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Fabrication, physicochemical properties and photocatalytic activity of $Ag_{0.68}V_2O_5$ hierarchical architecture assembled by ultrathin nanosheets

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ABSTRACT

The micro-nano structure control of Ag-based composite oxides is very important for improving the performance applied in advanced functional materials. In this work, the $Ag_{0.68}V_2O_5$ hierarchical architecture was fabricated by insertion of Ag^+ into layered V_2O_5 through a simple one-step hydrothermal method. The construction mechanism of this hierarchical architecture was proposed, which may be continuous intercalation reaction, Ostwald ripening and self-assembly process. Moreover, the light harvest range and separation efficiency of photogenerated electron-hole pairs based on $Ag_{0.68}V_2O_5$ photocatalyst are improved distinctly relative to that of pristine V_2O_5. It directly results in the superior photocatalytic performance for dye degradation over $Ag_{0.68}V_2O_5$ hierarchical architecture, which is also far higher than that of commercial V_2O_5 and TiO_2 (P25) for removing dye pollutants.

1. Introduction

The design and control of nanostructured materials are critical in investigating the shape and structure dependence on physicochemical properties, especially direct fabrication of complex nanoarchitectures including controlled morphology, orientation, dimensionality, crystal plane, interface, etc., which have attracted much attention in the advanced functional material fields [1–13]. For instance, GdOOH nanowires with sub-1 nm diameter and microscale length were electrospinningly processed into superstructures including smooth fibers and large-area mat, which not only exhibited both flexible texture and outstanding mechanical properties but also retained properties resulting from inorganic components [14]. The tetragonal Bi_2WO_6 with mesoporous single-crystal-like structure was obtained in the mixed molten salt system. This unique architecture originated from synergistic effect of mixed alkali metal nitrates and electrostatic attraction caused by internal electric field in crystal, which displayed superior photocatalytic activity of both organic dye degradation and O_2 evolution from water under visible light [15]. Therefore, it will distinctly improve performance of materials by means of controllably adjusting microstructure.

For the past few years, the plenty of Ag-based photocatalysts have been widely developed and researched, which were regarded as to be a kind of promising photocatalytic materials, and usually displayed the intense photocatalytic oxidation ability for using high-efficiency removal of organic contaminants and O_2 generation from the water under light irradiation [16–35]. As reported silver halides and their composite photocatalysts, they usually exhibited outstanding degradation activity for removing organic pollutants [16–19]. In addition, Ag-based composite oxides were another kind of photocatalytic materials, which generally had the more superior activity and resistance to light corrosion relative to silver halides. Two representatives were Ag familiar Ag_3PO_4 [21,22] and Ag_2CO_3 [23], and the former showed not only the superior liberating O_2 activity from water but also photocatalytic activity for degradating organic dyes as well as the latter displayed the universality for removing various dyes.

Up to now, the focus researches usually mainly concentrated on enhancing photocatalytic activity and stability by designing band gap engineering based on the hybridized and adjusted effects of Ag^+ ion as an effective electronic structure regulator [20], such as Ag_3PO_4 [21,22], Ag_2CO_3 [23], $AgNbO_3$ [24], $AgTaO_3$ [24], $AgVO_3$ [25], $AgInW_2O_8$ [26], $Ag_2V_4O_{11}$ [27], $Ag_2Nb_4O_{11}$ [28], $Ag_2Ta_4O_{11}$ [29,30], Ag_2ZnGeO_4 [31], Ag_3AsO_4 [32], Ag_3VO_4 [25,33], $Ag_4V_2O_7$ [25], $Ag_6Si_2O_7$ [34] and so on. However, the morphology control on account of micro-nano structure and its influence on photocatalytic performance still had less research reports. At present, there were some Ag-based materials that have exhibited distinctly improved

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photocatalytic performance by fabricating special morphology structure. A typical one was that tetrahedral Ag_3PO_4 submicrocrystals exhibited higher photocatalytic degradation activities than Ag_3PO_4 cubes [36], and the other was that the concave cubic AgCl possessed higher photocatalytic activity in O_2 evolution than cubic ones [37]. Although these researches about morphology have carried out, the structure-activity relationship was also lack of detailed discussions and needed to be further investigated.

Here, based on the layered crystal structure of V_2O_5 that easily took place intercalation reactions of metal ions [20,38], the $Ag_{0.68}V_2O_5$ hierarchical architecture assembled by ultrathin nanosheets was fabricated by one-step facile hydrothermal process. The crystal growth mechanism of $Ag_{0.68}V_2O_5$ hierarchical architecture was revealed in detail by time-dependent morphology evaluation experiments. The unique physicochemical properties and superior photocatalytic performance of $Ag_{0.68}V_2O_5$ hierarchical architecture as photocatalyst were discussed in depth. This work will provide a direction to realize the controllable construction of micro-nano structure for Ag-based composite oxides applied in advanced functional materials.

2. Experimental section

2.1. Synthesis and characterization

$Ag_{0.68}V_2O_5$ hierarchical architecture was synthesized using a typical hydrothermal reaction method. $AgNO_3$ of 0.170 g, V_2O_5 of 0.182 g and PVP of 0.1 g (Mr ≈ 1,300,000) were weighed out and added into a beaker containing distilled water (25 ml) under vigorous magnetic stirring for 30 min at room temperature. Then the suspension was transferred into a 30 mL Teflon lined stainless steel autoclave (filling volume of 80%) to perform a hydrothermal reaction of 1 h, 6 h, 12 h and 24 h at 140 °C. After being cooled down to room temperature, the precipitates were collected by centrifugation and washed with distilled water and ethanol for several times in turn, and then dried for 4 h at 60 °C. The final dark cyan products were obtained.

The phase of the $Ag_{0.68}V_2O_5$ sample was characterized by powder X-ray diffractometer (XRD, Rigaku D/max-2000) equipped with a Cu-Kα radiation at a scanning rate of 5° min^{-1} in the 2θ range of 10–90°. The morphologies of samples were characterized utilizing field-emission scanning electron microscopy (FESEM, MX2600FESEM) and transmission electron microscopy (TEM, FEI, Tecnai G2 S-Twin) techniques. X-ray photoelectron spectroscopy (XPS) analysis was measured on an American electronics physical HI5700ESCA system with X-ray photoelectron spectroscope using Al Kα (1486.6 eV) monochromatic X-ray radiation. The peak positions were corrected against the C 1 s peak (284.6 eV) of contaminated carbon. The UV–visible diffuse reflectance spectra (UV–vis DRS) of samples were recorded on a UV–vis spectrophotometer (PG, TU-1901) at room temperature with $BaSO_4$ as the background at 200–1000 nm. N_2 adsorption-desorption experiment was measured at 77 K using an AUTOSORB-1 Surface Area and Pore Size Analyzer. The photoluminescence (PL) spectra were carried out on the Horiba JobinYvon (FluoroMax 4) luminescence spectrometer. The time-resolved photoluminescence (TR-PL) spectra were obtained on a model FES 920 system with an excitation wavelength of 337 nm and detection wavelength of 469 nm.

2.2. Photocatalytic and photoelectrochemical measurements

The degradation experiment was carried out with 0.02 g sample suspended in the methylene blue (MB) dye solutions (10 mg/L, 100 ml) in quartz photochemical reactor. Then it was performed magnetically stirring for 30 min in the dark to complete the adsorption-desorption equilibrium between dye and sample.

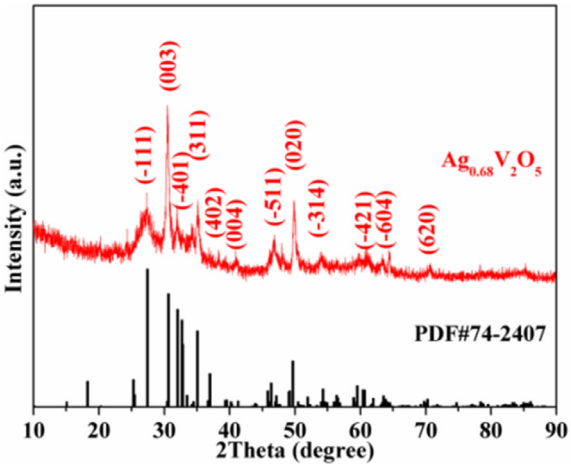

Fig. 1. XRD pattern of $Ag_{0.68}V_2O_5$ hierarchical architecture.

Lastly, adding 0.1 ml H_2O_2 to the reactor, the above suspension was exposed to visible light irradiation provided by a 300 W Xe arc lamp with band pass filter ($\lambda \geq 400$ nm) under magnetic stirring. UV–vis spectrophotometer (PG, TU-1901) monitored the absorbance of dye solutions at intervals of fixed time. Before measurement, the sample was removed from the reactor by centrifugalization. The detailed steps are as follows: after the first degradation reaction is completed, the photocatalyst is removed from the reaction system by centrifugalization. Then centrifugal photocatalyst is added in the MB dye solution and executed the next degradation reaction. It's worth noting that 0.002 photocatalyst (10%) was added into the reaction system to compensate for the loss of photocatalyst every performing after the second cycle.

The photocurrent responses and electrochemical impedance spectra were measured by using a standard three-electrode system. The as-prepared sample electrode, Pt plate and saturated Ag/AgCl electrode served as the working electrodes, counter electrode and reference electrode, respectively. Na_2SO_4 aqueous solution of 0.5 M was used as the electrolyte. The working electrode was prepared by the following method. The sample of 0.3 g, PVP of 0.01 g and oleic acid of 0.03 mL were dissolved in ethanol of 3 mL to form uniform suspension liquid, which was then performed spin-coated on indium tin oxide (ITO) conducting glass with the size of 15 × 20 mm by using drop-casting method. Thereafter, the working electrode was dried in the air.

3. Results and discussion

XRD was used to investigate the structure and phase compositions of as-prepared sample. From XRD pattern of $Ag_{0.68}V_2O_5$ sample in Fig. 1, it can be well-indexed as monoclinic $Ag_{0.68}V_2O_5$ crystal (JCPDS card No. 74-2407). Meanwhile, no diffraction peaks from the impurities are detected, which indicates that the pure $Ag_{0.68}V_2O_5$ product is obtained. The morphology of the as-prepared $Ag_{0.68}V_2O_5$ sample was revealed by FESEM. Fig. 2a shows that the typical two-dimensional (2D) $Ag_{0.68}V_2O_5$ nanosheets are obtained without any other shapes. The most of nanosheets overlap together to form equally distributed layered hierarchical architecture except a few scattered single nanosheets. The individual hierarchical architecture and nanosheet are further demonstrated by high-magnification FESEM images in Fig. 2b and c. We note that the hierarchical architecture exhibits orderly multi-layered characteristic, which can provide larger specific surface area and form abundant micro/nano- pores, thus availing adsorption, diffusion and transport of pollutant molecules to improve photocatalytic activity. In addition, the individual