrophenyl)furan (3a).[7d] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 - 8.21 (m, 2H), 7.80 - 7.75 (m, 2H), 7.57 (dd, *J* = 1.7, 0.5 Hz, 1H), 6.87 (dd, *J* = 3.5, 0.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.83, 146.50, 144.28, 136.55, 124.43, 124.04, 112.57, 109.12; MS (ESI) *m/z* 212 $[M + Na]^+$.

Typical procedure for synthesis of 5a

To a mixture of aniline (0.3 mmol) and $MeSO_3H$ (0.3 mmol) in acetone/H_2O (2:1, 3 mL) at 25 °C was added *t*-BuONO (0.45 mmol). The reaction mixture was stirred for 10 minutes at 25 °C. Then, enol acetate **4** (10 equiv.) and PANI-g-C_3N_4-TiO_2 (30 mg) were successively added. The mixture was then irradiated with a 14 W CFL and stirred at room temperature for 6 h. The distance of the reaction vial from the light is about 5 centimeters. After reaction, the mixture was diluted with EtOAc (10 mL) and H_2O (5 mL), and the solid catalyst was recovered by centrifugation. The aqueous phase was extracted with EtOAc (5 mL × 3). The collected organic extracts were dried on Na_2SO_4, filtered and evaporated to dryness. The crude was purified by flash chromatography on silica gel to give the pure product **5a** in 85% yield.

1-(4-Nitrophenyl)propan-2-one (5a).[7c] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.38, 147.16, 141.56, 130.59, 123.87, 50.15, 30.01; MS (ESI) *m/z* 202 $[M + Na]^+$.

Typical procedure for synthesis of 7a

To a mixture of aniline (0.3 mmol) and $MeSO_3H$ (0.3 mmol) in H_2O (3 mL) at 25 °C was added *t*-BuONO (0.45 mmol). The reaction mixture was stirred for 10 minutes at 25 °C. Then, enol acetate **6** (5 equiv.) and PANI-g-C_3N_4-TiO_2 (30 mg) were successively added. The mixture was then irradiated with a 14 W CFL and stirred at room temperature for 12 h. The distance of the reaction vial from the light is about 5 centimeters. After reaction, the mixture was diluted with EtOAc (10 mL) and H_2O (5 mL), and the solid catalyst was recovered by centrifugation. The aqueous phase was extracted with EtOAc (5 mL × 3). The collected organic extracts were dried on Na_2SO_4, filtered and evaporated to dryness. The crude was purified by flash chromatography on silica gel to give the pure product **7a** in 91% yield.

4'-Nitro-[1,1'-biphenyl]-2,5-dione (7a).[2j] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 6.97 - 6.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.98, 185.75, 148.74, 144.03, 138.88, 137.11, 136.71, 134.21, 130.43, 123.75; MS (ESI) *m/z* 252 $[M + Na]^+$.

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (21302014 and 21676030), the Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (BM2012110), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, and the Advanced Catalysis and Green Manufacturing Collaborative Innovation Center of Changzhou University of Changzhou University.

Notes and references

1 (a) S. Edmondson, S. J. Danishefsky, L. Sepp-Lorenzino and N. Rosen, *J. Am. Chem. Soc.*, 1999, **121**, 2147; (b) H. Yin, G.-i. Lee, H. S. Park, G. A. Payne, J. M. Rodriguez, S. M. Sebti and A. D. Hamilton, *Angew. Chem., Int. Ed.*, 2005, **44**, 2704; (c) A. R. Murphy and J. M. J. Fréchet, *Chem. Rev.*, 2007, **107**, 1066; (d) B. Schmidt and D. Geißler, *Eur. J. Org. Chem.*, 2011, 4814; (e) A. Perrier, F. Maurel and D. Jacquemin, *Acc. Chem. Res.*, 2012, **45**, 1173.

2 Selected examples for C-H arylation of heteroarenes: (a) S. Yanagisawa, T. Sudo, R. Noyori and K. Itami, *J. Am. Chem. Soc.*, 2006, **128**, 11748; (b) H. Kawai, Y. Kobayashi, S. Oi and Y. Inoue, *Chem. Commun.*, 2008, 1464; (c) B. Join, T. Yamamoto and K. Itami, *Angew. Chem., Int. Ed.*, 2009, **48**, 3644; (d) I. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, A. L. Sobel and P. S. Baran, *J. Am. Chem. Soc.*, 2010, **132**, 13194; (e) W. Han, P. Mayer and A. R. Ofial, *Chem. Eur. J.*, 2011, **17**, 6904; (f) N. Uchiyama, E. Shirakawa, R. Nishikawa and T. Hayashi, *Chem. Commun.*, 2011, **47**, 11671; (g) J. J. Dong, D. Roy, R. J. Roy, M. Ionita and H. Doucet, *Synthesis*, 2011, 3530; (h) M. Raduán, J. Padrosa, A. Pla-Quintana, T. Parella and A. Roglansa, *Adv. Synth. Catal.*, 2011, **353**, 2003; (i) A. Honraedt, M. Raux, E. L. Grognec, D. Jacquemin and F.-X. Felpin, *Chem. Commun.*, 2014, **50**, 5236; (j) H. Bonin, M. Sauthier and F.-X. Felpin, *Adv. Synth. Catal.*, 2014, **356**, 645; (k) S. Shaaban, A. Jolit, D. Petkova and N. Maulide, *Chem.*

View Article Online
DOI: 10.1039/C8GC00012C

Commun., 2015, **51**, 13902; (l) S. Crespi, S. Protti and M. Fagnoni, *J. Org. Chem.,* 2016, **81**, 9612; (m) S. Shaaban and N. Maulide, *Synlett*, 2017, **28**, 2707.

3 Selected examples for C-H arylation of enol acetates: (a) C. Molinaro, J. Mowat, F. Gosselin, P. D. O'Shea, J. Marcoux, R. Angelaud and I. W. Davies, *J. Org. Chem.,* 2007, **72**, 1856; (b) L. Li, *Synth. Commun.*, 2007, **37**, 985.

4 Selected examples for C-H arylation of benzoquinones: (a) J. Wang , S. Wang , G. Wang , J. Zhang and X. Yu, *Chem. Commun.*, 2012, **48**, 11769; (b) M.Lamblin, G. Naturale, J. Dessolin, F.-X. Felpin, Synlett, 2012, **23**, 1621; (c) A. Honraedt, F. L. Callonnec, E. L. Grognec, V. Fernandez and F.-X. Felpin, *J. Org. Chem.,* **2013**, *78*, 4604; (d) A. Deb, S. Manna, A. Maji, U. Dutta and D. Maiti, *Eur. J. Org. Chem.*, 2013, 5251; (e) S. E. Walker, J. A. Jordan-Hore, D. G. Johnson, S. T. Macgregor and A. Lee, *Angew. Chem., Int. Ed.*, 2014, **53**, 13876; (f) A. Ilangovan, A. Polu and G.Satish, *Org. Chem. Front.*, 2015, **2**, 1616.

5 (a) T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, **2**, 527; (b) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102; (c) Y. Ye and M. S. Sanford, *J. Am. Chem. Soc.*, 2012, **134**, 9034; (d) L. Shi and W. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687; (e) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (f) J. W. Beatty and C. R. J. Stephenson, *Acc. Chem. Res.*, 2015, **48**, 1474; (g) J. Chen, X. Hu, L. Lu and W. Xiao, *Chem. Soc. Rev.*, 2016, **45**, 2044; (h) X. Lang, J. Zhao and X. Chen, *Chem. Soc. Rev.*, 2016, **45**, 3026; (i) N. Corrigan, S. Shanmugam, J. Xu and C. Boyer, *Chem. Soc. Rev.*, 2016, **45**, 6165; (j) M. D. Levin, S. Kim and F. D. Toste, *ACS Cent. Sci.,* 2016, **2***,* 293; (k) S. Kim, J. Rojas-Martin and F. D. Toste, *Chem. Sci.,* 2016, **7***,* 85; (l) J. Xie, H. Jin and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2017, **46**, 5193; (m) W. Liu and C.-J. Li, *Synlett*, 2017, **28**, 2714; (n) M. Malacarne, S. Protti and M. Fagnoni, *Adv. Synth. Catal.*, 2017, **359**, 3826;

6 (a) I. Ghosh, L. Marzo, A. Das, R. Shaikh and B. König, *Acc. Chem. Res.*, 2016, **49***,* 1566; (b) S. Kindt and M. R. Heinrich, Synthesis, 2016, **48**, 1597.

7 (a) D. Kalyani, K. McMurtrey, S. Neufeldt and M. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 18566; (b) P. Schroll, D. P. Hari, and B. König, *ChemistryOpen*, 2012, **1**, 130; (c) T. Hering, D. P. Hari and B. König, *J. Org. Chem.,* 2012, **77**, 10347; (d) D. P. Hari, P. Schroll and B. König, *J. Am. Chem. Soc.*, 2012, **134**, 2958; (e) D. P. Hari and B. König, *Angew. Chem., Int. Ed.*, 2013, **52**, 4734; (f) D. Hari, T. Hering and B. König, *Angew. Chem., Int. Ed.*, 2014, **53**, 725; (g) J. Zhang, J. Chen, X. Zhang and X. Lei, *J. Org. Chem.*, 2014, **79**, 10682; (h) D. Xue, Z. Jia, C. Zhao, Y. Zhang, C. Wang and J. Xiao, *Chem. Eur. J.*, 2014, **20**, 2960; (i) D. Cantillo, C. Mateos, J. A. Rincon, O. de Frutos and C. O. Kappe, *Chem. Eur. J.*, 2015, **21**, 12894; (j) X. Zuo, W. Wu and W. Su, *Acta Chim. Sinica*, 2015, **73**, 1298; (k) J. Zoller, D. C. Fabry and M. Rueping, *ACS Catal.*, 2015, **5**, 3900; (l) L. Zhi, H. Zhang, Z. Yang, W. Liu and B. Wang, *Chem. Commun.*, 2016, **52**, 6431; (m) Y. Zhang, X. Feng, Y. Yang and B. Cao, *Tetrahedron Lett.*, 2016, **57**, 2298; (n) B. Alcaide, P. Almendros, E. Busto and A. Luna, *Adv. Synth. Catal*l., 2016, **358**, 1526; (o) F. Yang, J. Koeller and L. Ackermann, *Angew. Chem., Int. Ed.*, 2016, **55**, 4759; (p) N. Morimoto, K. Morioku, H. Suzuki, Y. Nakai and Y. Nishina, *Chem. Commun.*, 2017, **53**, 7226; (q) K. Rybicka-jasínska, B. König and D. Gryko, *Eur. J. Org. Chem.*, 2017, 2104.

8 (a) Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 12820; (b) S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro and L. Palmisano, *J. Am. Chem. Soc.*, 2008, **130**, 1568; (c) S. Yurdakal, G. Palmisano, V. Loddo, O. Alagoz, V. Augugliaro and L. Palmisano, *Green Chem.*, 2009, **11**, 510.

9 K. Bhattacharyya, S. Varma, A. K. Tripathi, S. R. Bharadwaj and A. K. Tyagi, *J. Phys. Chem. C*, 2008, **112**, 19102.

10 H. Tada, Q. Jin, H. Nishijima, H. Yamamoto, M. Fujishima, S. Okuoka, T. Hattori, Y. Sumida and H. Kobayashi, *Angew. Chem., Int. Ed.*, 2011, **50**, 3501.

11 Q. Jin, T. Ikeda, M. Fujishima and H. Tada, *Chem. Commun.*, 2011, **47**, 8814.

12 M. Harb, P. Sautet, P. Raybaud, *J. Phys. Chem. C*, 2013, **117**, 8892.

13 J. Tang, G. Grampp, Y. Liu, B. Wang, F. Tao, L. Wang, X. Liang, H. Xiao and Y. Shen, *J. Org. Chem.*, 2015, **80**, 2724.

14 A. J. Lennox, P. Bartels, M. M. Pohl, H. Junge and M. Beller, *J. Catal.*, 2016, **340**, 177.

15 K. Li, S. Gao, Q. Wang, H. Xu, Z. Wang, B. Huang, Y. Dai and J. Lu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 9023.

16 S. Obregón, Y. Zhang and G. Colón, *Appl. Catal. B*, 2016, **184**, 96.

17 (a) L. Wang, C. Wang, W. Liu, Q. Chen and M. He, *Tetrahedron Lett.*, 2016, **57**, 1771; (b) W. Liu, C. Wang, Y. Huang, Q. Chen, L. Wang and M. He, *Synth. Commun.*, 2016, **46**, 1268; (c) W. Liu, C. Wang and L. Wang, *Ind. Eng. Chem. Res.*, 2017, **56**, 6114.

18 P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 201.

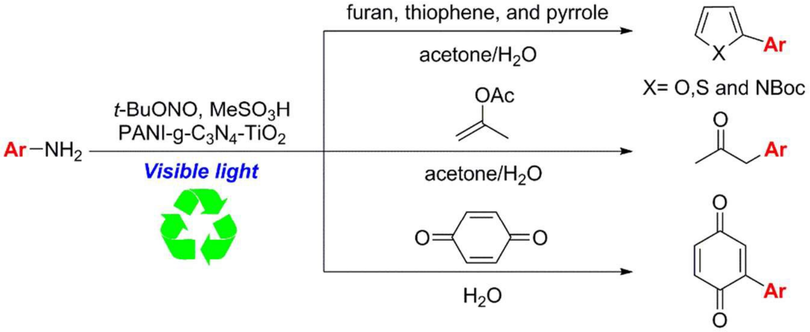
19 J. Rutherford, M. Rainka and S. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 15168.

20 L. Ge, C. C. Han and J. Liu, *J. Mater. Chem.*, 2012, **22**, 11843.

21 L. Ge, C. C. Han and J. Liu, *Appl. Catal. B*, 2011, **108**–**109**, 100.

View Article Online
DOI: 10.1039/C8GC00012C

Graphical Abstract



C-H arylation reactions under visible light in aqueous medium catalysed by PANI-g-C_3N_4-TiO_2 composite has been developed.