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Coupling plasmonic noble metal with TiO_2 for efficient photocatalytic transfer hydrogenation: M/TiO_2 (M = Au and Pt) for chemoselective transformation of cinnamaldehyde to cinnamyl alcohol under visible and 365 nm UV light

Yating Ma, Zhaohui Li [*]

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, PR China

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ABSTRACT

M/TiO_2 (M = Au and Pt) were prepared by a solvothermal method combined with an in situ photoreduction process and their photocatalytic performance for transfer hydrogenation of cinnamaldehyde (CAL) to form cinnamyl alcohol (COL) in the presence of isopropanol was investigated under visible light and 365 nm UV light. Although the photocatalytic transformation of CAL to COL can be realized over both Au/TiO_2 and Pt/TiO_2, they show different activity order under visible light and 365 nm UV light, ie, Au/TiO_2 show superior activity than Pt/TiO_2 under visible light, while an opposite activity order was observed under 365 nm UV light. The hydrogenation to form COL over Pt/TiO_2 reached a turnover frequency (TOF) of 197 h^{-1} under 365 nm UV light, which is among the highest in all the already reported systems for hydrogenation and transfer hydrogenation of CAL to form COL. The superior performance observed over Pt/TiO_2 at 365 nm can be ascribed to a synergistic effect of plasmonic Pt and the direct excitation of TiO_2. This study not only provides a green method for the transfer hydrogenation of CAL to form COL, but also highlights the great potential of coupling of plasmonic noble metal nanoparticles with semiconductor photocatalysts for light-induced organic transformations.

1. Introduction

Selective hydrogenation of α, β-unsaturated aldehydes to the α, β-unsaturated alcohols has received considerable attention recently since α, β-unsaturated alcohols are useful chemicals and intermediates in the manufacture of fine chemicals [1–3]. However, this reaction is usually challenging since two competitive hydrogenation routes, ie, the hydrogenation of the C=C bond to the saturated aldehydes versus the hydrogenation of the C=O bond to the unsaturated alcohols, coexist in the hydrogenation of α, β-unsaturated aldehydes. In particular, the desired selective hydrogenation of the C=O bond is thermodynamically unfavorable. Therefore, to obtain the desired unsaturated alcohols, the manipulation of the kinetic effects by choosing a suitable catalyst that favors C=O hydrogenation while keeping the C=C bond intact is important.

Traditional hydrogenation reactions are generally accomplished through thermal-based chemical processes using H_2 catalyzed by catalysts based on transition metals nanoparticles or organometallic complexes [4–13]. The use of metal hydrides like $LiAlH_4$ or $NaBH_4$ as the stoichiometric reducing agent for hydrogenation reactions has also been well documented [14]. To avoid using the flammable and explosive high pressure hydrogen and highly expensive metal hydrides, catalytic transfer hydrogenation, as a promising alternative to the traditional hydrogenation reactions, has also attracted extensive research interest. Catalytic transfer hydrogenation, which uses small molecules like alcohols, formic acid or its salts and other hydrogen sources, has the merit of operational simplicity, lower cost and is safer [15–22]. As a good hydrogen donor, isopropanol is among the most commonly used reagents for transfer hydrogenation reaction. Noble metal nanoparticles as well as organometallic complexes have both been reported to catalyze the transfer hydrogenation reactions [23–28]. For instance, a facile gold-catalyzed, isopropanol-mediated transfer hydrogenation strategy enabled a chemoselective hydrogenation of CAL to form COL with a high yield of 84% [29]. Iridium N-heterocyclic carbene complex exhibited a highly efficient transfer hydrogenation of aldehydes to alcohols [30]. However, most of the already reported transfer hydrogenation reactions occur in temperature (80–150 °C) that requires additional heating.

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[*] Corresponding author.
E-mail address: zhaohuili1969@yahoo.com (Z. Li).

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The use of light, in particular visible light, as the driving force for chemical reactions, is appealing and has attracted much current attention [31–36]. The application of photocatalysis in transfer hydrogenation reactions has also been reported. For example, transfer hydrogenation of carbonyl compounds under visible light has been realized over a hybrid photocatalytic system containing CdS as a sensitizer and $[Cp^{*}Ir(4,4'\text{-dihydroxy-bpy})(H_2O)]^{2+}$ as the hydrogenation catalyst [37]. Our group also reported that the coupling of CdS to a series of Ru carbonyl complexes showed photocatalytic activity for the hydrogenation of carbonyl compounds under visible-light [38]. In addition, the performance of the hydrogenation can be significantly influenced by irradiations mode, sacrificial agent, substrates as well as the structure of the Ru complexes. Very recently, Guo et al. reported that plasmonic Au nanoparticles supported on SiC can act as an efficient photocatalyst for transfer hydrogenation of CAL to form COL under visible light [39]. Similarly, Au/CeO_2 was also reported to exhibit high photocatalytic activity for selectivity hydrogenation of a series of organic compounds [40]. In both cases, the visible light generated "hot" electrons on the plasmonic Au nanoparticles enable the chemical reactions to be carried out under mild conditions [41].

In this manuscript, we reported the preparation of M/TiO_2 (M = Au and Pt) and studied their photocatalytic performance for transfer hydrogenation of CAL to form COL under both visible light and 365 nm UV light. It was found that the photocatalytic transformation of CAL to COL can be realized over both Au/TiO_2 and Pt/TiO_2. However, they show different activity order under visible light and 365 nm UV light, ie, Au/TiO_2 show superior activity than Pt/TiO_2 under visible light, while an opposite activity order was observed under 365 nm UV light. The TOF of the formation of COL over Pt/TiO_2 at 365 nm UV light is determined to be 197 h^{-1}. A synergistic effect of photocatalysis based on plasmonic Pt and the direct excitation of TiO_2 attribute to the superior performance over Pt/TiO_2. This study indicates that the coupling of plasmonic metal nanoparticles with semiconductors may be a promising strategy to realize the light-induced organic transformations.

2. Experimental

2.1. Syntheses

All the reagents and solvents were commercially available and used as supplied without further purifications. TiO_2 was prepared following previously reported procedures [42]. Pt/TiO_2 was prepared via a solution impregnation combined with an in situ photo-reduction process. The as-obtained TiO_2 (100 mg) was suspended in methanol solution (5 ml) containing 134 μL H_2PtCl_6 solution (19.3 mmol/L). The resulting mixture was stirred under N_2 atmosphere for 30 min and irradiated under four 4 W UV lamps with a wavelength centered at 365 nm. After illuminated for 5 h, the resultant sample was filtered, washed by methanol, and dried overnight at 60 °C in oven. A similar procedure was applied in the preparation of Au/TiO_2, except that H_2PtCl_6 was replaced with 132 μL $HAuCl_4$ solution (19.3 mmol/L).

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on an FEI Tecnai G2 F20 instrument. Ultraviolet–visible diffuse reflectance spectra (UV-DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA).

2.3. Photocatalytic reaction

The photocatalytic hydrogenation of CAL to COL was performed as following. In a typical process, a mixture of CAL (0.1 mmol, 12.60 μL) and isopropanol (2.0 ml) saturated with N_2 was transferred into a 10 ml Schlenk tube containing 10 mg of catalyst. For the reaction carried out under visible light, the reaction system was irradiated with a 300 W Xe lamp with a UV-cut filter to remove light with wavelengths less than 420 nm and an IR-cut filter to remove light with wavelengths longer than 800 nm. For 365 nm UV light irradiated system, four 4 W UV lamps with a wavelength centered at 365 nm were used as illuminating source. Apparent quantum efficiency (AQE) for photocatalytic hydrogenation of CAL to COL over Au/TiO_2 and Pt/TiO_2 was determined at 550 nm and 365 nm, respectively. The AQE% is represented as (2 × number of COL)/(number of incident photons) × 100%.

3. Results and discussion

Au/TiO_2 and Pt/TiO_2 were prepared from solvothermally obtained TiO_2 and $HAuCl_4$ and H_2PtCl_6 respectively by a photoreduction approach. The XRD patterns of the as-prepared Au/TiO_2 and Pt/TiO_2 show characteristics peaks of anatase TiO_2 (JCPDS, No. 99-0008). No peaks attributed to metallic Pt and Au are observed in the XRD patterns, probably due to the low amount of Pt and Au in the samples (Fig. 1). However, the XPS spectra of the as-obtained Pt/TiO_2 shows two peaks at 71.3 and 74.55 eV, corresponding to Pt^0 $4f_{7/2}$ and Pt^0 $4f_{5/2}$ respectively, while that of Au/TiO_2 shows two peaks at 84.1 and 87.77 eV, assignable to Au^0 $4f_{7/2}$ and Au^0 $4f_{5/2}$ (Fig. 2a and b). These indicate that Pt^{4+} and Au^{3+} have been successfully reduced to Pt^0 and Au^0 over TiO_2 via the photoreduction. The TEM images of Au/TiO_2 and Pt/TiO_2 show that Au and Pt nanoparticles with an average diameter of ca. 5 nm are deposited on the surface of TiO_2 (Fig. 3). Clear lattice fringe of 0.24 nm and 0.23 nm, which matches that of the (1 1 1) plane of face-centered cubic Au and (1 1 1) plane of face-centered cubic Pt, are clearly observed in the HRTEM images of Au/TiO_2 and Pt/TiO_2 (inset in Fig. 3). All these results confirm that small nanoparticles of Pt and Au have been deposited on the surface of anatase TiO_2.

The UV–vis diffuse reflectance spectra of the as-obtained Pt/TiO_2, Au/TiO_2 as well as TiO_2 were shown in Fig. 4. Theoretically TiO_2 has a band gap of 3.2 eV and is not responsive to the visible

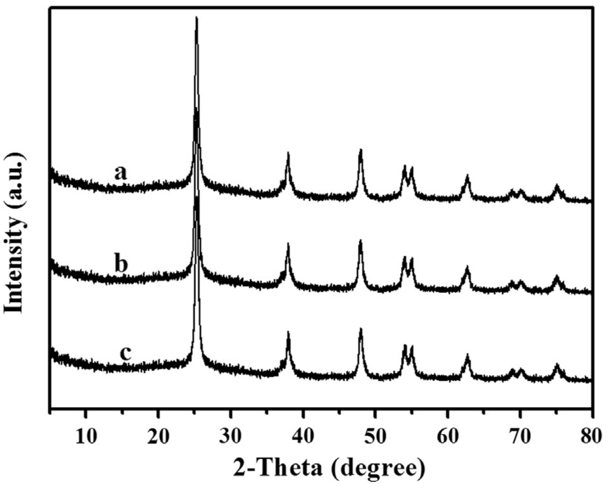

Fig. 1. XRD patterns of (a) Pt/TiO_2, (b) Au/TiO_2 and (c) TiO_2.