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Synthesis of hierarchical Mn_2O_3 microspheres for photocatalytic hydrogen production

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ABSTRACT

Hierarchical Mn_2O_3 microspheres have been prepared *via* polyol-mediated solvothermal method. The as-prepared hierarchical microspheres is about 8–10 μm in diameter assembled with porous nanosheets which favors charge transport. The formation process has been studied which is to form nanosheet first and then to self-assemble and finally to grow spheres. The band structure of Mn_2O_3 microspheres is confirmed through XPS valence spectrum and UV-vis,verfiying that it is suitable for hydrogen reduction. The H_2 production efficiency of hierarchical Mn_2O_3 microspheres is found to three time higher than that of Mn_2O_3 particles. The promoted photocatalytic hydrogen production efficiency could be attributed to the interesting hierarchical structure, large surface area and suitable band gap.

1. Introduction

Photocatalytic hydrogen production through semiconductors and solar energy irradiation is regarded as a promising technique to solve the energy crisis in future [1]. However, the current studies have not found an ideal semiconductor photocatalysts system with high efficiency because it is a complex reaction which refers many kinetic and thermodynamic process. The semiconductors as photocatalysts must satisfy some rigorous rules such as suitable band gaps, negative conduction band and so on [2]. During the past few decades, various photocatalysts including metal oxides, sulfides, oxynitrides and perovskites have been developed. [3–6] In order to enhance the photocatalytic activities, some strategies, for example constructing junctions, elemental doping and surface modifications, are tried and many of them exhibit promoted photocatalytic hydrogen production performance [7,8]. However, the design and synthesis of new materials for efficient photocatalytic hydrogen production is still the flash point of scientific research.

Manganese oxides, mainly including MnO_2, Mn_2O_3 and Mn_3O_4, have been widely studied for many years owing to their outstanding properties in catalytic, electrochemical, magnetic, optical, and electrocatalytic biosensors and their non-toxicity, abundance and cost effective feature [9,10]. Manganese is also the main ions of photosynthesis in green plants which could catalyze oxygen production. Some works have been shown that manganese oxides cluster displays excellent oxygen production ability in photocatalysis [11,12]. However, the photocatalytic hydrogen production performance of manganese oxides have been seldom investigated.

Surface area and morphology of photocatalysts could deeply affect their activities [13]. Hierarchical structure materials possess large surface area and the special structures that favors charge transport and promote the photocatalytic activity. To control the surface morphology of semiconductors is a great challenge. Solvothermal method is an effective approach to prepare hierarchical structure materials, and different oxides such as TiO_2, ZnO, titanates etc could be synthesized by solvothermal method [14–16].

To study the photocatalytic activity of manganese oxides, hierarchical Mn_2O_3 microsphere assembled with nanosheets have been controllably prepared through solvothermal method. The obtained hierarchical Mn_2O_3 microspheres show enhanced photocatalytic hydrogen production performance as compared to Mn_2O_3 particles. The promoted photocatalytic activity could be attributed to the hierarchical structure which favors charge transfer.

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2. Experimental section

2.1. Chemicals and reagents

All the reagents were of analytical grade and used as received without further purification. Deionized water was used throughout the experiment.

2.2. Synthesis of hierarchical Mn_2O_3 microspheres

2.45 g manganous acetate and 0.3 g sodium dodecyl sulfate (SDS) were dissolved in 40 mL ethylene glycol (EG) to form a clear pink solution, then the solution was stirring for 1 h to make the SDS completely dissolved. After that, the pink solution was transferred into 50 mL Teflon-lined stainless-steel autoclave, which was then sealed and heated at 160 °C for 12 h. After solvothermal process, the obtained dark pink precipitate was centrifuged and washed three times with absolute alcohol, and dried in vacuum at 60 °C for 4 h. The hierarchical Mn_2O_3 microspheres were obtained by annealing the precipitate at 500 °C for 2 h.

The Mn_2O_3 particles were prepared by annealing commercial MnO_2 particles at 500 °C for 2 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were obtained by Bruker D8. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument operating at 15 KV. The transmission electron microscopy (TEM) experiment was performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as the sample holders. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method using a Tristar II 3020 surface area and porosity analyzer (micromeritics). UV–vis absorption spectroscopy was recorded using a UV–vis spectrophotometer (SHIMADZU UV-2550). The X-ray Photoelectron Spectroscopy (XPS) was tested using a Kratos-AXIS ULTRA DLD apparatus with Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).

2.4. Evaluation of photocatalytic activity

The photocatalytic H_2 production experiment was conducted in an online photocatalytic H_2 production system (AuLight, Beijing, CEL-SPH2N) at ambient temperature (20 °C). In a typical experiment, 0.1 g of photocatalyst was suspended in a mixture of 80 mL distilled water and 20 mL methanol in the reaction cell by using a magnetic stirrer. 1 wt.% Pt loaded photocatalysts were prepared by known standard method of in-situ photodeposition method using H_2PtCl_6 aqueous solution. Prior to the reaction, the mixture was deaerated by evacuation to remove O_2 and CO_2 dissolved in water. The reaction was carried out by irradiating the mixture with visible light from a 300 W Xe lamp (AuLight, CEL-HXF300) with a UVCUT filter (AuLight, 400–780 nm). Gas evolution was observed only under photoirradiation, being analyzed by an on-line gas chromatograph (SP7800, TCD, molecular sieve 5 Å, N_2 carrier, Beijing Keruida Limited).

3. Results and discussion

X-ray diffraction (XRD) technique is regarded to be the most effective method to reveal the crystal structure of materials. Fig. 1 is the XRD patterns of prepared Mn_2O_3 precursor and products calcined at different temperature. It could be learned from the XRD of Mn_2O_3 precursor that the peak in low angle around 10° is the typical peak of metal glycolate which had been reported everywhere [5,14]. When the precursor calcined at low temperature of 300 °C, the product is amorphous because this temperature is lower than the minimum crystallization temperature of manganese oxides. After annealing at 500 °C, pure phase Mn_2O_3 is obtained. All of the XRD reflection peaks can be readily indexed to a bixbyite orthorhombic phase of $Mn_2O_3$with the calculated lattice constant a = 0.941 nm, b = 0.942 nm, and c = 0.940 nm, respectively, which are in good agreement with the literature results (JCPS No 41-1442) [17].

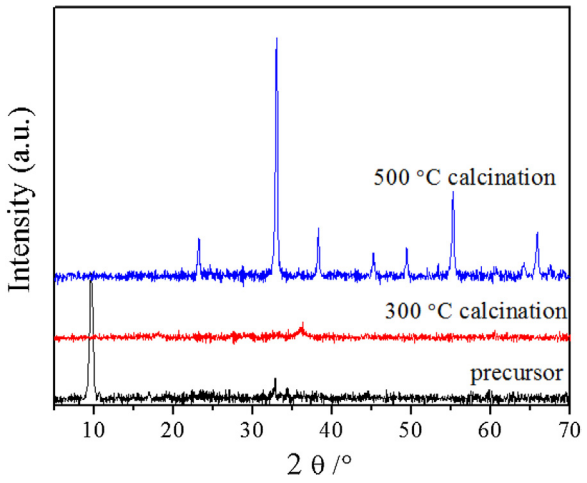

Fig. 1. XRD patterns of the prepared Mn_2O_3 precursor and products calcined at different temperature.

It could be learn from XRD, that the precursor possesses metal glycolate structure. To further study the organic groups in the precursor, FT-IR spectrum of the as-prepared Mn_2O_3 precursor is measured as shown in Fig. 2. The absorption peaks in the range of 2849 ~ 2924 cm^{-1} correspond to υ_{as} and υs (C—H) bands, at ~1572 cm^{-1} correspond to C=O bands, and in the range of 1050 ~1125 cm^{-1} is attributed to $\rho(CH_2)$, υ(C—O), and υ(C—C) bands [18]. These organic groups reveal that the precursor is metal-EG organic complex. It is well known that EG is a bidentate ligand and can react with metal ions to form the metal-glycolate polymer with chain like structure for its coordination ability with transition metal ions [19]. This means the precursor contains organic frameworks which could be removed and leaving holes when calcined.

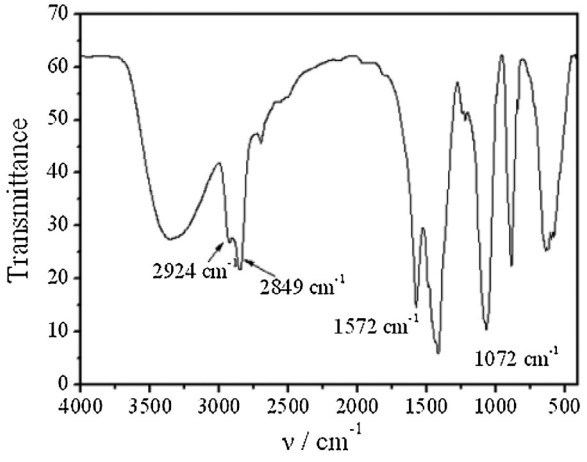

Fig. 2. FT-IR spectrum of prepared Mn_2O_3 precursor.