Chinese Chemical Letters xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Communication

The effect of surface electronic structures of Au/TiO_2 on sonophotochemical reactions

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ARTICLE INFO

Article history:
Available online xxx

Keywords:
Sonophotocatalysis
Localized surface plasmon resonance
Electronic structure
Water reduction
Au/TiO_2

ABSTRACT

Sonophotocatalysis combines ultrasonic and light irradiations to drastically boost the chemical reaction rate and has attracted many interests for its potential applications in the environmental remediation and protection. However, it still remains unclear whether the light irradiation could couple with the ultrasound to prompt the sonophotocatalytic process. Here, we selectively excited the TiO_2 and Au to manipulate the electronic structures of Au/TiO_2 and studied their influence in sonophotocatalytic water (H_2O) reduction. Surprisingly, no significant increase of the hydrogen (H_2) production rate was observed under either the UV light irradiation or the visible light irradiation, suggesting that the change in electronic structures of Au/TiO_2 does not prompt the generation of free radicals under sonication and the reaction is dominated by the recovery of active sites through ultrasound. Our findings established an in-depth understanding of the origin of the enhanced catalytic activity in sonophotocatalysis.

Sonication has been widely used for dispersing particles in liquids or cleaning glassware. Since Suslick proposed the concept of sonochemistry in the early 1990s [1], numerous studies have demonstrated the use of sonochemistry for materials synthesis [2,3], catalysis [4–8], and biological material deactivation [9,10]. The most important effects of ultrasound arise from acoustic cavitation: formation, growth, and implosive collapse of bubbles in liquid by passing ultrasonic waves through the medium [11]. It has been suggested that the implosive collapse of the bubbles generates the localized hot spots that greatly accelerated the H_2 evolution in H_2O sonolysis [4] and significantly enhanced the degradation rate of azo dyes [6]. Among these applications, sonophotocatalysis has attracted great attention due to its potential application in reactions involving environmental remediation and protection, such as environmental pollutant degradation [12–14] and H_2O reduction [15,16]. The combination of ultrasonic and light irradiations was believed to significantly prompt the chemical reaction rate. For examples, Mrowetz *et al.* observed the synergistic effect of sonolysis and photocatalysis towards the degradation of acid orange 8 in the presence of TiO_2, and they believed that the sonication induced the desorption of organic substrates as well as the degradation of the intermediates from the photocatalyst surface [17]. Wang *et al.* found that the high intensity sonication treatment was a simple and effective way to improve the performance of ZnO nanoparticles in the photoelectrochemical water splitting under the tungsten halogen lamp excitation [16]. However, to date, the description of the function of light irradiation in coupling with the ultrasound to facilitate the sonophotocatalytic process still remains ambiguous. Previous studies have suggested that a synergistic effect of photocatalysis and sonolysis might reduce the band gap energy via the high temperature and high pressure produced by the bubble collapse under the ultrasonic irradiation [18]. Others have proposed that both the light irradiation and ultrasound irradiation could generate reactive free radicals to directly increase the reaction activities [19].

Among these different understanding of the synergistic effect in sonophotocatalytic reaction, it has been generally accepted that the oxidizing species ($^\bullet OH$) generated on photocatalyst surfaces is necessary [20], suggesting that the surface charges on the photocatalysts might play a crucial role in prompting the surface chemical reactions. It has been known that the UV irradiation can generate hot carriers (electrons and holes) in semiconductors (*e.g.*, TiO_2) and alter their electronic structures [21]. Recent studies demonstrated that the visible light also can be used to produce hot carriers in metal/semiconductor heterostructures to initiate surface chemical reactions [22–24]. Upon irradiation, the surface plasmon resonance (SPR) of metal nanoparticles is excited and

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https://doi.org/10.1016/j.cclet.2018.03.027
1001-8417/

Please cite this article in press as: K. Qian, et al., The effect of surface electronic structures of Au/TiO_2 on sonophotochemical reactions, Chin. Chem. Lett. (2018), https://doi.org/10.1016/j.cclet.2018.03.027

then mediates the transfer of hot electrons across an interfacial Schottky barrier (φ_B) at the metal-semiconductor heterojunction, resulting different surface charge distributions on the metal/semiconductor heterostructures. Here, we use light irradiation of different wavelengths to manipulate the electronic structures of Au/TiO_2 investigate the roles of surface charges in enhancing the sonophotocatalytic water (H_2O) reduction reaction. Our study will improve the fundamental understanding of sonophotochemistry and promote its potential applications in real catalytic reactions.

Au/TiO_2 was prepared using a deposition precipitation (DP) method [25,26]. $HAuCl_4 \cdot H_2O$ (≥99.9%, Aldrich) was dissolved in Nanopure H_2O to prepare a 0.0191 mol/L aqueous solution. Then, the $HAuCl_4$ aqueous solution was mixed with TiO_2 powder (≥99.5% trace metals basis P25, Aldrich) and Nanopure H_2O in a flask and stirred at 323 K for 30 min. NH_4OH (28%–30% by weight, ACS reagent) was added to adjust the pH value of the system to *ca.* 9, after which it was stirred at 323 K for 2 h. The gel was centrifuged, washed with Nanopure H_2O three times, dried at 323 K for 12 h and calcined at 473 K for 4 h. The weight percentage (wt%) of Au on TiO_2 was estimated to be 1 wt%.

To test the sonophotochemical activity, 50 mg of as-prepared Au/TiO_2 and 15 mL Nanopure H_2O were added into a 50 mL three-neck round-bottom flask, followed by sonication for 20 min to achieve a better dispersion of the catalysts in the solution. Later, 5 mL methanol was injected into the solution. Schlenk line was used to evacuate atmospheric oxygen (O_2) and H_2O, followed by a gas flow of inert Argon (Ar) into the reactor. The flask was then placed in the middle of a sonicator (Fisher Scientific, FS30) throughout the reaction. The reactor was irradiated by a 300 W Xe lamp (Newport 6258) coupled with long pass filters (Newport) with specified wavelengths. The power intensities were measured to 1.0 W/cm^2 by a power meter (Newport, 1916-C). For each cycle, the reactor was sonicated for 1 min and then cooled down for 5 min to ensure the stabilization of the system temperature. Finally, 200 μL gas products were withdrawn by a gas-tight syringe at given reaction time and analyzed by a Gas Chromatography (GC, Shimadzu, GC2014) equipped with a 60/80 Mol Sieve 5A column. During the measurement, the thermal conductivity detector was maintained at 308 K with Ar as the carrier gas. Given that the intensities of both incident light and ultrasonic wave were greatly affected by the position of the reactor, the experiments under light irradiations of different wavelengths were carried out without changing the position of the reactor to ensure the validity of comparison.

Photoluminescence (PL) spectra were measured on a Horiba Aramis Raman system, which is a software-selectable multi-wavelength Raman/PL system. High-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) analysis was operated on a Hitachi HD 2700C. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Si substrate using a ULVAC-PHI 5000 VersaProbe III System. The binding energies in the XPS spectra were referenced to the Ti $2p_{3/2}$ binding energy in TiO_2 at 457.8 eV.

Fig. 1A presents a HAADF-STEM image of Au/TiO_2 catalyst. The average particle diameter of Au was measured to be 4.4 ± 1.1 nm over a hundred Au nanoparticles (Fig. 1C). The interface of the Au nanoparticle and TiO_2 support was also examined, in which the lattice fringes could be easily distinguished (Fig. 1B). The lattice fringes separated by 0.36 and 0.23 nm were assigned to anatase TiO_2 (101) and Au (111), respectively. An intact interface (which was marked by a white frame) between TiO_2 (101) and Au (111) was observed.

Fig. 2A shows the high-resolution XPS spectrum of Au 4f peaks acquired over the Au/TiO_2 heterostructures. The Au $4f_{7/2}$ peak consists of a single component with a binding energy of 83.7 eV, which is slightly red-shifted relative to $Au^{(0)}$ at 84.0 eV [27]. This indicates that a partially negative surface charge was imparted from the TiO_2 to the Au, as the Fermi level of two components must align during the formation of the Au-TiO_2 interface (Fig. 2C). Such strong interaction between Au and TiO_2 was further confirmed by the photoluminescence (PL) studies. As shown in Fig. 2B, Au/TiO_2 exhibits much weaker PL intensity than pristine TiO_2 under a 325-nm laser excitation.

If surface charges account for the enhanced catalytic activity during sonication, then the rate of H_2O sonolysis would be different when the electronic structures of Au/TiO_2 are altered. In our approach, different optical excitation was used to manipulate the surface charges of Au/TiO_2. As shown in Fig. 2D, when TiO_2 is excited by UV irradiation (*i.e.*, $\lambda < 400$ nm), hot electrons inject into Au due to a lower electronic potential, leading to the formation of a negative charge on Au and a positive charge on TiO_2 (marked as $Au^{(-)}/TiO_2^{(+)}$) [22,23]. Alternatively, when using visit light (*i.e.*, $\lambda > 435$ nm), Au LSPR is excited and facilitates the transfer of hot electrons into the conduction band of TiO_2, leaving positively charged Au and negatively charged TiO_2 (marked as $Au^{(+)}/TiO_2^{(-)}$) [22,23].

Following the methods outlined in previous literature [23,28], the catalytic activities of the Au/TiO_2 photocatalysts were tested for H_2O reduction. Fig. 3A shows that Au/TiO_2 by sonication alone produced (32.7 ± 1.7) $\mu mol_{H2}/g_{cat}$ H_2 within 1 min. Without sonication, the Au/TiO_2 photocatalysts still produced (11.3 ± 0.8) $\mu mol_{H2}/g_{cat}$ H_2 over $Au^{(-)}/TiO_2^{(+)}$ under UV excitation within 1 min. The above results suggest that both the sonication and UV excitation can assistant the H_2O reduction to produce H_2. However, under visible light, we did not detect H_2 production over $Au^{(+)}/TiO_2^{(-)}$ within 1 min. Such observation is consistent with our previous finding that the hot electrons transferred from the small Au nanoparticles to TiO_2 do not have enough potential energy to overcome the proton reduction potential [23].

To investigate the possible synergistic effect of the light irradiation and ultrasound irradiation and identify the role of surface charges, the sonophotocatalytic H_2O reduction was performed in the following sequence: (1) in the dark, (2) under UV excitation, (3) under visible excitation, and (4) in the dark

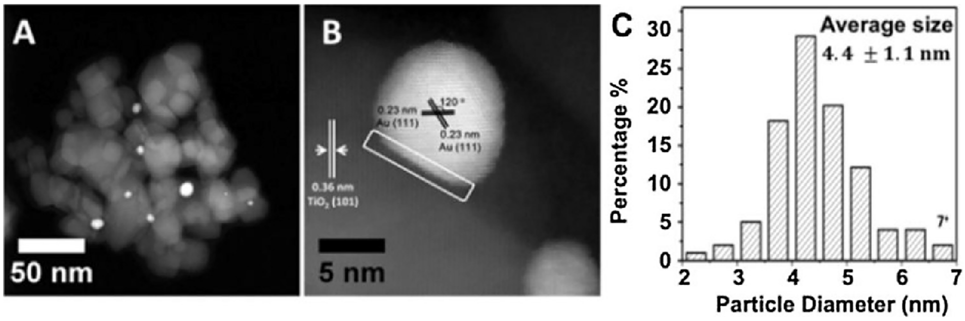

Fig. 1. (A) HAADF-STEM images of Au/TiO_2, (B) high-resolution image that shows the interface of Au-TiO_2, (C) size distribution of Au nanoparticles in Au/TiO_2.

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