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Single-site nickel-grafted anatase TiO_2 for hydrogen production: Toward understanding the nature of visible-light photocatalysis

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ABSTRACT

This work provides an engineering guide to constructing active sites on TiO_2 with the surface organometallic chemistry of nickelocene for unveiling the molecular nature of so-called "p–n heterojunction"-induced visible-light photocatalysis. H_2 evolution was used as a model reaction to evaluate the photocatalytic properties of Ni/TiO_2 materials containing different Ni-oxo species, which are prepared by three methods. Ni nuclearity-dependent H_2 evolution was shown by comparison of H_2 production rates over such Ni/TiO_2 photocatalysts. Detailed characterizations clearly revealed the triple role of atomically isolated Ni species as light-harvesting, electron-trapping, and hydrogen-evolving sites in the photocatalytic reaction. The Ti—O—Ni molecular junctions formed at the NiO–TiO_2 interface perform the function of p–n heterojunctions and create visible light absorption and photocatalysis. It was well established that visible light photocatalysis follows a physical mechanism of metal-to-metal charge transfer in Ti—O—Ni linkages severing as visible-light chromophores. Hydrogen gas is reduced and evolved at oxygen vacancies of the TiO_2 surface.

1. Introduction

As the ever-increasing energy crisis is spreading over the whole world, solar-to-chemical fuel conversion has been spotlighted recently as a process for producing renewable clean energy. Photocatalytic hydrogen generation from water and biomass, as one of the most promising alternatives to dependence on carbon-based fuels, has been paid a lot of attention [1–4]. The research focus in this domain is mainly on development of efficient photocatalysts that can work for conversion under visible light. Traditional photocatalysts such as TiO_2, ZnO, Ga_2O_3, and $SrTiO_3$ are only able to utilize very limited UV solar photons (ca. 4%) as a result of their large band gap of >3.2 eV. Many attempts have been made to engineer their band structures to match the solar electromagnetic spectrum by coupling these oxides with narrowing band gap semiconductors, or doping metal and nonmetal, or constructing heterostructures [2,5–7]. On such multicomponent photocatalysts, the modifiers were often highly dispersed or doped on semiconductor surfaces as nanoparticles, nanoclusters, and mononuclear complexes, depended on different preparation methods [2,8–11]. Identification of the pivotal contributors to improvement of photocatalytic efficiency and establishment of their structure–performance relationships are the key to designing highly efficient photocatalysts.

Among composite photocatalysts, Ni/TiO_2 is one of the classical nanomaterials, where NiO, an important p-type semiconductor with a wide optical band gap of 3.51 eV, was used as a promoter for charge separation [2,10]. There have been a huge number of reports on NiO-participated nanomaterials with excellent photocatalytic performance [11–14]. Wu et al. [12] have ascribed the enhancement of photocatalytic activity over NiO/TiO_2 photocatalysts to the formation of p–n junctions, which create an internal electric field to retard electron–hole recombination. Hu and Teng [13] have reported NiO-loaded $NaTaO_3$ photocatalysts and revealed the formation of a solid–solution transition zone at the NiO–$NaTaO_3$ interface by the interdiffusion of Ni^{2+} and Na^{+}, which allows charge tunneling through the interface barrier. Osterloh and co-workers [14] have reported on the NiO_x–$SrTiO_3$ system, which enables photocatalytic water splitting into H_2 and O_2. Recently, Tada et al. [11] found that NiO cluster-modified TiO_2 has a high level of visible-light photocatalytic activity and suggested that the visible-light response results from electron excitation from the Ni*3d* surface sub-band to the TiO_2 conduction band, and the NiO species can act as a mediator for electron transfer from the TiO_2 conduction band to O_2. It was well established according to these studies that loading Ni species can promote the photocatalytic efficiency of

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TiO_2, $SrTiO_3$, and $NaTaO_3$ and even extend the light response to visible light. However, their working mechanism is ambiguous. There is no consensus on this topic. But a hypothesis that the coupling may create a p–n heterojunction at the solid–solid interface is widely accepted for these nanomaterials with NiO participation. Such a heterojunction is considered the pivotal contributor to promote separation and transfer of charge carriers and to visible light absorption and photocatalysis. However, powerful evidence for the presence of p–n junctions in composite systems is. It is impossible to observe and visualize the chemical composites, structure, and configuration of heterojunctions directly by the present physical techniques, including high-resolution transmission electron microscopy (HRTEM). Insight at the atomic level into the chemical nature of p–n heterojunctions is a formidable challenge for chemists in the photocatalysis community. A promising strategy is to chemically construct heterobimetallic linkages with a well-defined M—O—M′ structure on semiconductor oxides to mimic structurally and functionally these so-called heterojunctions.

Loading NiO onto the TiO_2 surface by wet impregnation or mechanical mixing generally leads to a heterogeneous distribution of nickel species with different nuclearity (from isolated nickel cations to oxidic clusters, passing through dimers or small oligomers, even to nanoparticles). This greatly hinders definitive identification of contributors to the unique behavior of visible light absorption and photocatalysis. Compared to these typical preparation procedures, the surface organometallic chemistry (SOMC) method has the unique advantage of controlling the chemical states of metal modifiers and obtaining single surface complexes, in terms of the grafting reaction of organometallic compounds with surface groups of oxides, as proved by our previous studies [8,15–18]. A series of mononuclear metal-oxo (Fe, Ti, Cu, and Sn) complexes have already been obtained by this route [15]. More recently, atomically isolated tin-oxo species, as electron-capture sites, were successfully grafted onto the surface of anatase, TiO_2, by the SOMC method to form Ti^{IV}—O—Sn^{IV} molecular junctions [15]. Further coupling of these heterobimetallic linkages with the RuO_2—TiO_2 p–n junctions can enormously enhance the apparent quantum efficiency (AQE) of hydrogen production [18]. These findings inspired us to explore at the atomic level the role of Ni in visible-light photocatalysis via the preparation of single-site Ni-grafted TiO_2 photocatalysts using the SOMC strategy.

In the present work, we studied in detail the grafting chemistry of nickelocene, which is a precursor highly similar to ferrocene, reacting with the surface hydroxyls of anatase, TiO_2, and revealed the stepwise reaction pathways for the grafting process. By controlling the amount of nickelocene grafted, a series of Ni-grafted TiO_2 with different nickel content was obtained. Two other types of Ni/TiO_2 composites were also synthesized by wet impregnation and mechanical mixing for comparison. All as-prepared samples were characterized in detail by X-ray diffraction (XRD), N_2 physical adsorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV–visible diffuse reflectance spectrum (UV–vis DRS), in situ electron spin resonance spectroscopy (ESR), and X-ray absorption fine structure spectroscopy (XAFS). The photocatalytic activity of all samples for hydrogen evolution under visible and UV light irradiation was recorded and compared under the same conditions. The characterization results reveal clearly that the metal-to-metal charge transfer (MMCT) in Ti^{IV}—O—Ni^{II} linkages results in visible light photocatalysis. Owing to the well-matched redox potential, isolated Ni^{2+} cations can act as light harvesters, electron-trapping sites, and hydrogen-evolving catalysts, playing a triple role in photocatalytic hydrogen production. Hydrogen gas is reduced and evolved at oxygen vacancies of the TiO_2 surface under visible light irradiation. The Ti^{IV}—O—Ni^{II} molecular junctions formed at the NiO–TiO_2 interface are well established to be the transport channels of photogenerated electrons. This work definitively elucidates the origin of visible-light photocatalysis over Ni/TiO_2.

2. Experimental

2.1. Materials

Anatase, TiO_2 (99.7%, 15 nm, APS powder, CAS number: 1317-70-0), nickelocene, nickel oxide, and *n*-pentane (anhydrous, 99.8 + %, active dry) were purchased from Alfa Aesar (a Johnson Matthey company). Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, AR) was obtained from the Sinopharm Chemical Reagent Co. Ltd. All of the above chemicals were used without further purification.

2.2. Preparation of the catalyst

Three kinds of Ni/TiO_2 samples were synthesized by different methods as follows: (1) The samples denoted as Ni_x/TiO_2-S (x = percentage of Ni content) were prepared by the SOMC method that we have reported [8]. In a typical experiment, TiO_2 was first calcined at 653 K for 8 h under flowing dry oxygen, followed by treatment in a self-made glass reactor under dynamic vacuum (10^{-4} Torr) at 673 K for 2 h to remove adsorbed water and surface contaminants. After cooling to room temperature, a given amount of nickelocene dispersed in *n*-pentane was injected into the glass reactor to react with TiO_2 for 30 h at 403 K. The process of injection must take place in a glove box to protect the nickelocene from oxidization, and before the reaction, the majority of *n*-pentane must be removed by vacuum for 3 min. The unreacted nickelocene was removed by evacuation under dynamic vacuum at 403 K for 2 h. Finally, the organonickel-complex-grafted TiO_2 prepared was calcined at 723 K for 10 h in flowing dry oxygen, along with exposure to air at room temperature. (2) The sample denoted as $Ni_{1.0}/TiO_2$-I was prepared by the wetness impregnation (WI) method as a reference sample. Anatase, TiO_2, which was first calcined at 653 K for 8 h, was immersed into the qualified $Ni(NO_3)_2$ aqueous solution. After ultrasonic treatment for 5 min, the resulting solid was dried at 333 K for 6 h and then heated at 723 K for 10 h in flowing dry oxygen. (3) The sample denoted as $Ni_{1.0}/TiO_2$-M was prepared by the mechanical mixture of NiO with TiO_2 as another reference sample. The obtained sample was calcined at 723 K for 10 h in flowing dry oxygen. Elemental analysis indicates 1.0 wt.% Ni content in the two reference samples.

2.3. Catalyst characterizations

XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα_1 radiation (λ = 1.5406 Å). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. XPS spectra were carried out on a VG ESCALAB 250 XPS System with a monochromatized Al Ka X-ray source (15 kV, 200 W, 500 μm pass energy = 20 eV). All binding energies were referenced to the C1*s* peak at 284.6 eV of surface adventitious carbon. TEM and HRTEM images were obtained by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. In situ ESR spectra were measured using a Bruker Model A300 spectrometer equipped with a cylindrical cavity. The measurements were carried out in a cell that could be connected to a conventional high-vacuum system. A 200 W mercury–xenon lamp equipped with a high-pass (λ > 420 nm) filter and an IR-cut filter was employed as the light source (LC8, Hamamatsu Photonics K.K., Japan), and a light guide was used to direct the irradiation onto the powder sample through the quartz window of the cell for experiments. In situ FTIR experiments were performed in a special IR cell in conjunction with a vacuum system. The powders were first pressed