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Visible light-driven graphitic carbon nitride (g-C_3N_4) photocatalyzed ketalization reaction in methanol with methylviologen as efficient electron mediator

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ABSTRACT

Ketalization reaction, which is otherwise a typical acid catalyzed process, is herein firstly realized by a novel visible light driven photocatalytic reaction system with methylviologen (MV^{2+}) as an efficient electron mediator and graphitic carbon nitride (g-C_3N_4) as the visible light sensitizer. The photons utilization efficiency of g-C_3N_4 was maximized by simultaneous removal of the conduction band electrons and valence band holes by MV^{2+} and methanol, respectively. The turn over number of MV^{2+} reaches the remarkable high value of 31201/hour, with 72.7 mmol of cyclohexanone dimethyl ketal production in 1 h. The design strategy presented in this work could inspire the development of new and highly efficient photocatalytic reaction systems for broader purposes than usually expected.

1. Introduction

Semiconductor photocatalyzed organic functional groups conversion reactions have attracted increasing attention in recent years. *Via* this route, the abundant solar light can be directly employed as the energy source to drive the chemical reactions. Meanwhile, the novel reaction mechanism involved also contributes positively to the organic synthesis area [1–8]. Ketalization reaction is an effective way for protecting the carbonyl group during organic synthesis. Moreover, some of the ketals are valuable fine chemicals, such as cyclohexanone dimethyl ketal, which is a dehydration agent and also is a valuable intermediate for synthesis of perfumes and agricultural chemicals [9,10]. In terms of the production of dimethyl ketals, expensive reactant (trimethyl orthoformate), corrosive acid catalysts, and special reactors with water separation devices have to be involved to obtain satisfied yields and purities [9,11]. A novel, environmental benign photocatalytic method for ketalization of ketones with methanol is thereby highly desirable from the perspectives of both basic science and practical application.

Graphitic carbon nitride (g-C_3N_4), which is a conjugated polymer semiconductor with band gap of 2.7 eV, has raised intensive research interest, due to its physicochemical stability, metal-free composition made up from abundant elements, and most importantly, its visible light sensitivity [12–18]. However, achieving notable efficiency is challenging, because of the mutual influences and kinetic coupling within the complex electron transfer processes. Specifically, in semiconductors photo-catalyzed chemical conversion reactions, electrons are firstly exited to the conduction band by photons, leaving the oxidative holes in valence band; and these photo-generated charge-carriers, if not recombined in loss processes, drive the organic conversion reactions *via* electron and hole transfer with the reactants. Low conversion efficiency usually results from unwanted charge recombination, back electron transfer (BET) or a missing rate balance of the chemical reactions of electron and hole, *i.e.* the system has to “wait” for the slower reaction [19–23]. Interestingly, in bio-photosynthesis, the multisteps electrons transfer processes from PS II (Photosystem II) to PS I (Photosystem I) and PS I to $NADP^+$ (Nicotinamide Adenine Dinucleotide Phosphate) are able to realize high quantum yields [24,25]. This was mimicked *in vitro* by coupling semiconductor photocatalysis with enzyme biosynthesis *via* NAD^+ as an electron mediator, and the reported kinetic rates of 5 mmoles per hour speak for bio-like photon-to-reaction efficiencies exceeding 20% [26,27]. Accordingly, the improvement of the efficiency of the artificial photocatalytic reactions by virtue of a kinetically favourable electron mediator is particularly promising.

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Methylviologen (MV^{2+}) is a bipyridylium cation, which can capture one electron and change to reduced methylviologen (MV^{+}) (MV^{2+}/MV^{+}, −0.45 V *vs.* NHE) [28–31]. The quantum yield for MV^{+} generation with CdSe/CdS (Dot-in-Rod nanostructure) as photosensitizer could reach nearly unity [32]. MV^{+} readily donates one electron in the presence of Pt nanoparticles for hydrogen production in $Ru(bipy)^{2+}$ and CdSe/CdS photocatalytic systems with sacrificial electron donors [32,33]. Some enzymes and cofactors, such as formate dehydrogenase, flavin mononucleotide, and hydrogenase are also able to receive electron from MV^{+} and initiate the following reduction reactions [34–36].

Extending these observations to the more feasible graphitic carbon nitride, it is reasonable to expect high photocatalytic conversion efficiency, if the MV^{2+} could promptly capture the conduction band electrons on the surface of g-C_3N_4 particles. The left-alone valence band holes in carbon nitride possess strong oxidative power (1.40 V *vs.* NHE), which can be instrumentalized to drive many chemical conversion reactions [17,37,38]. Methanol, as a potential hole scavenger, can in principle quickly donate electrons to the hole and be oxidized to formaldehyde *via* the intermediate step of methoxy radical formation [39–41]. This methoxy radical is an active species, and could be a useful building block in organic synthesis, especially for C—O bond formation.

Herein, we apply the combination of the MV^{2+}/MV^{+} redox couple and methanol in the g-C_3N_4 system to explore a novel photocatalytic ketalization reaction of ketones. This reaction system is highly efficient when the positive and negative charges from g-C_3N_4 are taken up by MV^{2+} and methanol, respectively, with similarly high rates.

2. Experiments

2.1. g-C_3N_4 synthesis

g-C_3N_4 photocatalyst was synthesized with urea as the precursor in a furnace with nitrogen atmosphere. The urea was heat to 600 °C at a ramp rate of 5.5 °C/min, and the polymerized at 600 °C for 3 h. The as prepared yellow product was ground into fine powder followed by washing with methanol and water for 3 times each. The sample was then dried in the freeze-drier for 12 h. The yellow g-C_3N_4 powder was dried at 120 °C before used for reaction.

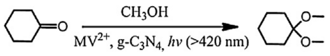
2.2. Photocatalytic reactions

The standard reaction conditions: Calculated amount of substrate, methylviologen chloride, g-C_3N_4, and toluene was mixed with anhydrous methanol in a 50 mL Pyrex glass reactor. The reactor was then sealed and connected to the Schlenk line, the reactor was flushed with nitrogen flow for 20 min. Then the reactor was placed on a magnetic stirrer, irradiated by 100 W white LED (10000 lm). A high power axial fan installed near the reactor kept the reactor at room temperature during light irradiation. Product was analysed by Agilent GC (6890) −MS (5975) with HP-5 capillary column.

3. Results and discussion

The typical SEM image, XRD pattern, and UV–vis absorption spectra of the graphitic carbon nitride are shown in Fig. S1. g-C_3N_4, with building block of tri-s-triazine, is electron rich and intrinsically negative, which is favourable for the surface absorption of the positive MV^{2+} [12]. As shown in Table S1, zeta potential of g-C_3N_4 in water and methanol is – 27.0 and – 0.4 mV, respectively. With the addition of the MV^{2+} in the solvents, zeta potentials positively shift to – 7.5 and 28.5 mV in water and methanol, respectively, indicating the surface adsorption of MV^{2+} on g-C_3N_4. The surface absorption of MV^{2+} on g-C_3N_4 directly promotes the electron transfer process between them under photon excitation. As shown in Fig. 1a, MV^{2+} is quickly reduced upon the visible light irradiation, showing fast rising of the distinctive absorption peak at λ = 605 nm. Meanwhile, after photo-irradiation, g-C_3N_4 in the dark blue solution shows the original yellow colour, indicating MV^{+} is more weakly absorbed on g-C_3N_4 surface (Fig. 1b and c). The spatial separation of the photo-induced charges could hinder direct reoxidation of the MV^{+} by the hole and contribute to the efficiency of this photocatalytic reaction system.

Table 1
Control experiments of the photocatalytic ketalization of cyclohexanone with methanol on g-C_3N_4.



Entry	Photocatalyst	Visible light Irradiation	MV^{2+} (μmol)	Conversion (%)
1[a]	g-C_3N_4	Yes	2.33	92.4
2[b]	g-C_3N_4	No	2.33	0
3	g-C_3N_4	Yes	0	0
4	–	Yes	2.33	0
5	TiO_2	Yes	2.33	0
6[c]	g -C_3N_4	Yes	2.33	0

[a] Standard reaction condition: 30 mg g-C_3N_4, 10 mmol cyclohexanone, 48 mL anhydrous methanol, nitrogen atmosphere, 1 h light irradiation with 100 W LED (λ > 420 nm), and room temperature (RT).
[b] The dark reaction was at 60 °C for 3 h.
[c] The reaction was in anhydrous isopropyl alcohol (IPA).

The reaction was successfully confirmed by the production of 1,1-dimethoxycyclohexane *via* one hour photocatalytic ketalization of cyclohexanone with 92.4% conversion and >99% selectivity (Table 1, entry 1; Fig. S2). To clarify the roles of each part in this reaction system, a series of control experiments was performed employing cyclohexanone as the substrate (Table 1). Without visible light irradiation, there was no reaction even at 60 °C (Table 1, entry 2), excluding the possibility of a thermal addition process. The control reaction under visible light irradiation without MV^{2+} gave no product, showing the critical role of the catalytic amount of 2.33 μmol MV^{2+} for the system (Table 1, entry 3). When g-C_3N_4 was removed from the system or substituted by the visible light inactive TiO_2 (Anatase), there was no product detected after 1 h visible light irradiation (Table 1, entries 4 and 5), demonstrating the role of g-C_3N_4 as visible light sensitizer in this system. To deduce the details of the reactions initiated by valence band hole, isopropyl alcohol (IPA), which is a secondary alcohol and could also work as hole scavenger, was employed for a comparison [42]. As indicated by the blue color of the reaction mixture, MV^{+} was produced in the reaction solution, demonstrating that the conduction band electrons and valence band holes had been trapped by MV^{2+} and IPA, respectively. However, there was no cyclohexanone conversion, which may due to the difference in the intrinsic reactivity of the methoxy and isopropoxy radicals (Isopropoxy radical changes to 2-hydroxy-2-propyl radical immediately after formation by hydrogen abstraction from isopropyl alcohol) [43,44]. The selectivity on the alcohol hole scavenger in the reaction system confirms again that the ketalization reaction herein is not acid-initiated, but photon-initiated. All the control experiments state that visible light, g-C_3N_4, and the presence of the cofactor MV^{2+} are all indispensible to the photocatalytic ketalization reaction.

Based on the analysis of the control experiments, we propose a possible reaction mechanism of the photocatalytic ketalization reaction with methanol on g-C_3N_4 (Scheme 1). Under visible light irradiation, methanol is oxidized to methoxy radical by the photogenerated hole. As an active species, the methoxy radical reacts