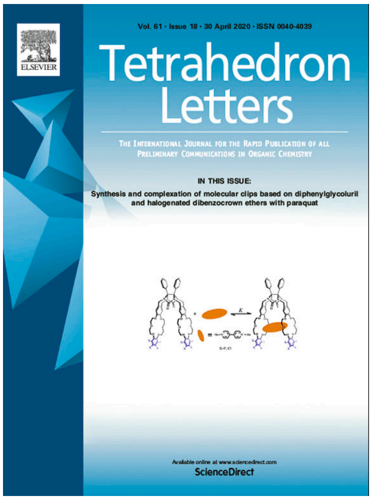

Photocatalyzed synthesis of unsymmetrical ureas *via* the oxidative decarboxylation of oxamic acids with PANI-g-C_3N_4-TiO_2 composite under visible light

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Graphical Abstract

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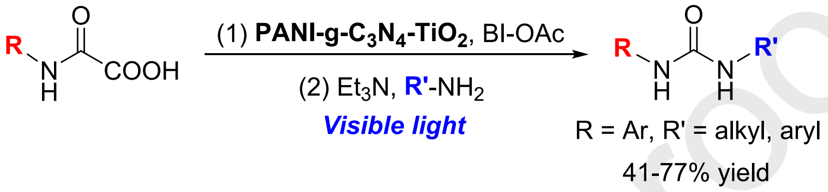
Liang Wang,[a,b,]* Hao Wang,[b] Yaoyao Wang,[b] Minggui Shen[b,c] and Shubai Li[a,]*



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Photocatalyzed synthesis of unsymmetrical ureas *via* the oxidative decarboxylation of oxamic acids with PANI-g-C_3N_4-TiO_2 composite under visible light

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ABSTRACT

The synthesis of unsymmetrical ureas *via* the photocatalyzed oxidative decarboxylation of oxamic acids has been developed. The carbamoyl radicals were generated from oxamic acids in the presence of a hypervalent iodine reagent and the PANI(Polyaniline)-g-C_3N_4-TiO_2 composite under visible light irradiation. The radicals were converted *in situ* into the corresponding isocyanates, which were then trapped by amines to afford the corresponding products in moderate to good yields. This protocol avoided the direct use of environmentally unfriendly isocyanates and a series of substrates were tolerated. Moreover, the photocatalyst could be readily recovered by simple filtration and be reused for several runs with only a slight decrease in the catalytic activity.

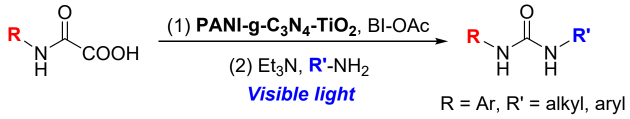
Urea derivatives are useful compounds that display attractive activities in pharmaceuticals and agrochemicals.[1] They have also found wide applications in molecular recognition[2] and organocatalysis[3] due to their high hydrogen bonding ability. Due to their significant importance in various research areas, a number of synthetic approaches have been developed. Traditionally, ureas are synthesized *via* the nucleophilic addition of amines to isocyanates,[4] which are generated by the phosgenation of arylamines or the Curtius rearrangement.[5] However, the use of toxic reagents (phosgene, triphosgene and azides), poor atom economy and limited substrate scope are the major drawbacks. Alternatively, ureas can be prepared *via* transition-metal-catalyzed coupling reactions such as the Pd-catalyzed amidation of aryl halides,[6] the Pd-catalyzed cross-coupling of aryl chlorides or triflates with sodium cyanate,[7] and Ir-[8] or Ru-catalyzed[9] reactions between amines and alcohols.

The transition-metal-catalyzed oxidative carbonylation of amines to access ureas in the presence of CO and an oxidant has also received interest.[10] However, these protocols gave symmetrical ureas as the major products, and only aryl amines were tolerated in some cases. To expand the substrate scope, Zhang and co-workers reported a Pd/C catalyzed carbonylation of azides in the presence of amines under a CO atmosphere.[11] Both aryl azides and alkyl azides were suitable for this methodology, providing unsymmetrical ureas in good yields. Wu and co-workers synthesized unsymmetrical ureas *via* sequential Pd-catalyzed carbonylation, Curtius rearrangement and nucleophilic addition reactions.[12] Similarly, our group reported a Pd/C-catalyzed domino synthesis of urea derivatives using chloroform as the carbon monoxide source in water.[13] While acknowledging these pioneering contributions in this field, there are still some issues that need to be addressed. Most of these protocols required the use of homogeneous noble metal catalysts and CO gas. Limitations such as the use of inconvenient substrates, narrow substrate scope, and harsh reaction conditions have also severely restricted their applications.

Recently, visible-light photocatalysis has served as a powerful and green synthetic technology for organic synthesis.[14] It provides environmentally benign and mild reaction conditions with good functional group compatibility. However, the reported photocatalyzed reactions mainly utilise heavy metal-based photocatalysts, which were either expensive or could not be easily recovered and reused. Further advantages such as low cost, high stability and recyclability make semiconductor photocatalysts more advantageous than the homogeneous ones. To date, numerous semiconductor photocatalysts have been prepared; however, they are mainly used for photo-degradation and their applications in organic sy

focused on photocatalyzed organic transformations employing semiconductor composites as the catalysts.[16] Titanium dioxide (TiO_2)-based composites such as TiO_2-MoS_2 and PANI-g-C_3N_4-TiO_2 displayed good photocatalytic activities in thiocyanation[16a] and arylation reactions,[16b] as well as in the synthesis of disulfides,[16c] *α*-chloro aryl ketones,[16d] and oxadiazoles.[16e] Particularly, for the PANI-g-C_3N_4-TiO_2 ternary composite, the addition of PANI greatly enhanced its catalytic activity and stability since PANI has high absorption coefficients in the visible-light range and good electrical conductivity. Moreover, PANI is a good electron donor and hole conductor upon photoexcitation.

To further expand their applications in photocatalyzed organic transformations, we herein report a PANI-g-C_3N_4-TiO_2 composite catalyzed synthesis of unsymmetrical ureas *via* the oxidative decarboxylation of oxamic acids under visible light (Scheme 1).



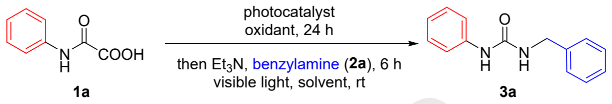
Scheme 1. PANI-g-C_3N_4-TiO_2 composite-catalyzed synthesis of ureas.

The PANI-g-C_3N_4-TiO_2 composite was prepared according to our previous report (see ESI for details).[16b,d,e] With the catalyst in hand, we began to explored its photocatalytic activity towards urea synthesis using 2-oxo-2-(phenylamino)acetic acid (**1a**) and benzylamine (**2a**) as the model substrates (Table 1).

Initially, a photocatalyst and an oxidant were utilized in order to achieve the radical decarboxylation of oxamic acid (**1a**).[17,18] The reaction was carried out in the presence of **1a** (1 equiv.), PANI(20%)-g-C_3N_4-TiO_2 (30 mg) and benziodoxole acetate (BI-OAc, 1.5 equiv.) in DCE (1,2-dichloroethane) at room temperature. After irradiation with a 14 W compact fluorescent lamps (CFL) for 24 h, Et_3N (3 equiv.) was added followed by the addition of benzylamine **2a** (0.5 equiv.). The mixture was further stirred for 6 h, and a 35% yield of the desired product **3a** was obtained (Table 1, entry 1). Encouraged by this result, different parameters were investigated in detail. It was found that the loading of PANI significantly affected the catalytic activity (Entries 1-4). The composite with 40 wt% of PANI gave the best result (75%, entry 2), which might be attributed to the fact that the addition of PANI can promote the absorption of visible light as well as the seperation of the electron-hole pairs. Moreover, among these PANI-g-C_3N_4-TiO_2 composites, the one with 40 wt% of PANI had the largest surface area (128 $m^2\ g^{-1}$, see ESI). The oxidants were then examined. Switching from BI-OAc to $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ afforded poor yields (Entries 5 and 6), presumably due to their low solubilities in DCE. Reactions using $(NH_4)_2S_2O_8$ in DCE/H_2O and DMSO/H_2O provided poor yields of the desired product (Entries 7 and 8). A 62% yield of **3a** was obtained when BI-OH was used, likely due to the poorer leaving group ability of OH compared with OAc. Other solvents were also surveyed (Entries 9-15). A comparable yield was obtained when the reaction was performed in dichloromethane, while the reactions in THF, 1,4-dioxane, acetonitrile, DMF and DMSO gave much lower yields. Different semiconductor photocatalysts were then evaluated (Entries 16-19). No reaction was observed in the presence of either PANI or TiO_2. When g-C_3N_4 was employed as the catalyst, a 22% yield of **3a** was obtained. The use of g-C_3N_4-TiO_2 provided the desired product in a comparable yield (25%).

of PANI-g-C_3N_4. These results indicated that a synergistic effect may exist in the ternary composite. The addition of both PANI and g-C_3N_4 could enhance the visible light absorption and electron–hole separation, thereby improving the photocatalytic activity. Control experiments also showed that no reaction occurred in the absence of either a photocatalyst or an oxidant (Entries 20 and 21). Finally, visible light was necessary for this reaction and 30 mg catalyst was sufficient (Entry 22).

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Oxidant	Solvent	Yield **3a** (%)[b]
1	PANI(20%)-g-C_3N_4-TiO_2	BI-OAc	DCE	35
2	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	DCE	75
3	PANI(60%)-g-C_3N_4-TiO_2	BI-OAc	DCE	64
4	PANI(80%)-g-C_3N_4-TiO_2	BI-OAc	DCE	60
5	PANI(40%)-g-C_3N_4-TiO_2	$K_2S_2O_8$	DCE	<5
6	PANI(40%)-g-C_3N_4-TiO_2	$(NH_4)_2S_2O_8$	DCE	17
7	PANI(40%)-g-C_3N_4-TiO_2	$(NH_4)_2S_2O_8$	DCE /H_2O[c]	25
8	PANI(40%)-g-C_3N_4-TiO_2	$(NH_4)_2S_2O_8$	DMSO /H_2O[c]	14
9	PANI(40%)-g-C_3N_4-TiO_2	BI-OH	DCE	62
10	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	CH_2Cl_2	70
11	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	THF	40
12	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	1,4-Dioxane	36
13	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	MeCN	37
14	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	DMF	15
15	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	DMSO	11
16	PANI or TiO_2(Anatase)	BI-OAc	DCE	0
17	g-C_3N_4	BI-OAc	DCE	22
18	g-C_3N_4-TiO_2	BI-OAc	DCE	25
19	PANI(40%)-g-C_3N_4	BI-OAc	DCE	42
20	–	BI-OAc	DCE	0
21	PANI(40%)-g-C_3N_4-TiO_2	–	DCE	0
22	PANI(40%)-g-C_3N_4-TiO_2	BI-OAc	DCE	0[d], 67,[e] 75[f]

[a] Reagents and conditions: **1a** (0.2 mmol, 1 equiv.), oxidant (0.3 mmol, 1.5 equiv.), catalyst (30 mg), solvent (2 mL), room temperature, irradiation with a 14W CFL for 24 h; then Et_3N (3 equiv.), benzyl amine **2a** (0.1 mmol, 0.5 equiv.), 6 h. [b]Isolated yield based on **2a**. [c]1:1 mixture. [d]Reaction without light. [e]20 mg catalyst was used. [f]40 mg catalyst was used.

The substrate scope of the developed method was then investigated and the results are summarized in Figure 1.[19]

Gen

proceeded smoothly under the standard reaction conditions, affording the desired products in moderate to good yields. Initially, the synthesis of aryl/alkyl ureas were evaluated. A series of aliphatic amines including benzylamine, cyclohexylamine, *n*-hexylamine, furan-2-ylmethanamine and thiophen-2-ylmethanamine reacted with oxamic acid **1a** to give the desired products **3a-3e** in 67-77% yield. Different aryl oxamic acids bearing functional groups such as alkyl, halo and nitro (**1f-1l**) also showed good reactivities, affording the corresponding products in moderate to good yields (**3f-3l**, 43-76%). The developed protocol was also suitable for the synthesis of aryl/aryl ureas, albeit in relatively lower yields (**3m-3u**).

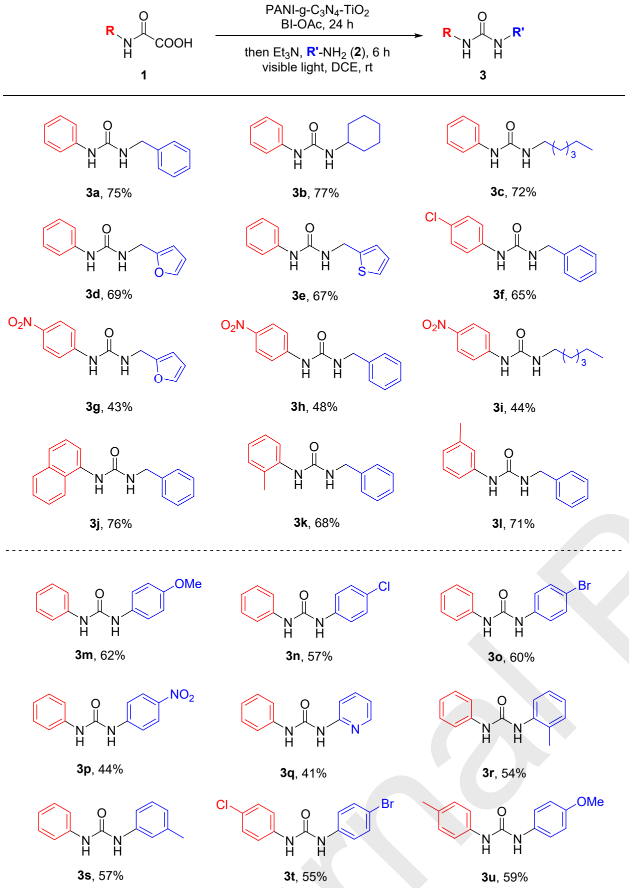
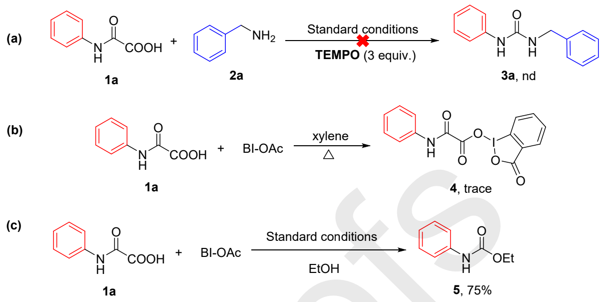


Figure 1. Reagents and conditions: **1** (0.2 mmol, 1 equiv.), BI-OAc (0.3 mmol, 1.5 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), DCE (2 mL), room temperature, irradiation with a 14W CFL for 24 h; then Et_3N (3 equiv.), amine **2** (0.1 mmol, 0.5 equiv.), 6 h. Isolated yield.

Importantly, the heterogeneous photocatalyst can be readily recovered and reused. A slight decrease in the catalytic activity was observed after five consecutive runs for the model reaction (75%, 75%, 73%, 71% and 70%, respectively).

To gain more detailed information about the reaction, some control experiments were then performed (Scheme 2). It was found that no desired product **3a** was obtained when 3 equiv. of the radical scavenger, 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) was added (Scheme 2, a). This result suggested that a radical reaction pathway might be involved in this process. Previously, Chen and co-workers reported a hypervalent-iodine-enabled radical decarboxylative alkenylation reaction under visible light.[20] They proposed that the benziodoxole vinyl carboxylic acid complex, as the key intermediate, was generated *in situ* from vinyl carboxylic acid and BI-OAc. The key intermediate was also isolated and confirmed. Similarly, Landais and co-workers also observed the formation of a

y, we were unable to isolate the benziodoxole–oxamic acid complex **4** in our reaction (Scheme 2, b). Instead, when the reaction was performed under the standard reaction conditions for 24 h, the addition of ethanol provided compund **5** in 75% yield (Scheme 2, c). This result might support the presence of the cationic species ($RNHC^+$=O).



Scheme 2. Control experiments.

On the basis of above results and related literature,[17,21] a plausible mechanism is proposed in Figure 2. Initially, the PANI-g-C_3N_4-TiO_2 composite absorbs photons and excites the electrons (e^-) and holes (h^+) under visible light. Meanwhile, oxamic acid **1** reacts with BI-OAc to form intermediate **I**, which abstracts an electron to generate radical-anion **II**. Then carbamoyl radical **III** and *o*-iodobenzoic acid anion form *via* the decarboxylation of radical-anion **II**. Afterwards, the carbamoyl radical **III** is oxidized by the holes (h^+) to give the corresponding protonated isocyanate **IV**. Finally, intermediate **IV** is attacked by amines **2** to deliver the corresponding ureas **3**.

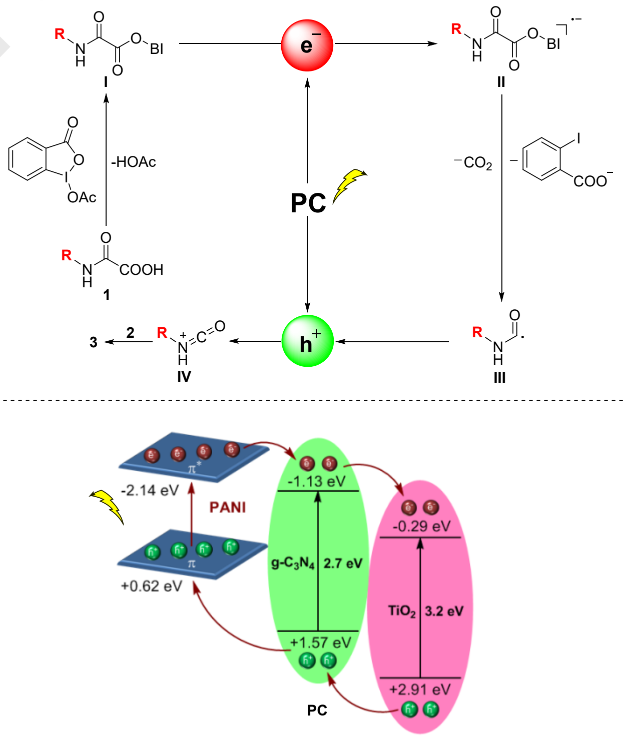


Figure 2. Proposed mechanism.

In summary, a PANI-g-C_3N_4-TiO_2 composite was prepared and employed as an efficient heterogeneous photocatalyst in the synthesis of unsymmetrical ureas under visible light. The carbamoyl radicals were generated from oxamic acids in the presence of a hypervalent iodine reagent and the PANI-g-C_3N_4-TiO_2 composite under visible light irradiation. The isocyanates, which were then trapped by amines to afford the corresponding products in moderate to good yields. This protocol avoided the direct use of environmentally unfriendly isocyanates. A broad scope of substrates were compatible with the reaction conditions and provided the desired products in moderate to good yields. Control experiments suggested that a radical pathway was involved in the reaction. Moreover, the photocatalyst could be readily recovered by simple filtration and reused for several runs with slight decrease in the catalytic activity.

Acknowledgments

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19 **General procedure for the synthesis of ureas and reuse of the catalyst:** A sealed tube equipped with a magnetic stirrer bar was charged with oxamic acid **1** (0.2 mmol, 1 equiv.), BI-OAc (0.3 mmol, 1.5 equiv.), PANI(40%)-g-C_3N_4-TiO_2 (30 mg), DCE (2 mL). The reaction mixture was then irradiated with a 14W CFL and stirred at room temperature (25 °C) for 24 h. The distance of the reaction vial from the light was approximately 5 centimeters. After reaction completion, the light was switched off and Et_3N (3 equiv.) was added to the

for 5 min. The amine **2** (0.1 mmol, 0.5 equiv.) was then added and the reaction mixture stirred for 6 h. Then the mixture was diluted with EtOAc (10 mL) and H_2O (5 mL), and the solid catalyst was recovered by centrifugation and filtration. The aqueous phase was extracted with EtOAc (5 mL × 3). The collected organic extracts were dried over Na_2SO_4, filtered and evaporated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of PE/EA to give the pure product **3**. The recovered catalyst was then washed with ethanol and deionized water, dried under vacuum, and reused for the next run.

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Highlights

- PANI−g-C_3N_4−TiO_2 composite-catalyzed the radical synthesis of unsymmetrical ureas under visible light is described.
- The semiconductor composite is readily prepared and cost-effective;
- The reaction conditions are mild, green, and the yields are satisfactory.
- The catalyst shows good stability and photocatalytic performance, and can be reused for several runs.

Conflict of interest statement

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Graphical Abstract

Photocatalyzed synthesis of unsymmetrical ureas *via* the oxidative decarboxylation of oxamic acids with PANI-g-C_3N_4-TiO_2 composite under visible light

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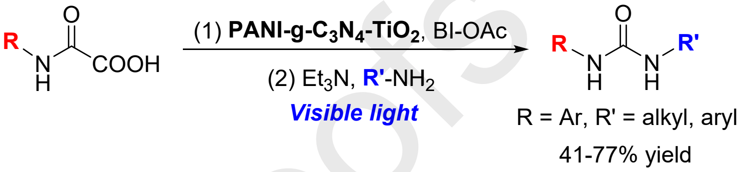

Synthesis of unsymmetrical ureas via photocatalyzed the oxidative decarboxylation of oxamic acids has been developed.