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TiO_2 nanosheets loaded with Cu: A low-cost efficient photocatalytic system for hydrogen evolution from water

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ABSTRACT

Rutile TiO_2 nanosheets were prepared by a simple solvothermal process, and Cu was loaded on the surface of TiO_2 nanosheets using the in situ photo-deposition method. Meanwhile, photocatalytic H_2 evolution from water over the as-prepared TiO_2 nanosheets loaded with Cu was explored using methanol as a sacrificial reagent. The results indicate that the TiO_2 nanosheets loaded with Cu is an efficient photocatalyst under UV irradiation. During the first 5 h, a rate of H_2 evolution of approximately 22.1 mmol g^{-1} h^{-1} was achieved under optimal conditions. Furthermore, for practical purposes, the photocatalytic hydrogen evolution was studied as a function of content of Cu, pH of solution, concentration of methanol and dosage of photocatalyst, respectively. At last, the photocatalytic mechanism was preliminarily discussed.

Introduction

Recently, photocatalytic H_2 production from water reduction has attracted much attention due to increasing anxiety about the global energy crisis and the environmental pollution. A lot of photocatalysts have been found for the H_2 evolution from water including TiO_2, ZnO, CdS etc. [1–7]. Particularly, because of high efficiency, high chemical stability, nontoxicity, low price, and availability, nanostructured TiO_2 has been one of the subjects which are investigated extensively [8–10]. Various nanostructured TiO_2 were prepared, such as nanoparticles [11], nanosheets [12], nanotubes [13], nanowires [14], nanorods [15], nanotube arrays [16] and so on. And their photocatalytic activities for H_2 production were widely explored. Therein, most of the studies were focused on the application of nanoparticles in the photocatalytic H_2 evolution. Although TiO_2 nanosheets showed considerable photocatalytic activity and began to arouse some interest recently, there are still relatively limited papers on the photocatalytic activity of TiO_2 nanosheets for H_2 evolution so far. It is well known that the properties of nanostructured TiO_2 including grain size, crystallization, morphology, specific surface area, surface state, and porosity obviously influence its photocatalytic activity [17–20]. TiO_2 nanosheets, as a two-dimensional nanomaterial, possess many attractive features which are favor to the transfer of photogenerated carrier and proceeding of the photocatalytic water reduction, including

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large specific surface area, nano-scaled thickness, and low defect density [21]. Therefore, it is meaningful to deeply investigate the photocatalytic behavior of TiO_2 nanosheets in photocatalytic H_2 production from water reduction.

Generally, TiO_2 nanosheets are synthesized by a hydrothermal process [22,23]. And HF is often used to control the morphology and enhance the photocatalytic activity of TiO_2 nanosheets when TiO_2 nanosheets are studied as a photocatalyst. HF is toxic and harmful to human and environment, implying that the future of the as-prepared TiO_2 nanosheets become doubtful. As a result, for practical purposes, it is desirable to develop a simple and F-freede method for synthesis TiO_2 nanosheets.

On the other hand, although some TiO_2-based efficient photocatalysts have been found, the photocatalytic activities of TiO_2-based photocatalysts need be further enhanced from the practical point of view. The experimental results reported previously indicate that the activities of photocatalysts can be effectively enhanced when noble metals or metal oxides, such as Pt [24], Pd [25], Au [26], Ru [26], RuO_2 [27] and so on, are used as a co-catalyst to improve the electron–hole separation. Therein, Pt is the commonest among the co-catalysts reported and regarded as one of the most efficient co-catalysts. However, Pt is expensive and rare, which is unfavorable to large scale applications [28]. It is reported that Cu can act as an efficient co-catalyst, and Cu loaded TiO_2 exhibits a high photocatalytic activity for the photocatalytic H_2 production from water [25]. Thus, it can be deduced that TiO_2 nanosheets loaded with Cu would possess high photocatalytic activity for the photocatalytic H_2 production from water. Unfortunately, to our best knowledge, there is no report on the application of TiO_2 nanosheets loaded with Cu in the photocatalytic H_2 production. It is still unclear whether TiO_2 nanosheets loaded with Cu is an efficient photocatalytic system or not.

In the present work, the rutile TiO_2 nanosheets loaded with Cu were prepared by a simple solvothermal process followed by in situ photo-deposition. And the photocatalytic activity of the TiO_2 nanosheets loaded with Cu was first explored for the photocatalytic H_2 production from water using methanol solution as a sacrificial agent. Moreover, the photocatalytic mechanism was preliminarily discussed.

Experimental

Materials

Titanium tert-butoxide, ethanol, concentrated hydrochloric acid and copper nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol was purchased from Shanghai Titan Scientific Co., Ltd. TiO_2 nanoparticles (P25) was purchased from Degussa AG Company (Germany). All reagents were of analytical grade and used as received. Deionized water was used as solvent.

Preparation of rutile TiO_2 nanosheets

Rutile TiO_2 nanosheets were prepared using a solvothermal method. In a typical procedure, titanium tert-butoxide (3 mmol) was added into a beaker containing ethanol (10 mL) at room temperature under stirring, and then the concentrated hydrochloric acid (5 mL) was dropped into the solution above. After the mixture was transferred into a Teflon-lined vessel (50 mL), the vessel was sealed in a stainless-steel autoclave and heated to 180 °C for 6 h. Subsequently, the autoclave was naturally cooled to ambient temperature. The white precipitate was collected by centrifugation and wash with deionized water for five times. Finally, the resulting product was dried at 60 °C for 2 h.

Photocatalytic activity test

The photocatalytic reaction was carried out in a gas-closed system with a reactor made of quartz. A 300 W xenon lamp equipped with an optical filter ($\lambda < 420$ nm) to cut off the light in the visible region was used as a light source. The distance between the lamp and the reactor is 1 cm. In a typical experiment, 10 mg of the as-prepared rutile TiO_2 nanosheets was added into 60 mL of the aqueous methanol solution (50 vol.%). The mixture was sonicated for 15 min to form a homogeneous suspension. Then, copper nitrate aqueous solution (25 μL, 0.1 mol L^{-1}) was dropped in the mixture above, and the suspension was deaerated using N_2. After the gas-closed system was vacuumed, the suspension was irradiated for 30 min to prepare the rutile TiO_2 nanosheets loaded with Cu. Finally, the gas-closed system was vacuumed again, and the amounts of hydrogen produced were measured with a gas chromatograph (GC-7900, China, molecular sieve 5 A, TCD) using N_2 as a carrier gas, after a certain period of irradiation.

Characterization

The X-ray diffraction (XRD) patterns were measured with a PANalytical Xpert Pro MRD X-ray diffractometer (Netherlands). The high-resolution transmission electron microscope (HRTEM) images were taken on a JEOL 2100F transmission electron microscope (Japan). The scanning electron microscope (SEM) image and the energy-dispersion X-ray analysis (EDX) were measured using a Hitachi S-4800 scanning electron microscope (Japan). The X-ray photoelectron spectra (XPS) were recorded with a Shimadzu Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Japan). The N_2 adsorption and desorption isotherm was measured on a Micromeritics ASAP-2020 nitrogen adsorption apparatus (USA). The UV–vis spectra were recorded on a Hitachi U-3900 UV–vis spectrophotometer (Japan).

Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared sample. It could be seen from Fig. 1 that the peak positions of the sample are matched well with those of rutile TiO_2 (JCPDS No. 21-1276) [29]. The diffraction peaks at 27.45°, 36.09°, 39.19°, 41.23°, 44.05°, 54.33°, 54.64°, 62.74°, 64.04°, 65.48°, 69.01°, 69.79°, 72.41°, 74.41°, and 76.51° are corresponding to (110), (101), (200), (111), (210), (211), (220), (002), (310), (221), (301), (112), (311), (320) and (202) planes of rutile TiO_2, respectively. Moreover, the diffraction peaks are very strong and sharp, meanwhile no evidence of crystalline impurities is found in the