Journal of Molecular Liquids 269 (2018) 211–216

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Effect of solvents and reaction parameters on the morphology of Ta_2O_5 and photocatalytic activity

Muhammad Nawaz [a], Fangzhi Mou [b], Leilei Xu [b], Jianguo Guan [b,*]

[a] Department of Nano-Medicine Research, Institute for Research and Medical Consultations(IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China

ARTICLE INFO

Article history:
Received 17 March 2018
Received in revised form 2 August 2018
Accepted 6 August 2018
Available online 07 August 2018

Keywords:
Ta_2O_5
Hierarchical structures
Catalysis
Hydrogen production

ABSTRACT

We report a facile and efficient hydrothermal method for the controlled preparation of tantalum oxide (Ta_2O_5) flower-like hierarchical structures. The formation of flower-like hierarchical structure is systematically studied by tuning the reaction parameters such as precursor amount, reaction time, reaction temperature, hydrofluoric acid (HF) volume, hydrochloric acid (HCl) concentration and propanol-HCl volume ratio. The results reveal that simply altering the reaction conditions can easily modulate the morphology of the resultant Ta_2O_5 product. The growth mechanism for the formation of flower-like hierarchical structures has been proposed, where HF and propanol play a key role. A comparative study for photocatalytic hydrogen production was conducted by calcinating the product at 450 °C and 700 °C. The product calcinated at 450 °C revealed a higher photocatalytic activity than that calcined at 700 °C. The successful and convenient preparation of flower-like hierarchical structures can be easily scaled up and extended for the designing and fabrication of 3D hierarchical structures and visible-light driven heterostructures nanomaterial for energy production, environmental remediation and optical devices.

1. Introduction

The shape-controlled preparation, design and fabrication of nanomaterials have attracted significant attention and providing new chances in exploring unique properties (chemical and physical) of nanomaterials. The properties and photocatalytic performances of nanomaterials are mainly reliant on their structure and shape of primary building blocks, their phases, size, size distribution and crystal facets [1–9]. Generally, the catalytic activities of nanocrystals mainly depend on their surface properties and structures. One can alter the reactivity and selectivity of nanoparticles by modulating the morphology as different exposed surfaces of the nanoparticles exhibit different catalytic activities [9–12]. Synthesis of nanocrystals with controlled morphologies has always been a challenge for the researchers. These materials are getting more interest due to their wide applications such as adsorbents, desiccants, separators, catalysts and catalyst supports [13–16]. The preparation of the complex structures that are preferably composed of nanostructures such as nanorods, sheets and particles assembled in a particular way have attracted more attention and interest. Such materials exhibit better properties and activities than their building blocks [17–21]. Hierarchical nanostructures have attracted attention due to their interesting properties in photocatalysis, adsorption, sensors, lithium ion batteries and dye sensitized solar cells [22–26]. Tantalum oxide (Ta_2O_5) is an important semiconductor and interesting material due to its many unique properties such as good conductivity, good thermal and chemical stability, good catalyst for variety of reactions and wide band gap (3.9 eV) [27–30]. Therefore, it is used as anti-reflection coating material for solar cells and capacitor material for dynamic random access memories [30–37]. Up to now, a few researchers have been reported Ta_2O_5 nanostructures with different morphologies including mesoporous [38], F-Ta_2O_5 [39,40], spheres [41,42], nanofibers [43], nanotubes [44], nanoparticles [45], employing different synthesis routes.

Herein, we demonstrate a facile hydrothermal approach to prepare controlled flower-like hierarchical structures of Ta_2O_5 for photocatalytic hydrogen production. A key strategy of this approach is to control the flower-like hierarchical morphology by varying reaction conditions and enhancing photocatalytic activity. We investigated and explored various parameters and their effect on morphology. The mechanism of flower-like hierarchical structures formation and mechanistic role of HF and propanol in reaction has also been proposed and investigated through a series of experiments. Furthermore, this works provides understandings about the growth mechanism of flower-like hierarchical

* Corresponding author.
E-mail address: guanjg@whut.edu.cn (J. Guan).

https://doi.org/10.1016/j.molliq.2018.08.026
0167-7322/

structures. It may extend to the synthesis of heterostructures materials with controllable morphology for visible-light driven photocatalysis.

2. Experimental

2.1. Chemical and materials

$TaCl_5$ (99.95%), propanol (99%), hydrofluoric acid (HF, 99.6%, 40 wt %), ethanol (99.7%) and hydrochloric acid (HCl, 37%) were purchased from commercial sources and used as it. Deionized water was used in all reactions.

2.2. Preparation of flower-like hierarchical Ta_2O_5

0.2 g $TaCl_5$ was added to a mixture of propanol and HCl (1.5 M) and 0.2 mL HF was added into this mixture. The solution was stirred and transferred into Teflon-line autoclave and heated in an oven at 180 °C for 24 h. Teflon-line autoclave was cooled at room temperature; the white precipitates formed were centrifuged. After washing several times with deionized water and ethanol, the product was dried at 60 °C for 12 h. In order to get a clean fluorine-free surface, the resultant product (Ta_2O_5) was calcined in air at 450 °C and 700 °C for 3 h.

2.3. Characterization

X-ray powder diffraction (XRD, Rigaku, Japan) analysis of Ta_2O_5 was performed on a X-ray diffractometer, using copper radiation (λ = 1.5418 Å). Field emission scanning electron microscope (Hitachi, S-4800) was used to observe the morphologies of the products and to determine the elemental composition by X-ray energy-dispersive spectrometer. JEM-2100F (Vender, Japan) was used to capture the TEM and HRTEM images of the products. An ultrahigh vacuum VG MultiLab 2000 X-ray photoelectron spectrometer was used to record the X-ray photoelectron spectra. BET surface area was determined on a Micromeritics ASAP 2020 nitrogen adsorption apparatus. UV–Vis diffuse reflectance spectra of the products were recorded on a diffuse reflectance UV–Vis spectrophotometer using barium sulfate as a reference [40].

2.4. Photocatalytic activity

Photocatalytic activity of Ta_2O_5 was studied in a closed gas circulation system under a 300 W xenon lamp. 50 mg of catalyst was added to aqueous mixture of Na_2S and Na_2SO_3 and dispersed ultrasonically. Prior to irradiation, the solution was evacuated for 20 min to remove the dissolved gases. After the evacuation, the suspension was exposed to xenon lamp. The hydrogen gas generated was determined *in situ* by a gas chromatogram [40].

3. Results and discussion

3.1. Characterization of Ta_2O_5 flower-like hierarchical structures

Ta_2O_5 flower-like hierarchical structures were prepared and morphology of the product was observed by SEM and TEM analysis. Fig. 1a and b show representative overview of flower-like hierarchical structures of Ta_2O_5 calcined at 450 °C and 700 °C and inset in Fig. 1a and b show high magnification view of Ta_2O_5, analyzed by SEM. It can be depicted that flower-like hierarchical structure is composed of small nanorods (200 nm) growing uniformly at acute angle and in a well-organized way. It is clear from SEM images that the product calcined at 450 °C and 700 °C didn't show much difference in size and morphology. Some more SEM images are given in Fig. S1 (Supplementary materials). TEM was employed to get further insight on morphology and detailed structural characteristics of Ta_2O_5 (Fig. 1c). The HRTEM image (Fig. 1d) shows crystal lattice fringes with an interplanar spacing of 0.348 nm, which can be ascribed to the (001) plane of orthorhombic Ta_2O_5. This is in combination with SAED pattern (insert in Fig. 1d) obtained on a single nanorod further confirms the single crystalline nature of Ta_2O_5.

The crystal structure of Ta_2O_5 was studied by X-ray diffraction. Fig. 1e shows the XRD pattern of Ta_2O_5 prepared at 180 °C for 24 h and calcinated at 450 °C and 700 °C. The sharp and strong diffraction peaks suggest a nanocrystalline structure and sharpness increases with increasing calcination temperature to 700 °C. All the diffraction peaks can be indexed as an orthorhombic phase of Ta_2O_5 (JCPDS card no. 25-0922). No impurities can be detected in this pattern, which implies orthorhombic phase of Ta_2O_5 can be obtained under the described experimental conditions. To further confirm the chemical states and chemical composition of the as-prepared product, X-ray photoelectron spectroscopy (XPS) was performed. As shown in Fig. 1d, the binding energies of Ta4f levels for the product appears at 28.5 eV and 26.8 eV for Ta $4f_{5/2}$, and $4f_{7/2}$ respectively, indicating that tantalum exists as Ta^{+5} in the product and it is same pattern as reported for the bulk Ta_2O_5 [46]. The full XPS spectrum of Ta_2O_5 is presented in Fig. S1c.

Energy-dispersive X-ray spectroscopy (EDX) was performed to confirm the composition of the as-prepared product. We selected different surfaces as collection areas and found the same results. Fig. 2a shows energy-dispersive X-ray spectroscopy (EDX) spectra of Ta_2O_5, confirming the presence of Ta and O in the product and also shows there is no impurity in the product. UV–visible diffuse reflectance (DRS) spectra of the as-prepared product calcined at 450 °C and 700 °C and commercial Ta_2O_5 are shown in Fig. 2b. The diffuse reflectance spectra of the product calcined at 450 °C and 700 °C demonstrated an absorption in the UV regions which is similar with commercial Ta_2O_5 spectra. Moreover, the product calcined at 450 °C and 700 °C show minor difference in light absorption abilities. The prepared product showed absorption in the region 335 nm which corresponded to band gap energy of 3.70 eV.

The surface area and porosity of the as-prepared products were determined by N_2-adsorption-desorption analysis. Fig. 2c shows the N_2-adsorption-desorption isotherms and pore size distribution of the products calcined at 450 °C and 700 °C. The shape of the isotherm indicates typical type-IV curve with a narrow H3-type hysteresis loop at relative pressure, indicating the presence of mesoporous particles [47]. The BET surface area of the products calcined at 450 °C and 700 °C was found 28.45 and 17.54 m^2/g respectively (Table S1). Temperature strongly influences on crystalline structure and texture properties of the material, when calcination temperature was increased from 450 °C to 700 °C, the surface area of material was decreased and pore size (Dp) was increased (Table S1). It is ascribed to the fact that at high temperature Ta_2O_5 loses its well-defined mesoporous structure as a result surface area is decreased. The BJH pore size distribution of the Ta_2O_5 calcined at 450 °C to 700 °C are shown in Fig. 2c. Compared with the product calcined at 450 °C, the pore size distribution in the product calcined at 700 °C is relatively broader. It indicates the demolition of original mesoporous structure by aggregation and crystallization at high temperature.

3.2. The influencing factors in the controlled preparation of Ta_2O_5 flower-like hierarchical structures

In order to elucidate and to get a full idea and understanding about the morphology evolution or origin of Ta_2O_5 flower-like hierarchical structures, we carried out a series of experiments under different experimental conditions, including precursor amount, reaction time, reaction temperature, HF volume, HCl concentration and propanol-HCl volume ratio. The morphology obtained under these different experimental conditions was investigated by high resolution SEM. The influences of the reaction conditions on the