

Solvothermal synthesis of a layered titanate nanosheets and its photocatalytic activity: Effect of Ag doping



Sibsankar Rahut, Ramdayal Panda, Jayanta Kumar Basu*

Department of Chemical Engineering, Indian Institute of Technology Kharagpur, 721302, India

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ABSTRACT

Photocatalytic activity of titanate nanosheets prepared by continuous hydrothermal flow system has been extensively studied earlier. Herein, for the first time, a thin layered titanate nanosheets were fabricated by one-step solvothermal approach. Descriptive study on solvothermal doping of Ag in titanate nanostructure and crystal growth mechanism of the material prepared by solvothermal synthesis has been discussed. Structure, morphology, crystallinity, electronic properties, optical properties and photoelectrochemical parameters have been studied with different level of silver incorporation. Charge transfer among Ti and Ag cluster and change of intermediate energy level results in an electronic renovation of the band structure. The material prepared by solvothermal doping was found to be visible light sensitive without addition of other minerals. Photodegradation of methyl orange and phenol has been observed under visible light irradiation, it shows excellent photocatalytic behavior.

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1. Introduction

Because of substantial industrialization in this current period, the amount of toxic effluent in water is increasing day by day as many dyes containing effluents and organic compounds are directly discharging to water bodies. Some of these effluents are highly stable in nature and resistant to aerobic digestion. Polluted water is not only harmful to aquatic creature but also to human lives. Nowadays, semiconductor based visible light photocatalyst got high attention for the debasement of those pollutants due to renewable, cheap and environment friendly nature [1–11]. Use of bimetallic oxide or metal metalate for degradation of organics shows very high affinity compared to the single transition metal oxide. The main reason behind the success of metal metalate is $M_1 - O - M_2$ bond, which further reduces the band gap of the semiconductor material for which it can be visible light sensitive. To enhance the photocatalytic activity, techniques like impregnation of metal ion and composites of metal oxides were evolved by tuning the band gap of the material. [12–15]

One of the leading metal metalates is sodium titanate nanostructure that received a high attention as a photocatalyst due to high external surface area and relatively cheap. But, there are same drawbacks for titanate due to its wide band gap which ranges from

3.4 to 3.7 eV. As a result, it shows better photocatalytic activity in UV region compare to the visible region [16,17]. Photocatalyst sensitive to visible region is more preferred since many natural and synthetic polymers and its products may crack or disintegrate by ultraviolet irradiation. There are also other drawbacks for visible light photocatalyst as there is a high probability of current leakage or photogenerated electron–hole recombination [18,19]. It has also been reported that other metal titanate with foreign impurity has been considered as an efficient route to enhance photocatalytic activity and tune the band gap to the desired level [20–22]. Nowadays layered sodium titanate with nanoflower, nanowire and nanotube morphology via hydrothermal route has been introduced for great photocatalytic performance due to high external surface area. A lepidocrocite type layered titanate nanostructure was also studied to find electronic properties of TiO_6 octahedra in titanate. Layered titanate via solvothermal route has never been studied earlier [23–33]. Change of structural, optical, electronic properties due to Silver doping in other semiconducting oxide has been discussed earlier which clearly depicts an improvement on tuning the band gap and restrict photocurrent leakage [34,35]. Photocatalytic study of titanate nanosheets prepared by continuous hydrothermal flow synthesis has been discussed earlier by Zhang et al. solvothermal synthesis of titanate nanostructure has never been studied before. Therefore, layered titanate via solvothermal route advances the key of interest for the forthcoming era of research on photocatalysis.

Herein, we investigated solvothermal synthesis of layered sodium titanate nanosheets. Effect of silver doping in the layered

* Corresponding author.

E-mail address: jkb@che.iitkgp.ernet.in (J.K. Basu).

titanate network has also been explored to achieve strong visible light absorption ability. Partial replacement of titanium atom by silver in the lattice was conducted by solvothermal doping which may effectively change its optical and electronic properties and enable visible light sensitivity. The structural and optical properties of the final products were controlled by adjusting the amount of silver doped. The photocatalytic activity of designed catalysts were examined under visible light by monitoring degradation of methyl orange and phenol in water.

2. Synthesis

Layered sodium titanate nanosheets (NT) were synthesized by simple solvothermal procedure. All chemicals are analytical grade. Typically 5 ml titanium isopropoxide (TIP) was mixed under stirring in 10 ml water/isopropanol mixture to form TiO_2 sol. 20 ml 3M NaOH aqueous solution was mixed under stirring to the previous suspension. Final white suspension is sonicated for 30 min and then kept under stirring for 1 h. Water/isopropanol ratio of final suspension has been maintained at 6:1. The resulting suspension was then transferred into a 50 ml Teflon-lined stainless steel autoclave and kept at 200°C for 24 h. A white color precipitate was obtained which was then filtered, repeatedly washed with hot water and ethanol followed by overnight drying at 60°C under vacuum. Afterwards, obtained yield was transferred to a silica crucible for further calcination treatment at 500°C for 2 h with a heating rate of $5^\circ\text{C}/\text{min}$. Similar procedure is followed to prepare violet colored Ag-doped titanate nanocrystals. Typically, 2 ml silver nitrate (AgNO_3) aqueous solution was mixed with 20 ml 3M NaOH aqueous solution. A gray suspension of silver hydroxide in excessive NaOH solution is formed which was added to the previously declared TiO_2 sol. The procedure is repeated with different mol% of AgNO_3 (Ag/Ti mol % = 1, 2, 5) and samples are designated as AT-1, AT-2 and AT-3 respectively. Note that isopropanol was used as a supercritical reducing agent at high temperature and pressure to promote the growth of titanate. Excessive isopropanol breaks the crystallinity due to the formation of anatase TiO_2 in this network (Fig.S1).

2.1. Characterization

A thermogravimetric (TG) analyzer (TGA-Q50, USA) is used to measure weight loss% with increasing temperature at nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. Powder X-ray Diffraction (XRD) patterns of the catalysts were obtained with a PAN analytical diffractometer (model: PW-3050/60, UK), using $\text{Cu-K}\alpha$ radiation at 40 kV and 30 mA with 2θ angle scanning from 5° to

70° . The powder sample was analyzed spreading on a conventional glass sample holder. Crystallinity and phases of the catalysts were identified by comparing the reported files from the International Centre for Diffraction Data. The surface morphology was scrutinized by field electron scanning electron microscope (FESEM-JEOL, Japan). Specific surface areas, pore size distribution and N_2 desorption isotherms were examined by Quantachrome (AUTOSORB 1, UK) instrument using Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) method where adsorption of nitrogen was observed at 77 K after degassing at 573 K for 2 h under high vacuum. Exact nanodispersion and particle size are determined by high-resolution transmission electron microscope image (HR-TEM) that has been captured by JEM-2100 HRTEM (JEOL, Japan) having point to point resolution of 0.194 nm and lattice resolution of 0.14 nm. Photoluminescence (PL) measurements were accomplished at room temperature by a He–Cd laser as an excitation source of 325 nm with an output power of 50 mW. A TRIAX-320 monochromator is used to record the signal which is detected signal by Hamamatsu R928 photomultiplier detector in the visible range. X-ray photoelectron spectroscopy (XPS, ULVAC PHI 5000 versaprobe II, Japan) with Al $\text{K}\alpha$ electrode was used to analyze the chemical and electronic state of designed sample. Raman spectroscopy (MODEL T64000, France) was investigated at room temperature with an excitation source of argon-krypton mixed ion gas laser (MODEL 2018 RM, USA) and detected by thermoelectric cooled front illuminated 1024 256 CCD (MODEL Synapse TM, France). Energy dispersive X-ray (EDX) spectroscopy (Oxford, UK) used to analyze atomic mapping. Electrochemical impedance spectroscopy (VersaStat-3, Princeton Applied Research, USA) were introduced to observe the charge transfer flexibility of photogenerated electron.

3. Result and discussion

Morphology, crystallinity, structure of the specimens subjected to the content of Ag were explored by SEM and TEM analysis. A typical titanate nanosheets were depicted in high magnification TEM image in which a particular lattice fringe of 0.72 nm with a sustainable selected area electron diffraction pattern has been clearly detected (Fig. 1a and b). similar morphology has been observed for Ag-doped titanate via higher magnification TEM image (Fig. 1c–e). Ag incorporation on titanate surface is explained by marking with red circles on TEM image which indicates that atomic positioning is consistent and well-arranged in the internal layers but, gradually fades near the surface of the nanosheets. FESEM image of pristine layered titanate and Ag-doped layered titanate confirm nanosheets

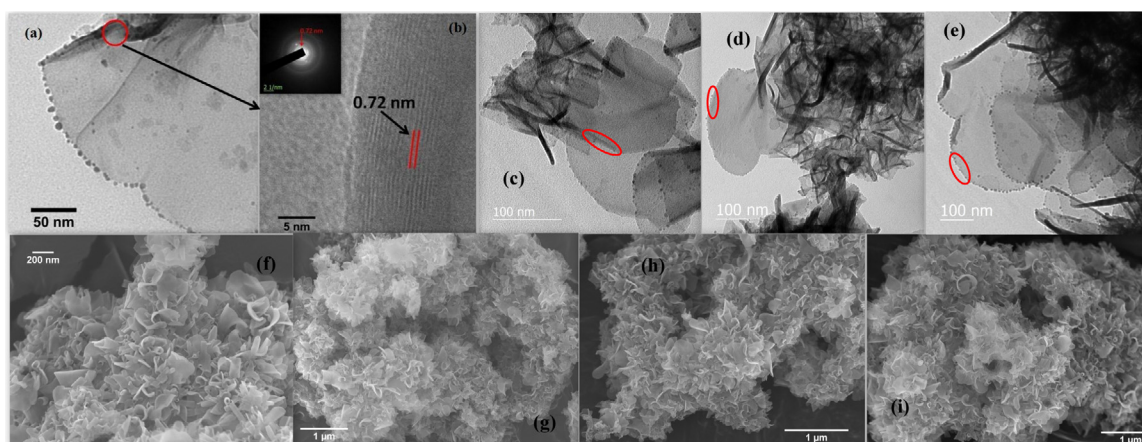


Fig. 1. (a) HRTEM image of titanate nanosheet (NT), (b) lattice fringes of pure titanate side view, (c) HRTEM image of AT-1, (d) HRTEM image of AT-2, (e) HRTEM image of AT-3, (f) FESEM micrographs of NT, (g) FESEM micrographs of AT-1, (h) FESEM micrographs of AT-2, and (i) FESEM micrographs of AT-3.

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