CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF YMnO$_3$ NANORODS FOR UV AND VISIBLE LIGHT PHOTOCATALYTIC APPLICATIONS

2.1 INTRODUCTION

Recently multiferroic materials, which exhibit both ferromagnetic and ferroelectric property, have received an intensive attention. The multiferroics has been extensively studied in several manganese oxides such as perovskite RMnO$_3$, hexagonal RMnO$_3$ and RMn$_2$O$_5$. The yttrium and rare-earth manganites RMnO$_3$ form an interesting family showing a wide variety of physical properties (Han et al 2006, Han et al 2011, Zhang et al 2007, Zheng et al 2010). However, multiferroics have applications in sensors, magnetoelectronics, magnetic data storage, nonvolatile memory, transducers, actuators and gate ferroelectrics in field effect transistors (Das et al 2011, Wang et al 2011, Zhu et al 2008, Bergum et al 2011, Wang et al 2010). YMnO$_3$ is also known to be a narrow-bandgap semiconductor and exhibits high catalytic activity for oxidation of carbon monoxide and various organic compounds (Wang et al 2011). In recent years, the photocatalyst YMnO$_3$ has attracted considerable attention because of its high catalytic activity, low cost, and environmental friendliness. It is observed that hexagonal YMnO$_3$ has simultaneous ferroelectric transition at Curie temperature $T_C = \sim 900$ K and anti-ferromagnetic transition at Neel temperature $T_N = \sim 80$ K (Zhang et al 2011, Wang et al 2011 and Marti et al 2007).
Photocatalytic degradation of organic pollutants by semiconductor photocatalysts is promising for environmental purification and energy conversion. To date, most investigations have focused on the photocatalyst TiO$_2$ because of its high photocatalytic activity, chemical stability, non-toxicity, and low price. However, its practical application has not yet run up to a satisfying extent due to its wide band gap (3.2 eV) and high recombination of electron–hole pairs (Stevens et al 2014, Yang et al 2011). To maximize the utilization of sunlight, a new type of photocatalyst with a perovskite structure has been recently used as a highly effective photocatalyst in the visible region (Hu et al 2014).

In this work, we demonstrate that YMnO$_3$ can be used as a photocatalyst for the decomposition of methyl orange (MO). Generally, the microstructure of a photocatalyst has an important influence on its photocatalytic activity; especially the creation of nanostructures offers great potential to achieve excellent photocatalytic efficiency since the photocatalytic reaction occurs dominantly on the catalyst surface and nanostructures can undoubtedly provide a large surface area to volume ratio. In the past several years, studies on YMnO$_3$ single crystals (Kim et al 2000) and thin films (Nakamura et al 2011, Marti et al 2010) have been carried out. But the nanomaterials such as nanoparticles, nanorods and nanowires have unique properties, which are expected to be critical to the function and integration of nanoscale devices (Zheng et al 2010). Many reports are focused on the synthetic approaches based on solution chemistry, such as sol-gel (Zhang et al 2011), citric acid method (Zhang et al 2004), polyacrylamide gel route (Wang et al 2011), hydrothermal (Zheng et al 2010) and chemical route synthesis methods (Bergum et al 2011). However sol-gel, citric acid, polyacrylamide gel route and chemical route synthesis method requires high temperature (>800 °C) for long duration, which results in poor homogeneity with micrometer particles. Herein a hydrothermal method is put forward for
the synthesis of YMnO$_3$ nanorods for the first time. In comparison with the other methods, the hydrothermal method requires lower temperature which produces the nanoparticles with good homogeneity. So it appears to be promising option for the synthesis of YMnO$_3$ nanorods due to its easy handling, fast and cost effective (Lin et al 2010). In addition, the possible reaction mechanism for the formation of YMnO$_3$ nanorods was discussed in detail.

2.2 EXPERIMENTAL DETAILS

All the reagents were of analytical grade and used without further purification. Synthesis was carried out by hydrothermal method using yttrium nitrate, sodium hydroxide, manganese acetate, potassium permanganate as source materials. In a typical experimental procedure 0.2M of Y(NO$_3$)$_3$·6H$_2$O, 0.5M of NaOH, 40 mmol of Mn(CH$_3$COO)$_2$·4H$_2$O and 10 mmol of KMnO$_4$ were dissolved in distilled water. The reaction mixture was stirred by a magnetic stirrer for 3 h with the solution pH of 9.2. Then the final homogeneous solution was transferred into 100 ml teflon-lined stainless steel autoclave with 80% of the volume filled. The autoclave was placed into a resistive heating furnace for the hydrothermal treatment at 200 ºC for 48 h. After reaction, the precipitate was collected and rinsed with distilled water for several times and then dried overnight at 100 ºC.

2.3 CHARACTERIZATION STUDIES

The crystal structure of the synthesized sample was characterized by XRD using (SEIFERT) JSO-DEBYEFLEX 2002 model diffractometer with CuKα$_1$ radiation ($\lambda=1.5405$ Å) in the scan range 2θ=10°-70°. The functional groups of synthesized sample have been studied by FT-IR analysis. The FT-IR measurements have been performed in the potassium bromide mode (KBR) using the model 6300 FT-IR spectrophotometer. The surface
morphology of synthesized samples and elemental presence has been studied by high resolution scanning electron microscopy (HRSEM) using FEI Quanta FEG 200 microscope operated at 20 kV. The particles size and morphology of the synthesized sample has been studied by high resolution transmission electron microscopy (HRTEM) using Tecnai G2 model T-30 s-twin electron microscope with an accelerating voltage of 300 kV. The atomic force microscopy (AFM) and magnetic force microscopy (MFM) measurements of the synthesized sample have been performed in non-contact mode at room temperature using XE 70 Park system. X-ray photoelectron spectroscopy (XPS) has been done to confirm the oxidation state of the elements present in the sample. The XPS data were collected using Omicron Nanotechnology instrument with a binding energy resolution of 0.7 eV. The optical absorption study of the synthesized sample has been carried out in the range of 200-800 nm using Cary 5E high resolution spectrophotometer. The vibrating sample magnetometer (VSM) measurements were recorded for two different temperatures (20 K and 300 K) along with ZFC and FC conditions using Lakeshore VSM 7410.

2.4 RESULTS AND DISCUSSION

2.4.1 X-ray Diffraction Studies

Figure 2.1 shows the powder XRD pattern of YMnO₃ sample. The peaks observed for the sample were compared and indexed with JCPDS file No. 25-1079. All the diffraction peaks were assigned to the pure phase of YMnO₃, indicating a hexagonal structure with space group of P6₃cm. The sharp and intense peaks indicate that the prepared YMnO₃ sample is highly crystalline. No traces of non-perovskite impurity phases like Y₂O₃ and various manganese oxides such as MnO, Mn₂O₃ and Mn₃O₄ are detected in the XRD pattern, which indicates that the product obtained in the present synthesis condition is highly pure.
2.4.2 FT-IR Studies

Figure 2.2 FT-IR spectrum of YMnO$_3$ nanorod sample
Figure 2.2 shows FT-IR spectrum of YMnO$_3$ sample. The broad absorption peaks in the range 600–400 cm$^{-1}$ corresponds to stretching and bending mode of metal oxygen bonds. The broad absorption peak at 596 cm$^{-1}$ is due to Mn–O stretching vibration, the sharp absorption peak at 535 cm$^{-1}$ corresponds to Y–O stretching vibration, and another sharp absorption peak at 499 cm$^{-1}$ is attributed due to O-Mn-O bending vibration. The stretching and bending vibration of all the three bands indicates the formation of YMnO$_3$ phase.

2.4.3 High Resolution Scanning Electron Microscopy Studies

![HRSEM images of YMnO$_3$ nanorods](image)

**Figure 2.3 HRSEM images of YMnO$_3$ nanorods**

Morphology of the YMnO$_3$ sample was examined by HRSEM analysis. Figure 2.3 shows low and high magnification HRSEM images of
synthesized YMnO$_3$ sample. From the HRSEM image it is clearly observed that the surface of the sample consists of high density rod-like morphology with uniform size distribution. Figure 2.3d shows individual YMnO$_3$ nanorod with average diameter of about 100 nm and length in several micrometers.

### 2.4.4 High Resolution Transmission Electron Microscopy Studies

![HRTEM images of YMnO$_3$ nanorods](image.png)

**Figure 2.4 HRTEM images of YMnO$_3$ nanorods**

The as-synthesized YMnO$_3$ sample morphology was investigated by TEM. The general TEM images, HRTEM image and SAED pattern of the as-synthesized YMnO$_3$ nanorods are shown in Figure 2.4. It can be observed from the TEM images (Figure 2.4 (a,b)) that the individual nanorod have smooth side wall with uniform diameter of about 100 nm and length in several micrometer. The HRTEM image (Figure 2.4c) shows clear lattice
fringe. Further the HRTEM study of the nanorod investigates that the interspacing between lattice planes was 0.296 nm, which agrees well with (002) plane. Figure 2.4d shows the SAED pattern of individual nanorod and hence the result suggests that the sharp diffraction spots in SAED pattern indicate that the individual rod of YMnO$_3$ nanostructure is single crystalline in nature.

### 2.4.5 Atomic Force and Magnetic Force Microscopy Studies

![AFM and MFM images of YMnO$_3$ nanorods](image)

**Figure 2.5** AFM and MFM images of YMnO$_3$ nanorods

Figure 2.5 shows the AFM and corresponding MFM images of YMnO$_3$ nanorods scanned at 500 nm X 500 nm area. The AFM image shows uniform distribution of nanorods with average diameter of about 100 nm. It was observed from the MFM image that major position of the rods interacts
magnetically with the MFM probe. The attractive magnetic interactions (dark regions) in the rods were clearly visible and it was found that the magnetic signal is evenly distributed along the rods.

2.4.6 Elemental Studies

![EDS spectrum of YMnO$_3$ nanorods](image)

**Figure 2.6 EDS analysis of YMnO$_3$ nanorods**

In order to determine the chemical composition of prepared YMnO$_3$ sample, EDX analysis was performed over the sample. Figure 2.6 shows the EDS spectrum of YMnO$_3$ nanorods. No elements other than yttrium, manganese and oxygen were detected which further confirms the purity of the synthesized sample.

2.4.7 Formation Mechanism of YMnO$_3$ Nanorods

YMnO$_3$ nanorods were formed by one step hydrothermal synthesis. Based on the experimental results, the possible reaction mechanism of YMnO$_3$ nanorods can be expressed as follows,

$$5[Y(NO_3)_3] + [KMnO_4] + 4[Mn(CH_3COO)_2] + 22 NaOH \rightarrow 5YMnO_3$$

$$+ 14NaNO_3 + KNO_3 + 8[Na(CH_3COO)] + 11 H_2O$$
Under high pressure hydrothermal condition Y(NO₃)₃ readily reacts with NaOH, KMnO₄, and Mn(CH₃COO)₂ to form the final products of YMnO₃.

2.4.8 X-Ray Photoelectron Spectroscopy Studies

Figure 2.7 XPS spectra of YMnO₃ sample (a) wide scan survey (b) core level of Y 3d region (c) core level of Mn 2p region (d) core level of O 1s region

XPS was performed in order to verify the oxidation states of Y 3d, Mn 2p and O 1s in the YMnO₃ samples. The binding energy resolution of the instrument is 0.7 eV and the recorded spectrum was shown in Figure 2.7. The peak position was reference to carbon at 284.6 eV. Figure 2.7a shows a wide scan spectrum of the sample, where peaks of Y, Mn, O, and C were detected.
Figure 2.7b shows the narrow scan spectra for Y 3d region where there are two characteristic peaks of Y were observed at the binding energy of 156.7 eV (Y 3d$_{5/2}$) and 158.6 eV (Y 3d$_{3/2}$), which are very close to the already reported binding energy values (Sivaraman et al 2011). Figure 2.7c shows peaks at 641.9 and 653.5 eV which were the characteristic peaks of Mn$^{+3}$ 2p$_{3/2}$ and 2p$_{1/2}$ respectively. Generally Mn is characterized to be +3 oxidation state in Mn based perovskite oxide materials. The absence of additional or shoulder peaks were found in Mn 2p XPS spectrum, which strongly indicates that Mn exists in +3 oxidation state in the prepared, samples (Das et al 2011). Figure 2.7d shows the narrow scan spectra for O 1s region where the characteristic peak of O was observed at the binding energy of 530 eV which are very close to the already reported binding energy values.

### 2.4.9 Magnetic Property Studies

Figure 2.8 shows the magnetization as a function of temperature in ZFC and FC conditions with applied magnetic field of 100 Oe for the YMnO$_3$ sample. The magnetization curve starts splitting at $T \sim 80$ K which shows that the sample appears to attain anti-ferromagnetic ordering at this temperature. However, ZFC and FC curves become virtually identical above 80 K, which shows paramagnetic behavior. Both the ZFC and FC curves showed an abrupt increase in magnetization at low temperature, meaning the anti-ferromagnetism at low temperature (Zhang et al 2011). According to Curie–Weiss law, the temperature ($T$) dependence of inverse susceptibility ($1/\chi$) above 140 K (paramagnetic state) in FC was fitted with a negative extrapolated temperature $\theta_{CW} \sim -310$ K (inset of Figure 2.8), which was higher than previous report and it may be due to morphology of the material (Zhang et al 2011).
Figure 2.8 Temperature dependent magnetization curves of YMnO$_3$ nanorods at 100 Oe

![Graph showing temperature dependent magnetization curves](image)

Figure 2.9 (a) M-H hysteresis loops of YMnO$_3$ nanorods at 300 and 20 K (b) Zoom view M-H hysteresis loops of YMnO$_3$ nanorods at 300 and 20 K

Figure 2.9a shows the dependence of the magnetization M(H) on the magnetic field between ±20 kOe at two different temperatures 20 K and 300 K in YMnO$_3$ nanorods respectively. The M(H) curve at 300 K shows
paramagnetic behavior and a very small hysteresis loop indicative of anti-ferromagnetism was observed for 20 K. Figure 2.9b shows the zoom view of M(H) hysteresis loop for 20 K and 300 K, and hence it was found that the coercivity (H_C) was about 435 Oe. Thus, in some temperature range the coexistence of both anti-ferromagnetic and ferromagnetic ordering is possible. Therefore anti-ferromagnetic behavior disappears and become paramagnetic above T_N which was already confirmed by temperature dependent magnetization curve.

2.4.10 UV-Vis Absorption Spectrum Studies

![Figure 2.10 UV-Visible absorbance spectra of YMnO_3 nanorods](image)

Figure 2.10 UV-Visible absorbance spectra of YMnO_3 nanorods

Figure 2.10 shows the UV-Vis absorption spectrum of YMnO_3 nanorods. It is observed that the present materials can efficiently absorb light over a wide range of wavelength including the entire visible spectrum (390–780 nm). The UV-Vis spectrum of YMnO_3 allows us to calculate the
optical band gap ($E_g$) of 1.63 eV based on the absorption which agrees well with previous experimental result. The result indicates that YMnO$_3$ nanorods prepared by hydrothermal method can absorb considerable amounts of UV and visible light, implying their potential applications as UV and visible light-driven photocatalysts.

2.4.11 Photocatalytic Property Studies

Figure 2.11 (a,b) shows the UV-Vis time dependent absorbance spectra during photocatalytic reaction of MO for YMnO$_3$ samples after UV and visible light irradiation. Under dark condition, the concentration of MO has no obvious change for long time in the presence of the catalysts. The methyl orange appears to be stable under irradiation without YMnO$_3$ photocatalyst, and the degradation percentage is less than 4% after 6 h UV irradiation and less than 5% after 16 h visible irradiation. Hence MO solution does not have any self-degradation under the radiation of both UV and visible light. The above results indicate that both the light and catalysts are necessary for effective photodegradation of MO.

For YMnO$_3$ sample as the irradiation time was extended from 0 to 6 h and 0 to 16 h the intensity of the absorption peak starts decreasing and slowly shifts to shorter wavelength; hence the result shows that the strength of the peak was reduced as the radiation time increases. After 6 h and 16 h, the absorption peak was low and the intense orange colour of the starting MO solution got faded (insert Figure 2.11(c,d)). Figure 2.11(c,d) shows the degradation percentage defined as ($C_0-C$)/$C_0$×100% as a function of time, where $C_0$ and C are the concentrations of MO before and after irradiation, respectively. As shown in Figure 2.11(c,d) about 64.3% and 61.5% of initial MO has been degraded while using YMnO$_3$ sample as a catalyst under UV and visible light irradiation for 6 h and 16 h respectively.
CONCLUSION

YMnO₃ nanorods have been successfully prepared by hydrothermal method. XRD analysis indicates that the as-prepared sample crystallize fully into perovskite YMnO₃ phase, with hexagonal structure. FT-IR spectrum confirms the presence of functional group present in the sample. HRSEM, HRTEM and AFM images shows that the surface morphology of the YMnO₃ samples were composed of uniform nanorods with an average diameter of about 100 nm and length of several micrometers. MFM confirms the
distribution of the magnetization in the individual rod. ZFC and FC magnetization curves of YMnO$_3$ show the magnetic transition at $T_N \sim 80$ K. Both the ZFC and FC curves showed an abrupt increase in magnetization at low temperature. The M(H) curves recorded for two different temperatures show paramagnetic at 300 K and anti-ferromagnetic at 20 K. XPS analysis confirms the oxidation state of all the elements. The optical band gap of the material was found to be about 1.63 eV. Interestingly, the as-prepared YMnO$_3$ nanorods exhibit a pronounced photocatalytic activity for the decomposition of methyl orange under ultraviolet and visible light irradiation, which is expected to widen the potential applications of YMnO$_3$. 