Journal of Catalysis 304 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Efficient visible-light-induced hydrogenation over composites of CdS and ruthenium carbonyl complexes

Xiaobin Liu, Dengrong Sun, Rusheng Yuan, Xianzhi Fu, Zhaohui Li *

Research Institute of Photocatalysis, Fujian Provincial Key Laboratory of Photocatalysis, Fuzhou University, Fuzhou 350002, PR China
Research Institute of Photocatalysis, State Key Laboratory Breeding Base, Fuzhou University, Fuzhou 350002, PR China

ARTICLE INFO

Article history:
Received 4 February 2013
Revised 27 March 2013
Accepted 6 April 2013
Available online 2 May 2013

Keywords:
Ru carbonyl complex
CdS
Photocatalytic
Hydrogenation
Visible light
Mechanism

ABSTRACT

Hybrid systems built by coupling CdS with a series of Ru carbonyl complexes ($[Ru(bpy)_2(CO)_2](PF_6)_2$ (**RC-1**), $[Ru(phen)_2(CO)_2](PF_6)_2$ (**RC-2**), $[Ru(bpy)(CO)_2Cl_2]$ (**RC-3**), $[Ru(Me_2bpy)(CO)_2Cl_2]$ (**RC-4**), and $[Ru(phen)(CO)_2Cl_2]$ (**RC-5**)) showed activity for the hydrogenation of carbonyl compounds under visible-light irradiations in the presence of appropriate sacrificial agent. The influences of the irradiations mode, sacrificial agent, substrates, and the structure of the Ru complexes on the hydrogenation performance of these composites were investigated. Results indicated that CdS act as the photosensitizer, while the Ru carbonyl complexes as catalytic active component. This study provides some guidance in the development of feasible hybrid photocatalytic systems encompassing visible-light-responsive semiconductors and redox-active transition metal complexes, which are expected to find great potentials in the photocatalytic organic transformations. It is believed that such photocatalytic systems can be built in a more controllable way based on our understanding on the structure–activity relationship of the molecular electro-catalyst.

1. Introduction

The depletion of fossil fuels and the impact of global warming have led to the utilization of solar energy as an abundant and renewable energy resource. The use of light, particularly visible light, as the driving force for chemical reactions, is appealing and has attracted much current attention [1–11]. However, the development of highly efficient photocatalysts for organic transformations that can function under visible-light irradiations is still challenging.

To mimic the natural photosynthetic systems, researchers have made a great effort to build artificial photocatalytic system by coupling a light-harvesting component (a photosensitizer), which captures the solar energy and initiates photochemical electron transfer, with a redox-active catalyst [10–16]. Combining semiconductors with transition metal complexes or dyes is a widely adopted strategy in building of such artificial photocatalytic systems. Most of the previously reported hybrid photocatalytic systems involve using dyes or transition metal complexes as photosensitizers and couple them to semiconductor photocatalysts for a variety of photocatalytic reactions. For example, metal-free dyes, ruthenium, or other transition metal complexes sensitized semiconductor photocatalysts have been used for the photocatalytic hydrogen generation or CO_2 reduction [2–4,10–15]. By activating O_2 and avoiding the generation of strong, nonselective hydroxyl radicals, photo-sensitized TiO_2 has also been used for the selective oxidation reactions [16]. Although well documented, these dyes-sensitized semiconductor photocatalysts usually suffer from poor stability due to the degradation of the photosensitizers under light irradiations. Besides this, dyes usually have narrow spectral absorption, which limit their absorption in most of the solar spectrum.

A more promising strategy recently reported in the development of the hybrid photocatalytic systems is to use narrow band-gap semiconductors as photosensitizers and combine them with redox-active transition metal complexes acting as electro-catalysts. Such hybrid photocatalytic systems can be built in a more controllable way since a rational design and modification of the molecular-based electro-catalyst is feasible based on a good understanding of its structure–catalytic activity relationship. Moreover, the replacement of the dyes with the semiconductor-based photosensitizers has two additional advantages. First, the spectral absorption range of the narrow band-gap semiconductors is usually broad and continuous, which is beneficial for an efficient absorption of the solar energy. Second, semiconductors are chemically more stable than organic or transition metal complexes dyes. Therefore, the use of semiconductors as photosensitizers is expected to improve the stability of the resultant photocatalytic

---

* Corresponding author at: Research Institute of Photocatalysis, Fujian Provincial Key Laboratory of Photocatalysis, Fuzhou University, Fuzhou 350002, PR China.
E-mail address: zhaohuili1969@yahoo.com (Z. Li).

0021-9517/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.04.004

systems. Actually, several hybrid photocatalytic systems developed via this strategy have recently been reported for photocatalytic H_2 production, CO_2 reduction as well as hydrogenation of carbonyl groups in ketones. For example, visible irradiations over N-doped Ta_2O_5 chemically combined with a ruthenium complex electro-catalyst ($[Ru(bpy)_2(CO)_2]^{2+}$ and its derivatives, bpy = 2,2′-bipyridine) can reduce CO_2 to give formate in the presence of triethanolamine (TEOA) acting as a sacrificial electron donor [17]. CdS/cobaloxime composite can photocatalytically produce H_2 under visible-light irradiations [18]. Hybrid systems built by coupling of CdS with iridium complex ($[Cp^*Ir(4,4'\text{-dihydroxy-bpy})(H_2O)]^{2+}$), a catalyst with excellent performance in transfer hydrogenation reaction, can photocatalytic hydrogenate carbonyl compounds under visible-light irradiations [19,20]. Although only a few such hybrid systems have been reported, their high potential in utilizing the solar energy to drive the chemical reactions has been demonstrated.

Since Ru carbonyl complexes are also capable of catalyze the transfer hydrogenation reaction as the already reported Ir complex, it is expected that the coupling of the Ru carbonyl complexes with CdS can also lead to efficient photocatalysts for the hydrogenation of carbonyl complexes under visible-light irradiations [21]. Therefore in this manuscript, we reported the development of a series of new hybrid photocatalytic systems by coupling CdS nanoparticles with Ru-based carbonyl complexes. As expected, these Ru complex/CdS composites showed activity for the hydrogenation of carbonyl compounds under visible-light irradiations in the presence of appropriate sacrificial agent. The influences of the irradiations mode, sacrificial agent, substrates and the structure of the Ru complexes on the photocatalytic hydrogenation performance of these composites were investigated. A mechanism of the photocatalytic hydrogenation over the Ru complex/CdS composites was also proposed.

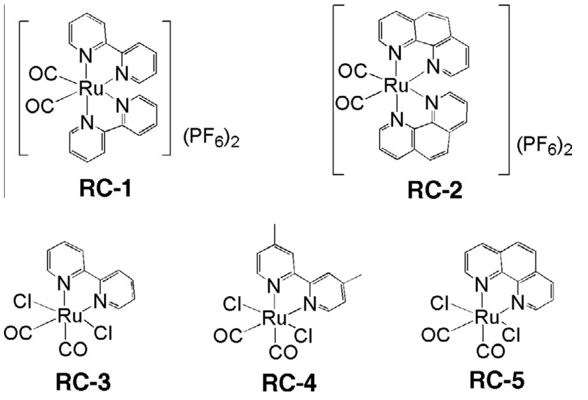
2. Experimental

2.1. Methods and materials

All the experiments were performed under an N_2 atmosphere by using standard Schlenk techniques unless otherwise stated. All the reagents were A.R. grade and used without further purification.

2.2. Preparations

$[Ru(bpy)_2(CO)_2](PF_6)_2$ (**RC-1**), $[Ru(phen)_2(CO)_2](PF_6)_2$ (**RC-2**), $[Ru(bpy)(CO)_2Cl_2]$ (**RC-3**), $[Ru(Me_2bpy)(CO)_2Cl_2]$ (**RC-4**), and $[Ru(phen)(CO)_2Cl_2]$ (**RC-5**) were synthesized following the methods reported in literature [22]. The structures of all these Ru-based complexes are shown in Scheme 1. CdS nanoparticles were prepared according to the previous literature [23]. $[Ru(bpy)_2(CO)H]PF_6$ (hydride derivative of **RC-1**) was synthesized according to the literature [24].



Scheme 1. Molecular structures of all the involved Ru complexes.

2.3. Characterizations

All the Ru-based complexes were characterized by IR and ^1H NMR, and the results were shown in Table S1. The IR experiments were carried out on a Nicolet 670 FT-IR spectrometer, and the samples were prepared as KBr pellets. NMR spectra were obtained on a 500 MHZ Bruker AVANCE III 500 M system. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scan rate of $0.02^\circ\ 2\theta\ s^{-1}$ in the 2θ range from 10° to 70°. UV–vis absorption spectra and UV–vis diffuse-reflectance spectrometry (UV–vis DRS) were obtained on a UV–vis spectrophotometer (Cary 500 Scan Spectrophotometers, Varian). $BaSO_4$ was used as a reflectance standard. The photoluminescence (PL) emission spectra were taken on a FL/FS 920 time-resolved fluorescence spectrometer.

2.4. Photocatalytic reactions

For the hydrogenation of cyclohexanone and acetophenone, CdS power (10 mg) and Ru-based complex (2 μmol) was introduced into a 25 mL Schlenk tube containing 5 mL degassed aqueous solution and 1 mL lactic acid. After an ultrasonic treatment on the suspension for 5 min, the substrate (0.2 mL, 2 mmol) was added. The reaction suspension was irradiated with Xe lamp equipped with a cutoff filter ($\lambda > 420$ nm). After reaction, the products were filtered and extracted by ethyl acetate, analyzed by a Shimadzu gas chromatograph equipped with a flame ionization detector and a ZB-WAX (30 m × 0.32 mm × 0.25 μm) capillary column. The amounts of the products were determined according to the commonly used external standard method.

The photocatalytic hydrogenation of ethyl pyruvate was carried out in a similar procedure except for the analytic method. The product was analyzed by a Waters HPLC equipped with a 254 nm UV detector and a Merck C18 capillary column. CH_3CN was chosen as the eluant.

3. Results and discussion

CdS nanoparticles in hexagonal structure were prepared via a precipitation–hydrothermal treatment. The UV–vis DRS of the as-prepared CdS nanoparticles show a strong absorption in the UV

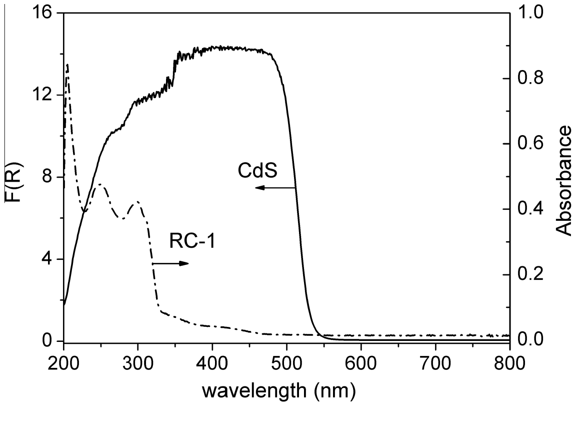


Fig. 1. UV–vis DRS of CdS nanoparticles and UV–vis absorption spectrum of **RC-1**.