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A visible-light-driven transfer hydrogenation on CdS nanoparticles combined with iridium complexes†

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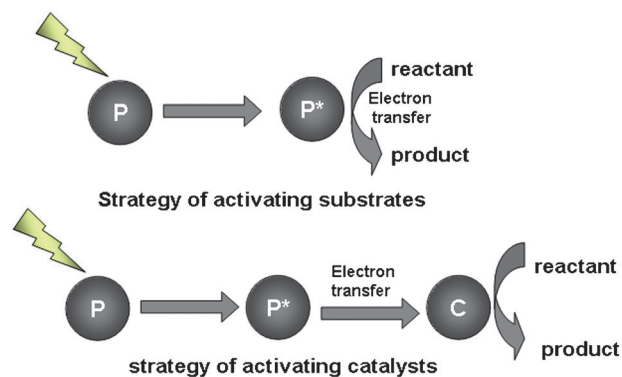
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A visible-light-driven transfer hydrogenation of carbonyl and C=C compounds has been developed by coupling CdS nanoparticles with iridium complexes, exhibiting high activities, excellent selectivities and a unique pH-dependent catalytic activity.

The use of light, particularly visible light, as the driving force for chemical reactions has attracted much attention of organic chemists.^{1,2} One fundamental impediment for classical photochemical reactions is the use of high-energy UV, which often induces undesired by-products due to the unselective excitation processes. The major present strategy to address this drawback is the use of photosensitizers or semiconductors to selectively activate reactants. For instance, the well-known photoredox catalyst tris(2,2'-bipyridyl)ruthenium(II) complexes $[\text{Ru}(\text{bpy})_3]^{2+}$ and its derivatives have been used as the electron transfer reagent to selectively activate special reactants such as aryl enones, α -carbonyl and α -aryl halogen derivatives, which initiate such photochemistry reactions as cycloaddition,³ dehalogenation⁴ and asymmetric alkylation reactions.^{5,6} Visible-light-response semiconductors have been mainly used for the selective oxidation reactions, by activating O_2 and avoiding the induction of strong, nonselective hydroxyl radicals.^{7,8}

Upon irradiation, the excited state of the molecules interacts with reactants, undergoing the electron-transfer processes, which plays a crucial role for the activation of reactants for most reactions. However, the direct electron-transfer between excited photosensitizers/semiconductors and reactants is often difficult. It is often limited by the oxidation/reduction potential of photosensitizers/semiconductors and needs to directly overcome the high energy barrier. The rational design of light-driven reactions using the strategy of activating reactants requires the insight of interaction between reactants and the excited state of photosensitizers/semiconductors. Thereby, the present strategy of activating reactants is restrained to reactions involving special molecules.



Scheme 1 Schematic illustration of the strategy of activating reactants or catalyst with a photoexcited electron-transfer process. P = photosensitizers/semiconductors, P* = the excited state of photosensitizers/semiconductors, C = catalysts.

An alternative solution is the introduction of the function-catalyzed molecules, such as organometallic complexes, as electron mediators between reactants and photosensitizers/semiconductors. These complexes can play a role as co-catalysts, activated by photoexcited electron-transfer processes and subsequently initiate the catalytic reactions (Scheme 1). It is well-known that organometallic complexes are very efficient catalysts for various organic reactions as well as excellent electron acceptors. The strategy to activate catalyst rather than reactants has inherent merits: (1) facilitating the charge separation process in space; (2) reducing the energy barrier of reactants by multistep electron-transfer; (3) ensuring the selectivities of reactions with complexes as active sites; (4) designing rationally the reactions according to the well-known research on organometallic chemistry. Herein, we report an example of photocatalytic transfer hydrogenation of carbonyl and C=C compounds under visible light irradiation, by coupling the semiconductor CdS with iridium complexes. The iridium complexes are activated by the photoexcited electron from CdS, and they play dual functions, acting as the acceptor of electron as well as the catalytic sites for organic transformation.

CdS was chosen because of its suitable conduct band and good visible-light-response ability. A series of half-sandwich iridium complexes **1–4** and $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ were chosen as electron acceptors (Fig. 1). For comparison, CdS supported iridium nanoparticles (Ir/CdS) were prepared by a photoreduction method.⁹ Reduction of cyclohexanone was chosen as a model

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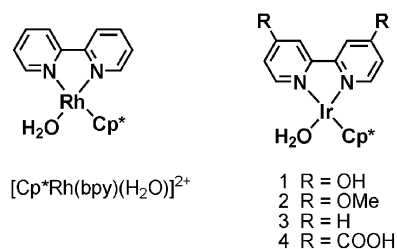


Fig. 1 The structure of complexes used in this study.

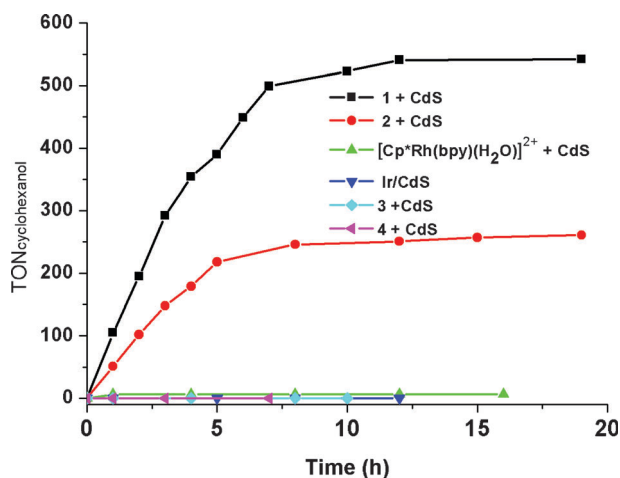


Fig. 2 TON for cyclohexanol formation as a function of irradiation time. The reactions were performed in 5 mL H₂O (containing 1 mL lactic acid) at 40 °C using a Xe lamp with a cut-off filter ($\lambda > 400$ nm). The concentrations of the complex and the substrate are 0.4 mM and 0.4 M, respectively. CdS is 10 mg. The loading of Ir/CdS is 0.3 wt%.

reaction. The reactions were investigated under continuous illumination with visible light from a Xe lamp with a power of 300 W equipped with a cut-off filter ($\lambda > 400$ nm). Lactic acid was chosen as a sacrificial reagent.

Whether or not under irradiation, no cyclohexanol is produced in the presence of complexes or CdS nanoparticles (Table S1, ESI[†]), showing that neither complexes nor CdS can catalyze the reduction reaction under the current conditions. The reaction profiles of reduction of cyclohexanone with coupling CdS with complexes are shown in Fig. 2. Complex [Cp*Rh(bpy)(H₂O)]²⁺, acting frequently as a shuttle in the regeneration of coenzymes,^{10–12} is thermodynamically capable of accepting electrons from CdS nanoparticles. However it showed very poor activity under irradiation, indicating that its hydride species cannot reduce cyclohexanone. When using iridium complex **1** with a hydroxyl group, the amount of the photocatalytic product (cyclohexanol) increased with increasing irradiation time. The iridium complex **1** delivered a turnover number (TON) of 541 in 12 h, and an initial turnover frequency (TOF) of 103 h⁻¹ based on per complex molecule. When switching the substituted group of iridium complexes from -OH to -OMe, a lower activity was observed, delivering a TON of 251 and an initial TOF of 51 h⁻¹. When the substituted group was changed to -H and -COOH, the reactions were completely inhibited. The electronic substituent effect shows that strong electron-donating ability facilitates the reaction. This trend is in agreement with those made with HCOONa as the reducing agent in water.¹³

The used CdS sample was filtered and further characterized. No iridium nanoparticles could be observed in the TEM image (Fig. S3, ESI[†]). Moreover, no iridium was detected by EDX and XPS analysis of the used CdS (Fig. S4 and S5, ESI[†]). The reduction of cyclohexanone was also performed in the presence of the Ir/CdS catalyst, and no activity for the reduction of cyclohexanone was observed (Fig. 2). These results distinctly confirm that the iridium complex instead of iridium nanoparticles adsorbed on CdS is responsible for the reduction of cyclohexanone.

In the absence of cyclohexanone, the hybrid system **1**/CdS can also efficiently catalyze the reduction of proton to H₂ under irradiation, yielding a TON of 681 in 6 h (Fig. S7, ESI[†]). However, only negligible H₂ was produced in the presence of cyclohexanone and cyclohexanol is a main reduced product (Table S2, ESI[†]). The linear sweep voltammetry test was performed to investigate the reduction ability of **1**/CdS for cyclohexanone and proton, as shown in Fig. 3. When adding cyclohexanone into an electrolyte, linear voltammetry scan displays a new wave centered at $E_{p,c} = 0.98$ V on the cathodic sweep of the CdS/FTO (FTO = fluorine tin oxide) electrode, attributed to the reduction of cyclohexanone. Sequentially adding complex **1** to the electrolyte, linear voltammetry scan displays a new cathodic wave centered at $E_{p,c} = 0.82$ V, attributed to the reduction of the iridium complex. Concomitantly, the reduction peak of cyclohexanone is increased sharply, suggesting a typical electrochemical/chemical process. The presence of complex **1** facilitates greatly the reduction of cyclohexanone prior to the reduction of proton.

Iridium complex **1**, using a chemical hydrogen donor like formate, shows strongly pH-dependent catalytic activity.¹³ This inspires us to improve the efficiency in the current photocatalytic system by the optimization of the pH value of solution. As shown in Fig. 4, the complex **1** in aqueous sodium formate showed a distinctive pH dependence in the reduction of cyclohexanone, as reported previously by Himeda *et al.*¹³

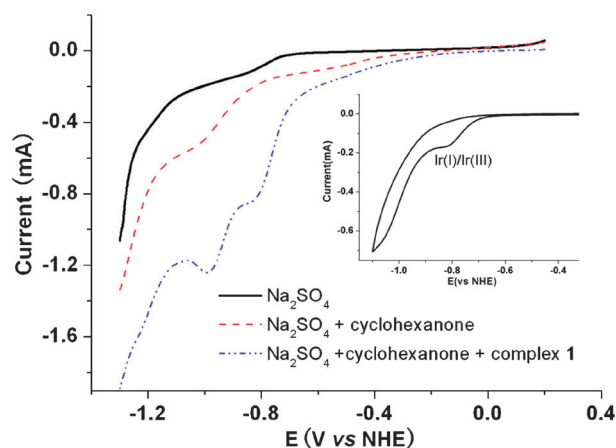


Fig. 3 Linear sweep voltammetry of solutions. Reaction conditions: (—) aqueous Na₂SO₄ (0.1 M); (---) aqueous Na₂SO₄ and cyclohexanone (0.2 mM); (· · ·) aqueous Na₂SO₄ and cyclohexanone in the presence of complex **1** (0.2 mM). The inset shows a cyclic voltammetry of iridium complex **1** in aqueous Na₂SO₄. Working electrode is CdS/FTO. Counter electrode is platinum wire. Reference electrode is Ag/AgCl. Scan rate is 0.05 V s⁻¹, and $T = 20$ °C.

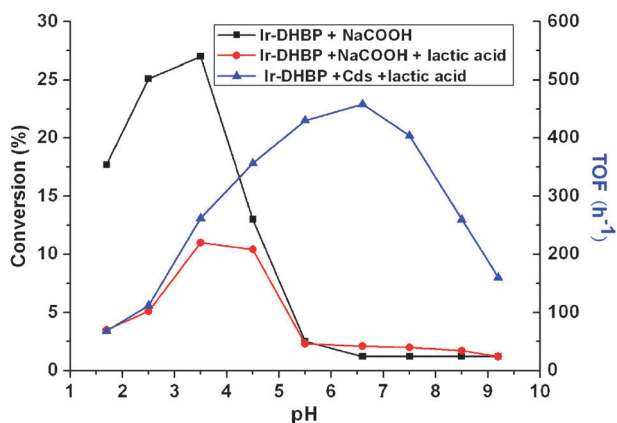


Fig. 4 Comparison of the activities of iridium complex **1** for the reduction of cyclohexanone at different pH conditions in water. Reaction conditions: (—■—) aqueous NaCOOH (1 mM); (—●—) aqueous NaCOOH (1 mM) and lactic acid (1 mL); (—▲—) CdS (10 mg) and lactic acid (1 mL) under irradiation ($\lambda > 400$ nm). TOF based on the conversion for 1 h.

The maximum TOF of 540 h^{-1} was obtained at pH 3.5 and the catalytic activity was diminished sharply at pH higher than 4. While adding lactic acid into aqueous HCOONa, the reaction showed a similar trend but lower activities at corresponding pH values. Interestingly, the photocatalytic system, coupling CdS with the iridium complex, responds contrarily to the pH change. The initial TOF is 100 h^{-1} , and the catalytic activity was steadily enhanced with the increase of solution pH. The peak appeared at *ca.* pH 6.5, delivering the maximum TOF of 400 h^{-1} . The different response to solution pH in the photocatalytic system indicates that the electron transfer between CdS and the iridium complex is affected greatly by the pH of solution. In contrast, we didn't observe similar pH-dependence using the iridium complex with the -OMe group under irradiation.

Iridium complex **1** with two phenolic hydroxyl groups existed as a protonated form at pH below 2.6, and a deprotonated oxyanion form at pH 7.3, as reported by Himeda *et al.*¹³ As shown in Fig. 5, the iridium complex **1** with oxyanion form has stronger adsorption ability than that with a phenolic hydroxyl at the surface of CdS. Furthermore, the oxyanion form of complex **1** possesses a unique conjugated structure between the oxyanion and the phenyl group, possibly favoring the electron transfer between CdS and complex **1**.

A series of other substrates were tested with the coupled **1**/CdS system under neutral conditions, and the results are summarized in Table 1. For example cyclohexanecarboxaldehyde was reduced efficiently, giving a TON of 381 in 6 h. Acetophenone was reduced with a TON of 220 in the same time. The C=C bond was selectively reduced for benzylideneacetone in neutral conditions, giving a TON of 318. Particularly α -ketoester shows much higher activity. For instance, ethyl

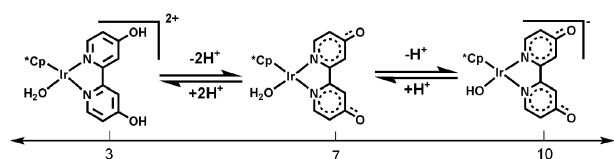


Fig. 5 Acid-base behavior of complex **1** at different pH.

Table 1 Reduction of various substrates with coupling CdS and complex **1** under irradiation^a

| Substrate | Product | Time/h | Selectivity (%) | TON |
|-----------|---------|--------|-----------------|-----|
| | | 6 | 100 | 381 |
| | | 6 | 100 | 220 |
| | | 6 | 100 | 320 |
| | | 3 | 100 | 790 |

^a The initial pH of solution of water/lactic acid is 6.5. See Fig. 2 for other conditions.

pyruvate delivered a TON of 790 in 3 h, and initial TOF exceeds 500 h^{-1} .

In summary, we developed a highly selective photocatalytic system for organic reduction reaction under visible light irradiation, by coupling CdS nanoparticles with iridium-based complexes. In the hybrid systems, the semiconductor harvests light energy, and complexes are activated by the photo-driven electron, and catalyze the subsequent reactions. The strategy of activating catalysts by photoexcited electron-transfer provides a promising method for various photocatalytic organic reactions, particularly for reductions and oxidation reactions. Furthermore, the strategy can be expanded to the utilization of solar energy to produce H_2 and chemicals from H_2O and CO_2 .

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