Materials Letters 186 (2017) 252–255

Contents lists available at ScienceDirect

Materials Letters

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

Optical properties of hydrophilic surfaced self-assembled $Cd_2V_2O_7$ hollow sphere shape architecture

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ARTICLE INFO

Keywords:
Hydrophilic-surfaced
$Cd_2V_2O_7$
Microstructures
Band gap
Semiconductor

ABSTRACT

In this study, hydrophilic-surfaced $Cd_2V_2O_7$ microstructures were synthesized *via* a simple and efficient surfactant-assisted hydrothermal route using $Cd(NO_3)_4 \cdot 4H_2O$, $NaVO_3 \cdot 2H_2O$ and NaOH as the starting materials at pH 8 and various temperatures. The products were characterized by X-ray powder diffraction (XRD), Fourier Transform infrared (FT-IR) and ultraviolet–visible spectroscopes (UV–Vis), and scanning electron microscopy (SEM). SEM images illustrated the optimized material that synthesized at pH 8 and 180 and 200 °C displays good dispersion of small-sized and the product consisted of a large amount of similar spherical superstructures with mean diameters of about 2–3 µm in which an individual spherical particle composed of a large number of nanorods with a diameter about 60–80 nm. A band gap of about 2.88–2.95 eV was estimated by the diffuse reflectance spectroscopy (DRS) for as-synthesized samples, which can be appropriate for photocatalytic activity in the visible region of the solar spectrum as a semiconductor.

1. Introduction

Complex vanadium(V) oxides have been the focus of intense research as electrode materials, catalysts and also show potential application in optics [1,2]. Vanadium 3d orbitals are usually located below the analogous d orbitals of other transition metals in the energy spectrum. Therefore, the bottom conduction band is lowered to a more positive position. This makes vanadium an important elemental photocatalyst candidate in the visible-light region [1]. In addition, $Cd_2V_2O_7$ is a proper material for solid-state source of cadmium atoms [3]. It is well known that the synthesis of low-dimension nanostructures and their complex functional architectures ordered superstructures lead to novel properties and the construction of nanoscale devices. In the hierarchical architecture, the rough surfaces, high surface area and permeability could provide ideal activity sites for photocatalytic reactions [4,5]. Also, due to demand for hydrophilic surface of complex vanadium(V) oxides for use in various applications, it is desirable to develop a fast and economical route for their preparation. Specifically, synthesis of complex vanadium(V) oxides with hydrophilic surface and defined morphology remains as a challenge. In this context, we have developed a simple method for the synthesis of hydrophilic surfaced nanocrystals of cadmium pyrovanadate with various sizes and shapes in large-scale by tuning reaction temperature *via* the hydrothermal reaction of an aqueous mixture containing corresponding metal cation (Cd^{2+}) and anion (VO_3^-) in the presence of 6-aminohexanoic acid ligand and investigated their energy band structure and optical properties. It is well known that the optical property of $Cd_2V_2O_7$ changes along with the morphology and size of the as-synthesized samples, which is related to the variation of energy band structure [1,6,7].

2. Experiment

For the synthesis of samples, $Cd(NO_3)_2 \cdot 4H_2O$ (0.47 g, 1.52 mmol) and 6-aminohexanoic acid (0.40 g, 3.05 mmol) were dissolved in 50 mL distilled water. A 0.06 M aqueous solution of sodium mono vanadate (50 mL) was added to the above solution under stirring for 10 min at room temperature. The pH of solution was adjusted to a desired pH value (8) using 1 mol L^{-1} NaOH solution. The resulting reaction mixture (100 mL) was transferred to 175 mL Teflon-lined stainless steel autoclaves and treated to 180 °C for 20 h. The obtained samples were filtered out and washed by distilled water, and dried at 60 °C for 2 h or further. The various self-assembled $Cd_2V_2O_7$ superstructures with various subunits have been controlled by varying temperature of synthesis solution ranging from 160 to 240 °C. The structure of as-synthesized $Cd_2V_2O_7$ samples were characterized by powder X-ray diffraction on Philips X′pert X-ray diffractometer using Cu Kα radiation (wavelength, λ=1.5418 Å). Fourier transform infrared

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http://dx.doi.org/10.1016/j.matlet.2016.09.121
Received 13 July 2016; Received in revised form 1 September 2016; Accepted 28 September 2016
Available online 29 September 2016
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spectra of superstructures were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. The scanning electron microscopy analysis of the samples were recorded by TESCAN (VEGA3) instrument. UV–vis absorption spectra were measured on Shimadzu-UV-2550-8030 spectrophotometer in the range of 190–800 nm at room temperature.

3. Results and discussion

XRD patterns of the as-prepared $Cd_2V_2O_7$ samples at various temperatures are shown in Fig. 1. All diffractions can be clearly indexed as a pure monoclinic phase of cadmium pyrovanadate and matched well with the reported data (JCPDS card File no. 38-0250). No diffraction peaks of other phases or amorphous cadmium compounds were observed in XRD patterns, indicating a high purity and crystallinity of the samples.

The morphologies of as-prepared samples were also examined by low and high SEM. SEM images of the $Cd_2V_2O_7$ that prepared at 160 °C demonstrates hallow sphere-shape architecture with a diameter of about 3–5 µm (Fig. 2a), in which an individual sphere is composed of large numbers of similar nanosheets with thickness of 50–60 nm. As can be seen, a few individual nanosheets and nanoparticles are also visible in micrographs. Low magnification SEM image of the obtained products at 180 °C (Fig. 2b), shows hallow sphere-like morphology for products with a mean diameter of about 3 µm, consisting of a large number of nanorods with diameters of about 60–80 nm. Interestingly, as processing temperature was raised to 200 °C, the morphology of the products (Fig. 2c) appeared as a mixture of hollow sphere-shape and flower-like structure. Notably, an individual hollow sphere is composed of nanorods with a mean diameter of 60–70 nm. Meanwhile, mean diameter of an individual hollow sphere is about 2–3 µm and an individual flower-like structure are composed of similar sheets in nanoscale. The morphologies of as-prepared samples at 220 °C (Fig. 2d) have a hallow sphere-like and a flower-like architecture. As Figure shows, an individual sphere or flower is composed of a large number of thick and short rods with a diameter of about 50–120 nm. Finally, low magnification SEM images of the $Cd_2V_2O_7$ prepared at 240 °C demonstrate that the sample was a mixture of sphere-like and flower-like architecture with a few individual nanosheets (Fig. 2e). As can be seen, an individual sphere or flower is composed of a large amount of nanosheets with thickness of 10–100 nm and rods with a mean diameter of about 1 µm and an individual nanosheet has a thickness of 10–1 µm.

Interestingly, the SEM micrographs in Fig. 2(a–e), clearly demonstrates that the optimized materials were synthesized at pH 8 and at 180 and 200 °C, displayed good dispersion of small-sized gold and the products consisted of a large amount of similar hallow spherical superstructures and this products are more uniform than other products in morphology.

Li et al. reported the formation mechanism of $Cd_2V_2O_7$ at pH 8 in format of a simple hydrothermal ripening process and using phase transformations [1]. It seems in present synthetic method phase transformations do not occur because of absence of the NH_4Cl and hydrolysis of this precursor in synthetic solution and stability of the $V_2O_7^{4-}$ in a neutral or alkaline environment under identical hydrothermal temperatures. Therefore, a possible growth mechanism for sphere-like or flower-like architecture, in which an individual sphere or flower is composed of a large amount of nanosheets based on of time-dependent experiments reported in literature was considered [8,9]. The effect of Ostwald ripening [10], lateral-aggregation [11], and dissolution/recrystallization [8] processes apparently dominate the transformation of dense aggregates of primary particles into $Cd_2V_2O_7$ nanosheets. These processes probably can be ascribed to the presence of 6-aminohexanoic acid molecules in the reaction. To clarify the assembly mechanism of sphere-like and flower-shape architecture, FTIR spectra of free 6-aminohexanoic acid (AHA) and AHA-capped $Cd_2V_2O_7$ were measured to assess the interaction between 6-aminohexanoic acid and nanosheets. For instance, FT-IR spectra of synthesized AHA-capped $Cd_2V_2O_7$ at 200 °C and free 6-aminohexanoic acid (AHA) (S_1, not shown) clearly demonstrated that the amino ($-NH_2$) group of AHA molecules capped on the surface of $Cd_2V_2O_7$ nanosheets and the free carboxylic (-COOH) terminus resulted to the hydrophilic surfaced nanocrystals and also, confirmed that the $Cd_2V_2O_7$ nanosheets were accumulated by the self-assembly due to existence the polypeptide chains. These surface agents were formed through the interaction between the uncoordinated carboxylic group on the $Cd_2V_2O_7$ nanosheet surface and the amino group of residual 6-aminohexanoic acid in aqueous solution. Therefore, the sphere-shape and flower-shape morphology can be controlled by adjusting the concentration of AHA [12]. On the other hand, purposed mechanism for sphere-shape or flower-shape architecture is composed of a large amount of nanorods, based on literature, involves two well-known mechanisms of Ostwald ripening and oriented attachment [7,11]. A possible growth mechanism of this nanocrystals is schematically illustrated in S_2. For formation of the $Cd_2V_2O_7$ superstructures, the $Cd_2V_2O_7$ particles accumulated by the self-assembly as well as the sphere-shape and flower-shape $Cd_2V_2O_7$ architecture composed of nanosheets *via* the purposed self-assembly mechanism for this sample.

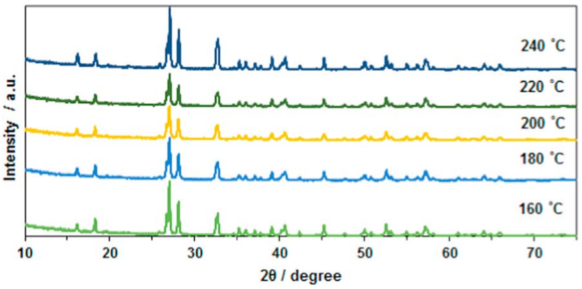

Fig. 1. XRD patterns for $Cd_2V_2O_7$ synthesized at different temperatures.

Fig. 3 shows diffuse reflection spectra (DRS) of $Cd_2V_2O_7$ at different temperatures. As can be seen in Fig. 3(a–e), the absorption spectrum of the as-synthesized samples show two absorption peaks about 295 and 364 nm and then falls sharply in 368–432 nm region [1,7]. The *Eg* values of the $Cd_2V_2O_7$ samples according to Tauc relation, are evaluated by extrapolating the linear portion of the curve [7]. As shown in the insert of Fig. 3a–e, $Cd_2V_2O_7$ samples show direct band gaps with *Eg* of about 2.88–2.95 eV [1]. Despite being in nano-scale of the $Cd_2V_2O_7$ samples, these nanoparticles have visible light absorbance that is of great significance for its practical application point of view.

4. Conclusion

In summery self-assembled $Cd_2V_2O_7$ hollow sphere-shape superstructures with hydrophilic surface have successfully been synthesized *via* a simple route based on surfactant-assisted hydrothermal. The results indicated that by simply controlling temperature, different morphologies could be obtained, and the optimized materials that were synthesized at 180 and 200 °C with 60–80 nm subunit nanorods displayed good dispersion of small-sized gold. The possible growth mechanisms for the formation of single-crystalline as-product nanocrystals are proposed where the process of crystal growth was dominated by a crystallization-dissolution-recrystallization growth mechanism for nanosheets and Ostwald ripening and oriented attachment for nanorods. Finally, the optical properties of the $Cd_2V_2O_7$ samples also have been investigated and results were compared with earlier reports for $Cd_2V_2O_7$. The as-synthesized samples in this work with appropriate band gaps and surface areas can have potential application for photocatalytic activity in the visible region of the solar spectrum.

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