

Accepted Article

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Authors: Meifang Zheng, Jiale Shi, Tao Yuan, and Xinchen Wang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201800319 Angew. Chem. 10.1002/ange.201800319

Link to VoR: http://dx.doi.org/10.1002/anie.201800319 http://dx.doi.org/10.1002/ange.201800319

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Metal-Free Dehydrogenation of N-Heterocycles by Ternary *h*-BCN Nanosheets with Visible Light

(a) previous work

Meifang Zheng, Jiale Shi, Tao Yuan, and Xinchen Wang*

Dedicated to Professor Xintao Wu on the occasion of his 80th birthday

Abstract: An efficient metal-free catalytic system has been developed using hexagon boron carbon nitride (h-BCN) nanosheets for the dehydrogenations of N-heterocycles with visible light, while releasing hydrogen gas (H₂), and thus no proton acceptor is needed. This acceptorless dehydrogenation of hydroquinolines, hydroisoguinolines or indolines to the corresponding aromatic Nheterocycles has been achieved with excellent yield by visible light irradiation under the ambient temperature. With h-BCN as the photocatalyst and water as the solvent, this protocol shows broad substitution tolerance, environment benign and high efficiency. This metal-free photoredox catalytic system for organic synthesis expands our knowledge of chemical reactivity and enables new environmentally friendly synthetic protocols.

Compared to thermo-derived reactions, visible light (400-800 nm) energy as driving force for chemical reactions is appealing, since it is a kind of clean, infinitely available, safe and easy-to-handle energy resource.1 Photochemical synthesis of organic molecules has thus attracted significant attention, and in the last few years, spectacular advancements in photoredox organic transformations have been made.² However, most of the photocatalytic organic bond-forming reactions require the involvement of precious metals³ or organic dyes⁴, which face the drawbacks of high cost or unrecyclable problems or even both. Metal-free heterogeneous catalysis can be the ease to address the abovementioned issues. Among the reported metal-free semiconductor photocatalysts,⁵ g-CN and *h*-BCN presented as a new family of efficient light harvesters for sustainable utilization of solar energy by water splitting, CO₂ reduction and environmental remediation, which draw broad interdisciplinary attention.⁶ It is certainly desired to introduce these metal-free semiconductors in the realm of molecular transformations with visible light irradiation.

Catalytic dehydrogenation reactions play a significant role in organic transformations and manufacturing commodity chemicals.7 those acceptorless Amona reported, dehydrogenation reactions have recently become a rapidly growing area of research, not only because they avoid the use of stoichiometric oxidants as proton couplers in the process, but also exhibit potential applications for hydrogenstorage materials. Recent reports of computational and experimental data display that the nitrogen atom facilitates dehydrogenation process by decreasing the the endothermicity of the reaction.⁸ Contributions from the group

 [a] Dr. M. F. Zheng, J. L. Shi, T. Yuan, Prof. X. C. Wang State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116 (China)
E-mail: xcwang@fzu.edu.cn
Website: https://wanglab.fzu.edu.cn

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of Fujita,^{9a,9b} Xiao^{9c} and Li^{9d} presented iridium and ruthenium complexes as co-catalysts, which are competent for acceptorless dehydrogenation of N-heterocycles as well as the reverse process, that is, the hydrogenation of the corresponding heteroarenes. Crabtree and Jones reported that base metals such as nickel, iron, and cobalt are also potent photocatalysts or electrocatalysts for the dehydrogenation of N-heterocycles, however, it is difficult to reuse them." reuse them. 10 Kanai and coworkers have previously developed $B(C_6F_5)_3\mbox{-}catalysts$ for dehydrogenation of Nheterocycles.¹¹ These advances are impressive, to the best of our knowledge, these previous works have employed conventional transition metal catalysts with designed complex ligands, thus requiring operation temperature higher than 120 °C and cost increases due to the use of expensive noble metals and the chemical synthesis of organic ligands. In view of the importance of heterocycles in natural products,¹² and liberating energetic H₂ as the only byproduct.¹³ the development of a recyclable heterogeneous metal-free catalytic system with high efficiency at mild conditions would be of significant synthetic utility, but it remains challenge.



Scheme 1. Strategies for the acceptorless dehydrogenation of THQs.

Based on previous reports, the oxidative potential of hydroquilonines are below 1.0 V.^{9d} g-CN and *h*-BCN, with band gap of 2.7 eV and valence band level of -1.3 V versus normal hydrogen electrode (*vs* NHE), are thermodynamically capable of running the dehydrogenation reactions upon illumination of visible light.⁶ Considering this, we develop a

system based on heterogeneous photocatalysis *via* radical pathway from tetrahydroquinolines (THQs) to quinolines, testing the efficiency of recyclable heterogeneous catalysts as idea compensate for noble metals. Herein, the first acceptorless metal-free dehydrogenation of THQs, isoTHQ, indolines and other saturated N-heterocycles was presented by merging sustainable semiconductor photoredox catalysis with organic synthesis under mild reaction conditions.

In this report, h-BCN was synthesized by nitridating the mixture of urea and glucose with flowing ammonia gas at 1523K for 5h, with a refluxing treatment in acetonitrile and 0.1M HCl at 353K (see the SI for details). To get insights into the local structure of the as-obtained h-BCN materials, the chemical states of B, C, and N elements were investigated using X-ray photoelectron spectrometer (XPS) (Figure S2) and transmission electro microscope (TEM) (Figure S3). Figure S2 (c) and (d) show typical N1s and B1s spectra for h-BCN, respectively. The binding energy of N1s is 398.6 eV, while the B1s signal is at 191.1 eV. The shoulder at 192.5 eV in the B1s spectrum is assigned to the structure terminating B-O bonds. This minor peak is due to the oxygen-defects in h-BCN structure. This metal-free h-BCN was applied for the photoredox organic transformations with blue LED light irradiation.

 Table
 1.
 Screen
 of
 photocatalysts
 for
 dehydrogenation
 of
 1,2,3,4

 tetrahydroquinoline

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	N H	cat. solvent	\rightarrow	
entry	cat.	solvent	hv	yield ^[a]
1	g-CN	EtOH	Blue LEDs	2%
2	g-CN	EtOH	-	n.d.
3	-	EtOH	Blue LEDs	n.d.
4	c-CN	EtOH	Blue LEDs	2%
5	B-CN	EtOH	Blue LEDs	1%
6	<i>h</i> -BCN	EtOH	Blue LEDs	5%
7	<i>h</i> -BCN	MeOH	Blue LEDs	6%
8	<i>h</i> -BCN	EtOH	Blue LEDs	10%
9	<i>h</i> -BCN	EtOH	Blue LEDs	5%
10	<i>h</i> -BCN	<i>i</i> PrOH	Blue LEDs	86%(83%)
11	<i>h</i> -BCN	TFE	Blue LEDs	41%
12	<i>h</i> -BCN	HFP	Blue LEDs	22%
13	<i>h</i> -BCN	H ₂ O	Blue LEDs	80%(79%)
14	Ru(bpy) ₂ Cl ₂	H ₂ O	Blue LEDs	7%
15	Ir(bpy) ₂ Cl ₂	H ₂ O	Blue LEDs	trace



We first selected 1,2,3,4-tetrahydroquinoline (1a) as a model substrate (Table 1). As expected, in the absence of a photocatalyst, formation of quinoline (2a) was not detected. To further study the effect of visible light irradiation on the reaction, experiments with alternating light sources and dark phases were conducted (entries 2-3). After screening different catalysts and solvents (entries 4-9), other systems were shown less effective. To our delight, primary solvent investigation found that dehydrogenation of 1a afforded 2a with the release of two molecules of H₂ in quantitative yield, both in *i*PrOH and water within 12 hours (Table 1, entries 10

and 13). Besides, it was proved that *i*PrOH and water could not produce H₂ under the reaction conditions. To our delight, 86% yield of 2a was obtained along with releasing H_2 in isopropanol after 12h irradiation (entry 10). To the best of our knowledge, such mild reaction conditions are very rare for potential H₂ storage materials. When H₂O was used as the solvent, the yield of 2a is good with the yield of $65 \% H_2$ with respect to 1a (with respect to the dehydrogenated product 2a, the yield is 82%) (Figure S4), with an quantum efficiency of 2.0 % at 420 nm. Other organometallic photosensitizers were also explored as comparisons, and results revealed that and Ir(bpy)₂Cl₂ dyes $Ru(bpy)_2Cl_2$ showed inferior photochemical efficiency comparing with h-BCN in this system (entries 14 and 15).





[a] $\overline{1}$ (0.30 mmol), *h*-BCN (10 mg), H₂O (2.0 mL), irradiation with blue LEDs for 12 h at room temperature. Yield is that of isolated product.

Having the preferred dehydrogenation optimization in hand, we next investigated the scope of substrates (Table 2). Similar to THQ, 2-MeTHQ displayed excellent reaction efficiency (**2a**, **b**). A variety of the substituents, from methyl to fluoro, at the 6-position of THQ cannot affect the yields and achieved excellent yields (**2c-h**). 7-nitro groups also went through the transformation smoothly (**2e**). Moreover, 6fluoro-2-methyl-THQ bearing two substituents, displayed excellent yields (**2g**). Besides, the developed method was also extended to the dehydrogenation of isoTHQ to afford isoquinolines (**2i-I**) in excellent yields. isoTHQ bearing phenyl groups on the 2-position resulted in **2I** in excellent yields.

Dehydrogenation of indolines with substitutions at different positions was studied further (Table 2). NH free indoline had been successfully dehydrated to indole **2m** with the yield of 67%. Indolines bearing 2-methyl group also resulted in corresponding indole **2n** with a good yield.

In the next set of experiment, the reaction was monitored for 2a with light on/off over time. Smooth transformation of THQ to quinoline was observed with irradiation by blue LEDs, but the organic transformation stopped when the light is turned off. This suggested that the reaction was induced through a photoredox catalytic pathway (Figure 1a). For repeated cycles, catalyst was recovered by simple filtration and reused in subsequent reactions. Results revealed that there is only a slight decrease in catalytic performance due to the slight loss of the catalyst in the sample recovering process. Nevertheless, after four repeated cycles, it showed similar yield as the first cycle (Figure 1b), indicating the high stability of *h*-BCN during the prolonged photochemical operation, which is also reflected by the virtually identical XRD patters of the sample before and after the reaction (Figure 1c).

Based on the observed oxidation potential of 1j and 2methyl-1,2-dihydroquinoline (6,7-diOMeDHQ; 1j; E1j⁺/1j =+0.44 V vs. SCE and E1k^{+/}/1k = +0.53 V vs. SCE, respectively; see Figures S5 and S6 in the SI), the release of the second H₂ would be more difficult than the first one. But the release of the second H₂ might be easier than the first one because of the aromatization. The mechanism of the dehydrogenation was studied by electron spin resonance (ESR) and control experiments. In the initial step of the reaction, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was employed as a spin trap. It is clearly shown in Figure 1d that when the solution of DMPO, h-BCN, and 1a in anaerobic CH₂Cl₂ were irradiated with a 15W blue LED, intense ESR signals (Figure 1d, red) were observed exhibiting general 1:1:1:1:1:1 patterns. On basis of our observations together with the literature reports,¹⁴ the above signals should be attributed to the adduct of DMPO with carbon radical.



Figure 1. (a) Profile of **2a** with the light on/off over time. Yields were determined by GC-MS. (b) Evaluation of Catalyst Recycling. (c) XRD of *h*-BCN before and after reaction. (d) ESR spectrum of a solution of *h*-BCN (3.0×10^{-3} M), **1a** (0.10 M), and DMPO (0.50 M) in anaerobic CH₂Cl₂.

An outline of a possible reaction mechanism for photocatalytic dehydrogenation and hydrogen-evolution is

illustrated in Scheme 2.^{9d} Upon visible light irradiation, oxidative valence band holes and reductive conduction band electrons are produced by the excitation of the *h*-BCN semiconductor. The hole oxidizes the substrate to the corresponding cation radical **A**. Subsequent deprotonation affords intermediate **B** (equivalent to a radical anion). Then, the intermediate **C** is obtained from the intermediate **B** by the release of one proton (H⁺) and one electron (e). The released electron is captured by the produced valence band hole. Isomerization of the intermediate **C** affords **D** and **E**, which might be induced by the same dehydrogenation reaction or the aromatization of **E** to the final product. The formed protons (H⁺) are reduced by the reductive conduction band electrons of *h*-BCN to generate H₂, which is similar to the formation of H₂ by water splitting.



Scheme 2. The proposed mechanism for the photocatalytic dehydrogenation of isoTHQ by *h*-BCN with visible light.

In summary, we have developed the heterogeneous acceptorless dehydrogenation of THQs, indolines and other related heterocycles by metal-free photoredox catalysis using *h*-BCN photocatalysts. Distinct from traditional systems, this photocatalytic process avoids the employment of metals and stoichiometric oxidants, which provides a convenient and cost-effective protocol for heterocycle synthesis and H₂ production at ambient environment. The clean and mild synthetic approach provides a potential extension to synthesize a number of other N-containing aromatic motifs using sustainable solar irradiation.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (grant nos. 21425309, 21702030 and 21761132002) and the 111 Project.

Keywords: Heterogeneous Catalysis • Organocatalysis • Acceptorless Dehydrogenation • 2D Materials • Radical

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This protocol provides a green heterogeneous route to synthesize Nheterocycles by metal-free photoredox catalysis, with hydrogen gas as the only byproduct. Nitro, carboxyl and hydroxyl substitutions can be tolerant in this organic transformation with excellent yields under mild conditions.



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