# Photocatalytic Water-Splitting Coupled with Alkanol Oxidation for Selective *N*-alkylation Reactions over Carbon Nitride

Yangsen Xu[+],[a] Zhaofei Zhang[+],[a] Chuntian Qiu,[a] Shaoqin Chen,[b] Xiang Ling,[a] and Chenliang Su*[a]

Photocatalytic water splitting technology (PWST) enables the direct use of water as appealing "liquid hydrogen source" for transfer hydrogenation reactions. Currently, the development of PWST-based transfer hydrogenations is still in an embryonic stage. Previous reports generally centered on the rational utilization of the in situ generated H-source (electrons) for hydrogenations, in which photogenerated holes were quenched by sacrificial reagents. Herein, the fully-utilization of the liquid H-source and holes during water splitting is presented for photo-reductive *N*-alkylation of nitro-aromatic compounds. In this integrate system, H-species in situ generated from water splitting were designed for nitroarenes reduction to produce amines, while alkanols were oxidized by holes for cascade alkylating of anilines as well as the generated secondary amines. More than 50 examples achieved with a broad range scope validate the universal applicability of this mild and sustainable coupling approach. The synthetic utility of this protocol was further demonstrated by the synthesis of existing pharmaceuticals via selective *N*-alkylation of amines. This strategy based on the sustainable water splitting technology highlights a significant and promising route for selective synthesis of valuable *N*-alkylated fine chemicals and pharmaceuticals from nitroarenes and amines with water and alkanols.

Photocatalytic water splitting technology (PWST) offers a direct and environmentally benign approach for renewable $H_2$ production.[1–4] Overall water splitting into hydrogen and oxygen over semiconductors is a "Holy Grail" and a challenging task that is generally hampered by the sluggish $O_2$-producing half reaction. To achieve efficient photocatalytic $H_2$ evolution, most reports have been centered on accomplishing the half reaction by adding sacrificial electron donors (such as $CH_3OH$, triethanolamine, lactic acid, and ascorbic acid) to scavenge the holes,[5–9] while in these cases, the output values are generally less than the input values (Figure 1a). Replacing the consumption of sacrificial agents by valuable organic transformation is a promising approach to address these issues by simultaneously $H_2$ fuel evolution coupled with production of value-added fine chemicals (Figure 1b).[10–23] For examples, Kasap et al. reported a couple solar $H_2$ generation with concomitant selective oxidation of benzylic alcohols to aldehydes over cyanamide surface functionalized polymeric carbon nitride (PCN).[17] PCN could be also designed to drive water splitting for $H_2$ evolution and simultaneously oxide the biomass derived 5-(hydroxymethyl) furfural (HMF) to a more valued platform chemical, 2,5-diformylfuran (DFF).[21] Reisner group developed an impressive photo-reforming of nonrecyclable plastic waste [poly (ethylene terephthalate) and poly(lactic acid)] to clean $H_2$ fuel and a variety of organic chemicals under alkaline aqueous conditions.[22] Besides, rational utilization of the *in situ* generated active hydrogen species (i.e. adsorbed hydrogen, $H_{ad}$) from water for transfer hydrogenation reactions towards value-added fine chemicals and pharmaceuticals to increase the output value is also highly desired (Figure 1c).[19,24] For example, we and others recently demonstrated a series of PWST-based transfer hydrogenations of olefins,[25,26] alkynes[27,28] and halides[29–32] towards fine chemicals production with water as the "liquid hydrogen source". Generally, in these PWST-based transfer hydrogenations, only "half story", photogenerated electrons, are involved in generating active $H_{ad}$ for transfer hydrogenations, whereas holes are quenched by sacrificial agents, resulting in relatively limited application ranges. Thus, it is highly attractive and desired to design synergistic systems to fully-utilize the in situ generated H-source (electrons) from water and holes for complex photocatalytic transformations towards value-added fine chemicals and pharmaceuticals to further increase the output values (Figure 1d).

Photocatalytic reduction of nitroaromatic compounds towards anilines, azo- or azoxy-compounds have been explored over semiconductor photocatalysts or the supported plasmonic metal nanoparticles.[33–35] For example, full reduction of nitroarenes for the synthesis of anilines has been demonstrated by using inorganic semiconductor photocatalysts such as $TiO_2$[36] and CdS.[33,34] Interestingly, Su et al.

[a] Y. Xu,[+] Z. Zhang,[+] C. Qiu, X. Ling, Prof. C. Su
SZU-NUS Collaborative Center and International Collaborative Laboratory of 2D Materials for Optoelectronic Science & Technology of Ministry of Education
College of Optoelectronic Engineering
Shenzhen University
Shenzhen, Guangdong 518060 (P. R. China)
E-mail: chmsuc@szu.edu.cn
[b] S. Chen
Department of Materials Science and Engineering
Southern University of Science and Technology
Shenzhen, Guangdong 518055 (P. R. China)
[+] These authors contributed equally to this work.

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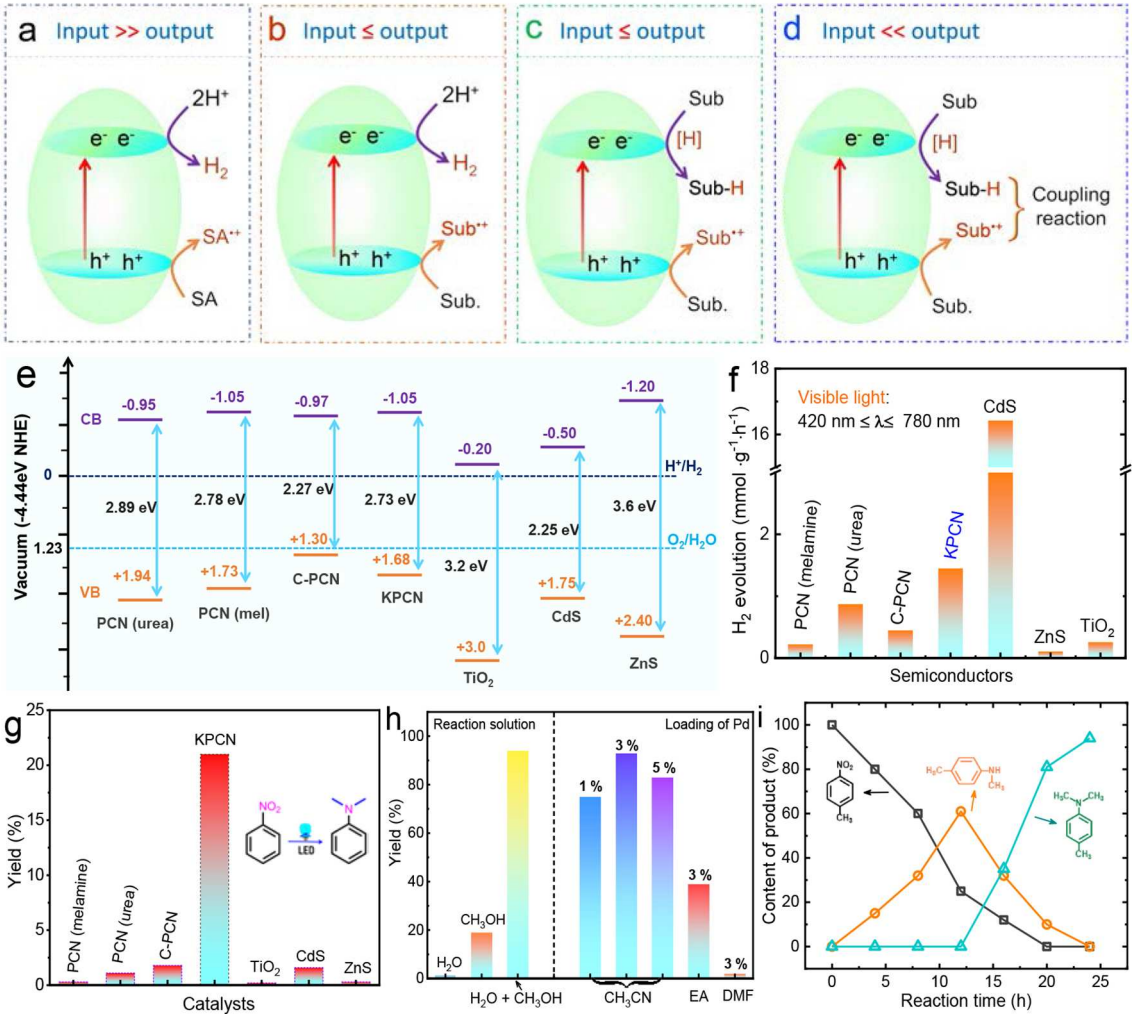


**Figure 1.** Representations of semiconductor-based photoredox catalytic reaction modes based on water splitting and the corresponding energy efficiency. (a) Water splitting; (b) hydrogenation of chemicals; (c) $H_2$ evolution and oxidation of chemicals; (d) integration of oxidation and reduction by water splitting. SA: Sacrificial agent. (e) Band-gap energies and relative band positions of different semiconductors relative to the water oxidation/reduction potential (vs. NHE). (f) $H_2$ evolution rate from water over various materials with ~1 wt% Pd as co-catalyst in 10% TEOA solution. (g) *N,N*-dimethylation of 4-nitrotoluene over different catalysts under visible light (420 nm LED) by water splitting at 20 °C. (h) The yield of *N,N*-dimethyl-4-methylaniline over KPCN achieved by the coupling photocatalytic redox process. (i) Time-dependent p-nitrotoluene photoconversion and the corresponding products over 3 wt% Pd/KPCN.

reported a novel method for the controllable synthesis of a series of azo- and azoxy-aromatic compounds from the corresponding nitroarenes under visible light by using a PCN photocatalyst.[37] Azobenzene has also been synthesized at room temperature over Au-supported $ZrO_2$ under UV light.[38] In these reports, isopropanol, $HCOONH_4$,[34,39] and TEOA[35] were generally the hydrogen source for the photocatalytic transfer hydrogenations of nitroaromatic compounds. However, the direct use of water as the most sustainable H-donor for photocatalytic reduction of nitroaromatic compounds remains rarely explored. To further include the function of the photoexcited holes, photoredox centers induced photocooperative reduction of nitroaromatic compounds followed by coupling reactions which could be designed and developed towards valuable fine chemicals.

To this end, herein, selective *N*-alkylation of nitroaromatic compounds with water and alkanols are designed over visible-light-active $K^+$ inserted polymeric carbon nitride (KPCN) semiconductors.[40] In the integrated system, photoexcited electrons are utilized to reduce water to furnish active H-species for hydrogenation of nitroarenes to the corresponding anilines, while photoexcited holes are proposed to oxidize alkanols to furnish aldehyde intermediates. The sequential condensation of anilines and aldehydes followed by hydrogenation produces *N*-alkyl amines, which are widespread in a series of bioactive compounds as well as pharmaceutical derivatives.[41–43] Control experiments with or without water, as well as the deuterium-labeling experiments, have attested to the significant role of water in *N*-alkylation of nitroarenes. Importantly, selective mono-alkylation and di-alkylation of nitroarenes have been effectively demonstrated by fine-tuning the reaction time and alkylating reagents. Selective *N*-alkylation of amines for the synthesis of existing pharmaceuticals is also well-presented. In total, the


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water-splitting based synergistic strategy highlighted by broad reaction scope, excellent functional group tolerance, high yield and selectivity, and scalability is therefore a promising alternative to conventional *N*-alkylation processes.

First, the visible-light-response semiconductors such as PCN, KPCN, CdS, etc. with sufficient reduction potential for water reduction were chosen as the photoredox catalysts (the preparation procedures and corresponding characterization details are provided in the Supplemental Experimental section and Figures S1–S8) (Figure 1e). As shown in Figure 1f, under visible light illumination, both CdS and KPCN enabled high $H_2$ evolution activities in the presence of sacrificial reagents. Low $H_2$ was produced over ZnS (~3.4 eV) and $TiO_2$ (~3.2 eV) due to their limited absorption of visible light. With these initial results, photoredox centers cooperative catalytic water-splitting coupled with methanol oxidation for selective *N*-methylation of nitrobenzene is evaluated (Figure 1g). The reaction was performed under visible light (420 nm LED) with 0.4 mmol of nitrobenzene, methanol and $H_2O$ (1.5 ml/1.5 ml) and 0.3 mmol of $AlCl_3$ as the acidic additive over Pd (1 wt%)/semiconductors. Among a variety of semiconductors, KPCN was screened out as the most active material to effectively drive the cascade di-alkylation of nitrobenzene to produce *N,N*-dimethyl-4-methylaniline (Figure 1h). $CH_3CN$ has been demonstrated as the best solvent compared with DMF and ethylacetate (EA) (more details can be found in Table S1). The different loading of Pd cocatalyst (1 wt%, 3 wt%, 5 wt%) has little impact on the reactivity and selectivity. Interestingly, the control experiment without water showed a remarkably decreased yield from 94% to 19%, attesting to the significant role of water in this N-methylation reaction. Time-dependent experiments were carried out with the optimized conditions. As shown in Figure 1i, the p-nitrotoluene was exhausted gradually, along with the formation of a mono-methylation product at the initial period (0–12 h), which could undergo another methylation step by prolonging the reaction time to produce *N,N*-dimethyl 4-methylaniline with excellent yields.

To evaluate the generality of our proposal, various nitro compounds and alcohols were tested under optimized conditions as shown in Scheme 1. Initially, the di-alkylation of different substituted nitroarenes with methanol was explored. Reactions of nitroarenes bearing electron-donating groups (*p*–Me, *p*–OMe) or electron-withdrawing groups (*p*–CN, *p*–F, *p*–Cl) proceeded smoothly with methanol to afford the desired *N,N*-dimethylated anilines in good to excellent yields (61–94% yields) (2aa-2ak). In particular, sterically hindered ortho-substituted substrates were also active (2ag-2ai), giving the corresponding products with excellent yields. Besides, substrates with a series of functionalities such as aryl fluoride (2ab), chloride (2ac, 2af, 2ah), nitrile (2ag), carbonyl (2aj) and sulfhydryl (2ak) substituents were well-tolerated. This protocol was also applicable for the synthesis of heteroaromatic dimethylanilines (2al-2am), which are important substructures in bioactive molecules, agrochemicals and advanced materials. For example, 4-dimethylaminopyridine (DMAP, 2am), a useful nucleophilic catalyst for a variety of reactions was obtained in 86% yield. Derivatives of tocopherol (product 2an), L-menthol (product 2ao), indomethacin (product 2ap), adamantane (product 2aq) and mefenamate (product 2ar) underwent reductive di-methylation in good to excellent yields. To extend the applicability of this methodology, *N,N*-di-methylation of a variety of biologically active molecules with nitro moieties was investigated. For example, di-methylation of nimesulide (a non-steroidal anti-inflammatory drug, 2as)[44] and flutamide (2at) proceeded smoothly in good to excellent yields (78% and 90% yields) without affecting the amide and sulfamine functionalities. Gram scale synthesis of 2at proved the good practical utility of our protocol. A rhodamine derivative (2 au), which is widely used as a fluorescent probe, was successfully obtained in good yield. Next, we explored the possibility of applying different alkanols as the alkylation partner. To our delight, this strategy could be well-extended by using ethanol as the alkylation reagent, affording the di-ethylated anilines (2ba–2bd) in good yields. Interestingly, when applying this strategy to substituted benzyl alcohols, mono-alkylated products were obtained in acceptable yields with high selectivity (2ca–2cd). Finally, aliphatic nitro compounds were also tested, but unfortunately these substrates cannot function in this system.

On the basis of these obtained results, we are interested in exploring the applicability of mono-methylation of nitroarenes. To this end, stepwise *N*-methylation of flutamide was investigated in greater detail (Scheme 2A). By controlling the reaction time, flutamide-$NH_2$ (3aa), flutamide-NHMe (3ab) and flutamide-$N(Me)_2$ (2at) were successfully obtained, which was very helpful to understand the reaction process as well as the mechanism. With these stepwise results, the generality of a mono-alkylation protocol was studied. As shown in Scheme 2B, several nitroarenes were subjected to the optimized conditions with carefully controlled reaction time, which smoothly afforded the N–Me and N–Et anilines in 45–81% yields.

*N*-alkylation is an important tool to regulate the biological and pharmaceutical activities of life science molecules, especially, *N*-alkylation reactions are of significance in the synthesis of existing pharmaceuticals that belong to the 200 top selling drugs. Since our photocatalytic protocol is also applicable to N-alkylation of amines from the stepwise results, a variety of important bioactive or pharmaceutical-related secondary amines were examined by utilizing this mild strategy. First, late-stage functionalization of pharmaceutical amines was evaluated (Scheme 2C). Methylation of vortioxetine and paroxetine, ethylation of paroxetine and atomoxetine and benzylation of fluoxetine (3ca-3ce) all proceeded smoothly in good to excellent yields without affecting the core structures of the pharmaceutical molecules. Acyclic amines, piperazine and piperidine rings all worked well. Furthermore, our process could enable access to several important pharmaceutical amines in a single step with high efficiency and selectivity. For example, Benadryl (3cf), an antihistamine, was prepared in 88% yield in a straightforward manner. Loxapine (3cg), an antipsychotic


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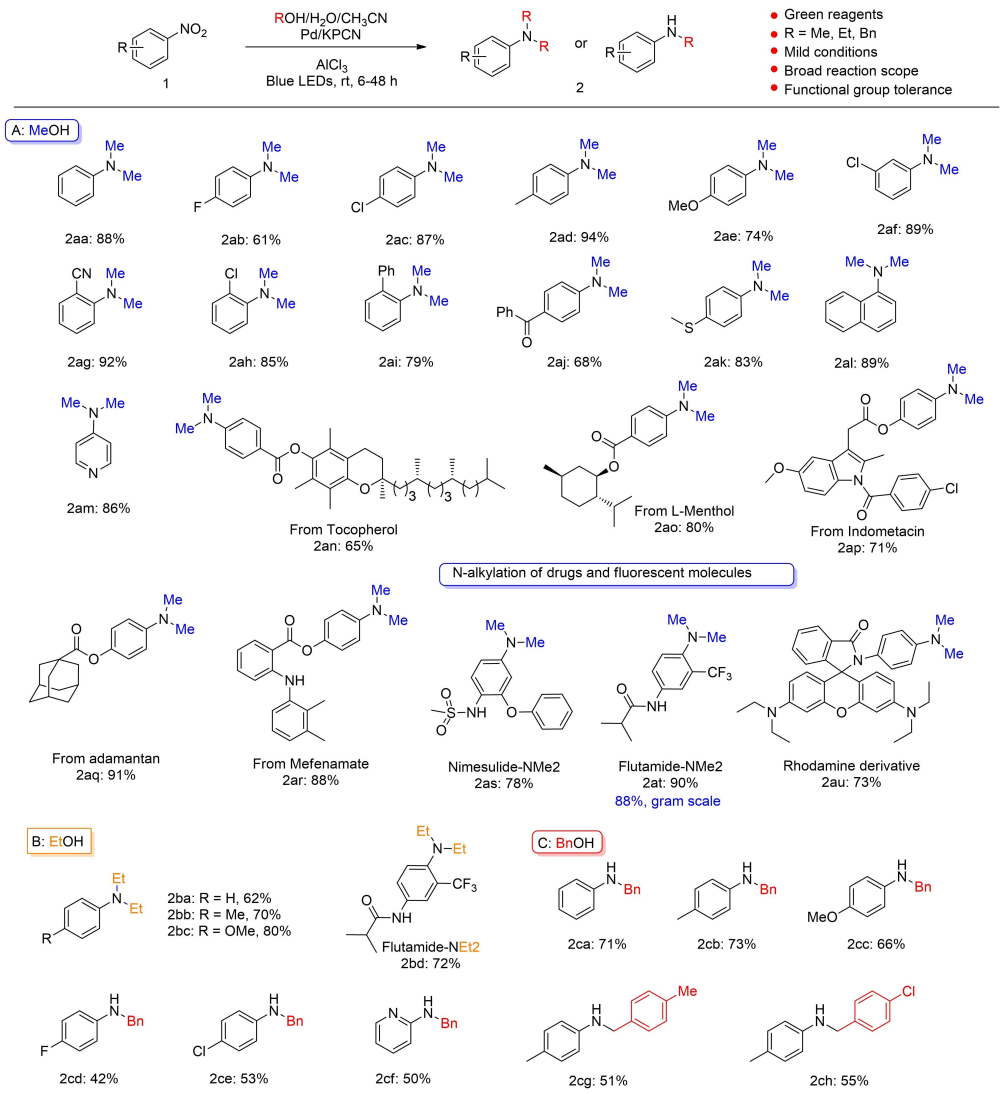


**Scheme 1.** Substrate scope in the integrated selective *N*-alkylation of nitroarenes over Pd/KPCN catalyst based on PWST. Reaction conditions: 0.4 mmol nitroarene, 25 mg of Pd/KPCN, 0.3 mmol $AlCl_3$, 2 mL Acetonitrile, 1.5 mL $H_2O$, ROH (1.5 mL MeOH or 1.5 mL EtOH or 40 equiv. $ArCH_2OH$), Blue LEDs, 20 W, rt. Isolated yields. A: ROH=MeOH; B: ROH=EtOH; C: R=$ArCH_2OH$.

drug, was successfully synthesized from its metabolite amoxapine. This process was also effective in the synthesis of alverine (3ch) by using ethanol as the coupling partner. Moreover, piperazine derivatives were treated with the corresponding benzyl alcohols to produce 1-(3,4-methylenedioxybenzyl)piperazine (MDBZP, 3ci), piribedil (3cj) and budizine (3ck) in good yields, which further demonstrated the excellent applicability of our photocatalytic coupling method.

To shed more light on the mechanism, the bandgap structures of the semiconductor photocatalysts were examined to understand their photoredox potentials from the viewpoint of thermodynamics. From Mott-Schottky experimentation, the lowest unoccupied molecular orbital (LOMO) of KPCN is identified as −1.05 V, more negative than the reduction potential of $H^+/H_2$ (Figure 2a). The highest occupied molecular orbital (HOMO) of KPCN is more positive than those of the utilized alkanols (i.e. methanol, ethanol and benzyl alcohol, Figure 2c). To determine whether the *in situ* formed active hydrogen species ([H] or $H_{ad}$) from water splitting could be observed, 2,2,6,6-tetramethyl-l-piperidine-*N*-oxyl (TEMPO)-trapping experiments were performed by electron spin resonance (ESR). As shown in Figure 2b, the characteristic triplet TEMPO peaks with intensity of 1:1:1 were observed in both KPCN and Pd/KPCN systems. The intensity of those peaks decreased dramatically over Pd/KPCN under visible light irradiation for 10 min, indicating the reduction of TEMPO by [H] to form the corresponding hydroxylamine (TEMPOH), which is consistent with the reported literature.[45,46] In the bare KPCN system, no changes were observed, suggesting the necessity of co-catalyst Pd nanoparticles to accelerate the reduction of water (as confirmed by the obvious quenched PL peaks on Pd/KPCN in Figure S5) and trap the [H]. Isotope-labeling experiments


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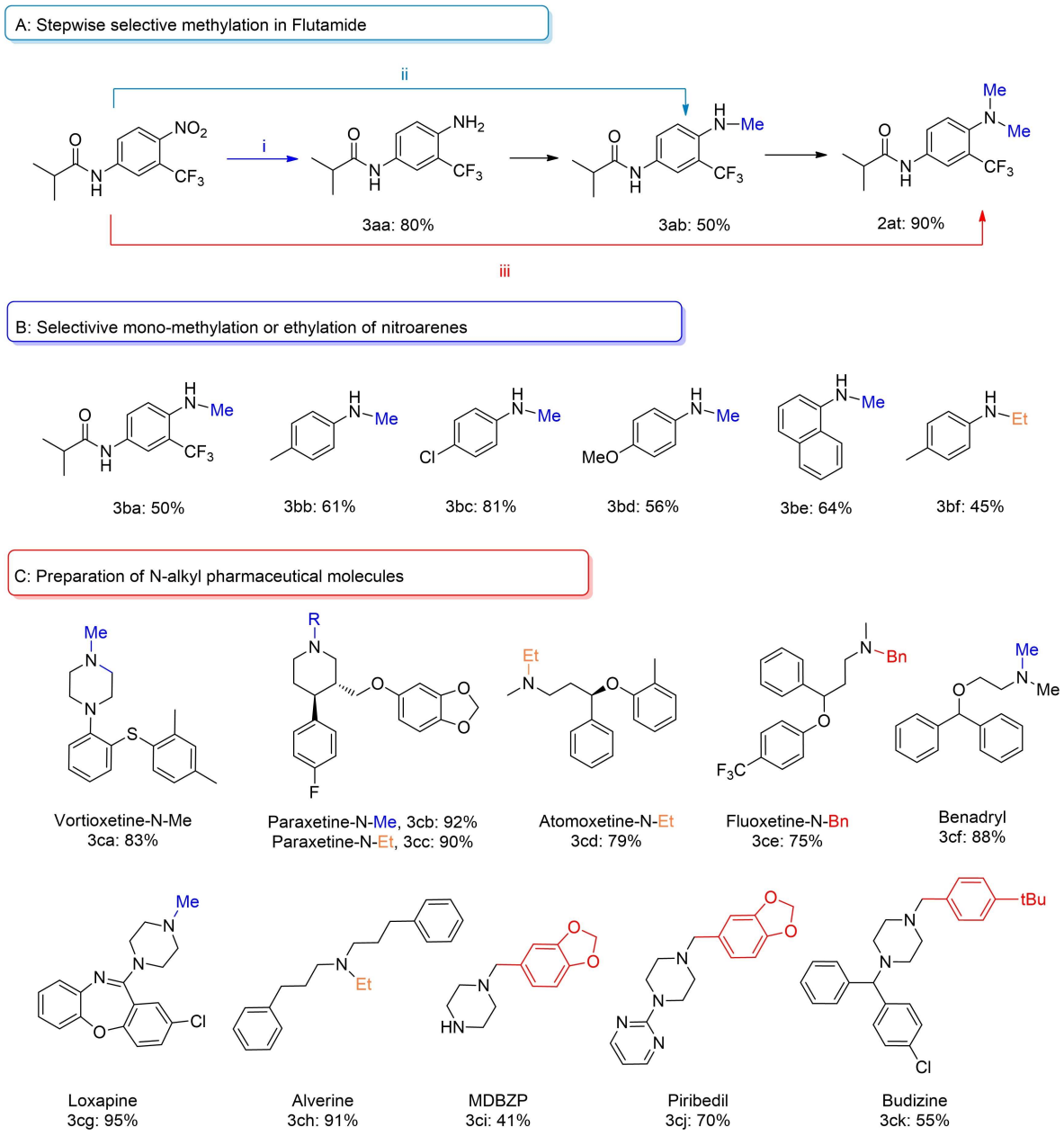


**Scheme 2. A**. Stepwise selective methylation in Flutamide (i, ii, iii). (i) Reaction time: 4 h. (ii) Reaction time: 11.5 h. (iii) Reaction time: 18 h. **B**. Selectivity towards mono-methylation or ethylation. **C**. Preparation of N-alkyl drugs. Reaction conditions: 0.4 mmol nitroarenes or amines, 25 mg of Pd/KPCN, 0.3 mmol $AlCl_3$, 2 mL Acetonitrile, 1.5 mL $H_2O$, ROH (1.5 mL MeOH or 1.5 mL EtOH or 40 equiv. $ArCH_2OH$), Blue LEDs, 20 W, rt. Isolated yields.

were performed to understand the roles of water and methanol in greater detail. As displayed in Figure 2d, using the $H_2O/CD_3OD$ as combined methylating reagent, the *N*–$CD_2H$ unit was introduced in good yield with high D-content. This result pinpointed that 4-nitroanisole was reduced to 4-anisidine, which coupled with [$D_2C$=O] from isotopic methanol to produce imine intermediate, which was sequentially reduced by [H] species from water splitting, giving *N,N*–di–$CD_2H$-anisidine. Consistently, when using the $D_2O/CH_3OD$, *N,N*–di–$CH_2D$-anisidine was obtained.

On the basis of these results, the probable mechanism was proposed as shown in Figure 2e. Nitroarenes are firstly reduced by the in situ generated [H] from water splitting to produce anilines. Simultaneously, alkanols are oxidized by photogenerated holes to produce aldehydes. Then, aldimine condensation occurs to produce imine intermediates, which undergo Pd-catalytic hydrogenation by [H] to furnish the secondary amines. The secondary amines could undergo another aldimine condensation with aldehydes generated from alkanols oxidations by holes, furnishing iminium ions, which undergo Pd-catalytic hydrogenation with [H] to produce the tertiary amines. The stepwise N-alkylation of nitrobenzene (Figure S9), N-alkylation of secondary amines


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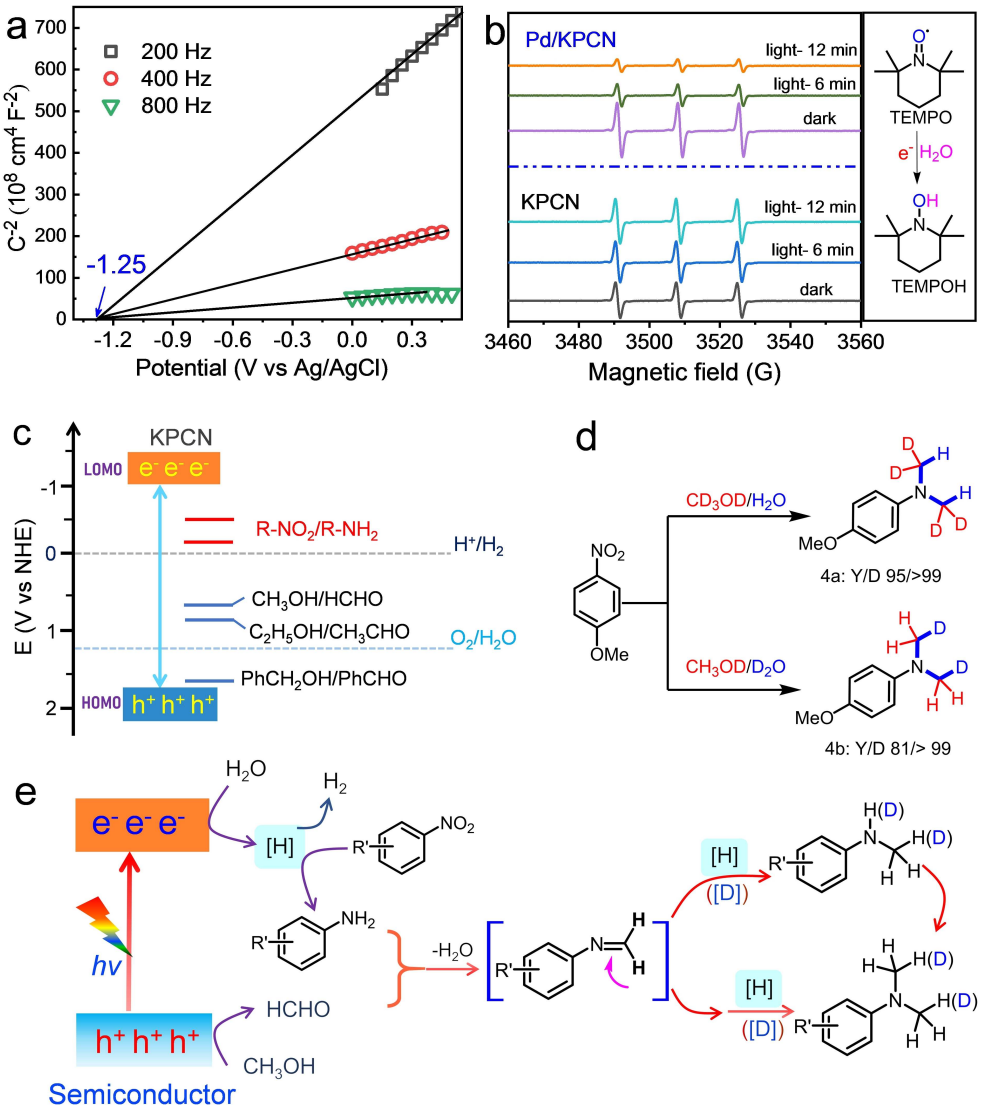


**Figure 2.** Mechanisms of photocatalytic *N*-alkylation of nitro-compounds: (a) Mott-Schottky plots of KPCN obtained in 0.5 M $Na_2SO_4$ aqueous solution. (b) ESR spectra of detecting photoexcited electrons in an aqueous solution of KPCN and Pd/KPCN under visible light irradiation, with the mechanism of trapping TEMPO radicals shown on the right. (c) Energy diagram of the conduction and valence bands of KPCN and redox potentials of relevant reactions. (d) Mechanistic analysis by photocatalytic deuteration of nitro compounds. (e) Schematic representation of a closed redox system for solar-driven simultaneous proton reduction, alcohol oxidation and *N*-alkylation of nitro-compounds in $CH_3CN$ solution.

(Scheme 2B) and isotopic experiments (Figure 2d) clearly verified the proposed mechanism.

In conclusion, semiconductor photoredox catalytic selective *N*-alkylation of nitroarenes and amines with water and alkanols was successfully achieved under by synergistic utilization of the photogenerated redox centers over KPCN. With this system, water could serve as the green "liquid hydrogen source" via photoexcited electron-induced reduction; alkanols could serve as green precursors of aldehydes synthesized by photoexcited holes-induced oxidation. This strategy presents a clear "whole story" of photocatalytic water splitting-based organic transformations for photosynthesis of high-valued *N*-alkyl fine chemicals and pharmaceuticals from nitroarenes or secondary amines with high selectivity, good functional group tolerance, wide reaction scope and mild conditions. We can imagine that photocatalytic water splitting simultaneously coupled with organic oxidations in a closed system will offer great potential in large scale artificial photosynthesis of valuable products with water and organics in the near future.

## Experimental Section

### Preparation of Pd/KPCN catalysts

The employed KPCN semiconductor was synthesized following our previous work.[40] Typically, melamine (3.0 g, Alfa Aesar) was ground with KCl (2.25 g, Alfa Aesar) in 2 mL EtOH in an agate mortar. The dry mixture was heated to 580 °C for 3.5 h with the rate of 3.3 K $min^{-1}$ in a tube furnace in an air atmosphere. The yellow


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product was washed with boiling deionized water, followed by drying at 70 °C under vacuum. Pd/KPCN (Pd = 1.0, 3.0, 5.0 wt%) catalysts were prepared by photoreduction of $H_2PdCl_4$. Briefly, the as-synthesized KPCN (0.4 g) was dispersed in a mix solution with 100 mL deionized water and 30 mL glycol. After untrasonication treatment for 2 h, 112 μL of 1.0 M $H_2PdCl_4$ was added into the mixture, then the mixture was illuminated under 300 W Xe lamp illumination for 1 h under anoxic quartz bottle to reduce $Pd^{2+}$. The gray slurry was centrifuged and washed with deionized water, and finally dried in an oven at 70 °C overnight.

### Photocatalytic $H_2$ evolution

The photocatalytic water splitting was carried out in a Pyrex flask reactor (Labsolar VIAG, Perfectlight Technology Co., Ltd., Beijing, China) via top-irradiation with a 300 W Xenon lamp (XE300 C) under visible light (420 nm ≤ λ ≤ 780 nm) or UV-vis light (250 nm ≤ λ ≤ 780 nm). The reaction system was controlled at 10 °C by the circulated water. For each experiment, 30 mg photocatalyst was suspended in an aqueous solution containing 10 vol % TEOA solution. Pt cocatalyst (~1.0 wt%) was in situ loaded on the photocatalyst by photo-deposition of $H_2PtCl_6$. The produced gas was quantified online using a gas chromatograph (Fuli 9890II, Zhejiang) equipped with a thermal conductivity detector (TCD) detector with argon as the carrier gas.

### General procedure for the photo-catalyzed N-alkylation reaction

25 mg of Pd/KPCN and 0.4 mmol of nitroarenes and $AlCl_3$ (0.3 mmol) were dispersed in a mixture solution with $CH_3CN/H_2O$ = 2 mL/1.5 mL and ROH (1.5 mL MeOH or 1.5 mL EtOH or 40 equiv. $ArCH_2OH$). Then the reaction mixture was irradiated with a LED lamp (20 W, λ = 420 nm,) and stirred at room temperature until the full consumption of the substrates (typically 12 h–48 h). The mixture was filtered to remove photocatalyst. The supernatant was extracted by adding 5 mL of $CH_2Cl_2$. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to furnish the corresponding product.

### Gram scale synthesis of Flutamide-$NMe_2$ (2 at)

250 mg of Pd/KPCN, 5.0 mmol of Flutamide and $AlCl_3$ (3 mmol) were dispersed in a mixture solution with Acetonitrile/MeOH/$H_2O$ = 20 mL/15 mL/15 mL, and then sonicated for 10 min. The reaction mixture was then irradiated with a LED lamp (20 W, λ = 420 nm) for 36 h under Argon at 20 °C by using a flow of cooling water during the reaction. After reaction, the mixture was centrifuged to remove photocatalyst. The supernatant was extracted by adding 50 mL of $CH_2Cl_2$. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to furnish the Flutamide-$NMe_2$ (**2 at**) (1.2 g, 88%).

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** alkanol oxidation · carbon nitride · *N*-alkylation reaction · photocatalysis · water splitting

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# COMMUNICATIONS

**Nothing left to waste**: Full utilization of the liquid H-source and holes during water splitting was realized for selective *N*-alkylation of nitro-aromatic compounds, including pharmaceuticals, under visible light with high selectivity, good functional group tolerance, and wide reaction scope.