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Simple electrochemical synthesis of black metal oxides for enhanced visible light absorption

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ABSTRACT

Hydrogenation of oxides such as TiO_2 is so far considered as a time consuming and complex process which requires high temperature annealing in hydrogen atmosphere. In this work, an electrochemical method for the hydrogenation of metal oxides is introduced. The electrochemical hydrogenation process is a low cost process which requires only a few seconds for synthesizing the black semiconducting oxides. Water with small amount (0.2 vol%) of ionic species like fluorine ions is used as electrolyte. The black semiconducting oxides prepared using the electrochemical hydrogenation process exhibit very good absorption of light in visible region.

1. Introduction

Metal oxides, such as TiO_2, SnO_2, ZnO, etc., are considered to be promising materials for different applications like photocatalysis [1], dye sensitized solar cells (DSSCs) [2,3], electrochemical sensors [4] etc. due to their photo-induced reactivity and semiconducting properties. Tailoring the material to increase its absorption in the visible and infrared region of the solar spectrum is expected to increase its photo-conversion efficiency. Typically, metal oxides like TiO_2, SnO_2, ZnO, etc. are white in color, have a band gap in the range of 3–3.8 eV and thus absorb in the ultraviolet region of the solar spectrum. Black semiconducting oxides show enhanced absorption of visible and infrared light. Conventional way to produce black oxides is annealing of metal oxides in hydrogen atmosphere under high pressure [5,6].These processes lead to the production of oxygen vacancies in the metal oxide films resulting in the black color metal oxide [7]. This process is time consuming, and has stringent process control requirements.

In this work, electrochemical synthesis of black semiconducting metal oxides is reported. Titanium dioxide nanotubes and fluorine doped tin oxide (FTO) films were successfully converted into black oxides with a simple electrochemical process which takes less than 10 s. It was observed that the absorption of light by the black oxides is significantly enhanced in the visible and infrared regions. Room temperature electrochemical method of conversion of semiconducting oxides into black oxides is a safe, low cost, less energy intensive and fast process and can be adapted for large scale synthesis.

2. Experimental section

Titanium foils (0.6 mm thick, 99.2%, TIMET, grade 2) of 2.0 cm × 1.5 cm dimension were used for preparing TiO_2 nanotubes by anodization. Electrochemical anodization was carried out as per details mentioned in a previous article [8]. The black semiconducting oxides were synthesized using a simple electrochemical process. The above anodized titania nanotubes, TiO_2 nanoparticle films prepared using Degussa P25 TiO_2 nanoparticle (Evonik) on FTO and commercially available bare FTO (TEC8, sheet resistance 8–9 Ω/sq, Pilkington) were hydrogenated by the electrochemical process. In this process semiconducting oxide films such as Tio_2, SnO_2, etc. are connected to the terminal with negative potential. The titanium sheet was used as terminal with positive potential. 100 ml of deionized water with 0.2 vol% of NH_4F was used as electrolyte. Presence of ionic species like F^- enhances the conductivity. The electrochemical process was performed at 50 V, 100 V, 120 V and 140 V for 2, 10 and 60 s at 25 °C with an electrode distance of 3 cm using a DC power source (APLAB, Mumbai). The converted black oxide films were washed in ethanol and dried in air for further characterization.

Morphology of the nanostructured oxide layers was characterized using JEOL JSM 7600F Field Emission Scanning Electron Microscope (FEG-SEM). Energy dispersive X-ray spectroscopy (EDX) analysis was carried out at a working distance of 15 cm, 20 kV and the collection time was 90 s. UV-spectroscopy (Jasco V-650 spectrophotometer) was utilized to measure the diffused reflectance spectra of TiO_2 nanotube. The X-ray photoelectron

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spectroscopy (XPS) analysis was performed using a spectrometer (PHI 5000 Versaprobe II) with monochromatized Al Kα radiation. All binding energies were referenced to the adventitious C 1s line at 284.6 eV.

3. Results and discussion

It was observed that the as-anodized TiO_2 nanotubes were fully coverted to black color after 10 s of electrochemical hydrogenation (Fig. 1a). The rate of conversion and hydrogen bubbling is mainly dependent on the current density during the process. Thus, rate of conversion can be easily adjusted by changing the voltage or by changing the concentration of F^- ions in the electrolyte. But to attain hydrogenation within a minute, a minimum current density of approximately 50 mA/cm^2 is required which is achieved under conditions mentioned above. It was noticed that the current density decreased exponentially as the hydrogenation process progressed. The electrochemical hydrogenation of florine doped tin oxide film converted it to brown colored film in 10 s (Fig. 1a). It was also observed that crystalline TiO_2 nanotubes (anodized TiO_2 nanotubes heat treated at 500 °C for 3 h) converted into a dark blue color oxide in 10 s and it took approximately 1 min for the full conversion of nanotubes into black TiO_2 nanotubes. This suggests that the crystallinity of the material plays an important role in the kinetics of conversion of metal oxides. Overall, it is confirmed that this electrochemical hydrogenation process is applicable to a wide variety of semiconducting oxides.

XPS studies of as anodized and hydrogenated TiO_2 surface were performed to examine the effect of hydrogenation at different voltages and durations. As expected, the as-anodized TiO_2 nanotubes showed presence of F^- ions which are one of the main constituents of the anodization electrolyte. The peak at 684.5 eV (Fig. 1b) was assigned to physically adsorbed F^- ions on the surface of TiO_2. The intensity of the peak decreased with increase in voltage possibly due to migration of fluoride ion towards anode during the electrochemical process. The absence of peak at 688.9 eV ruled out the substitution by F^- ion at oxygen sites in the TiO_2 crystal lattice [9]. Peaks corresponding to Ti $2p_{3/2}$ (around 458.8 eV) were slightly shifted toward lower binding energy with higher voltages and increased time duration (Fig. 1c and d), suggesting increased formation of Ti^{3+} sites in the hydrogenated TiO_2 sample [6].

The change in absorbance due to hydrogenation of TiO_2 nanotubes and FTO at 120 V and for 10 s was verified by recording the UV–visible spectrum. The UV–visible spectra (Fig. 2) showed that the black TiO_2 nanotubes and brown FTO exhibited enhanced light absorption in the visible region. The reflected light from TiO_2 nanotubes on Ti substrate after conversion was reduced by 57% (from 20*R*% to 8.5*R*% at 550 nm). FTO also absorbs 25% extra light at 550 nm. Hydrogenation process even for duration as low as 10 s enabled dramatic enhancement of visible light absorption.

FEG-SEM characterization has been performed to study the effect of electrochemical hydrogenation process on morphology of

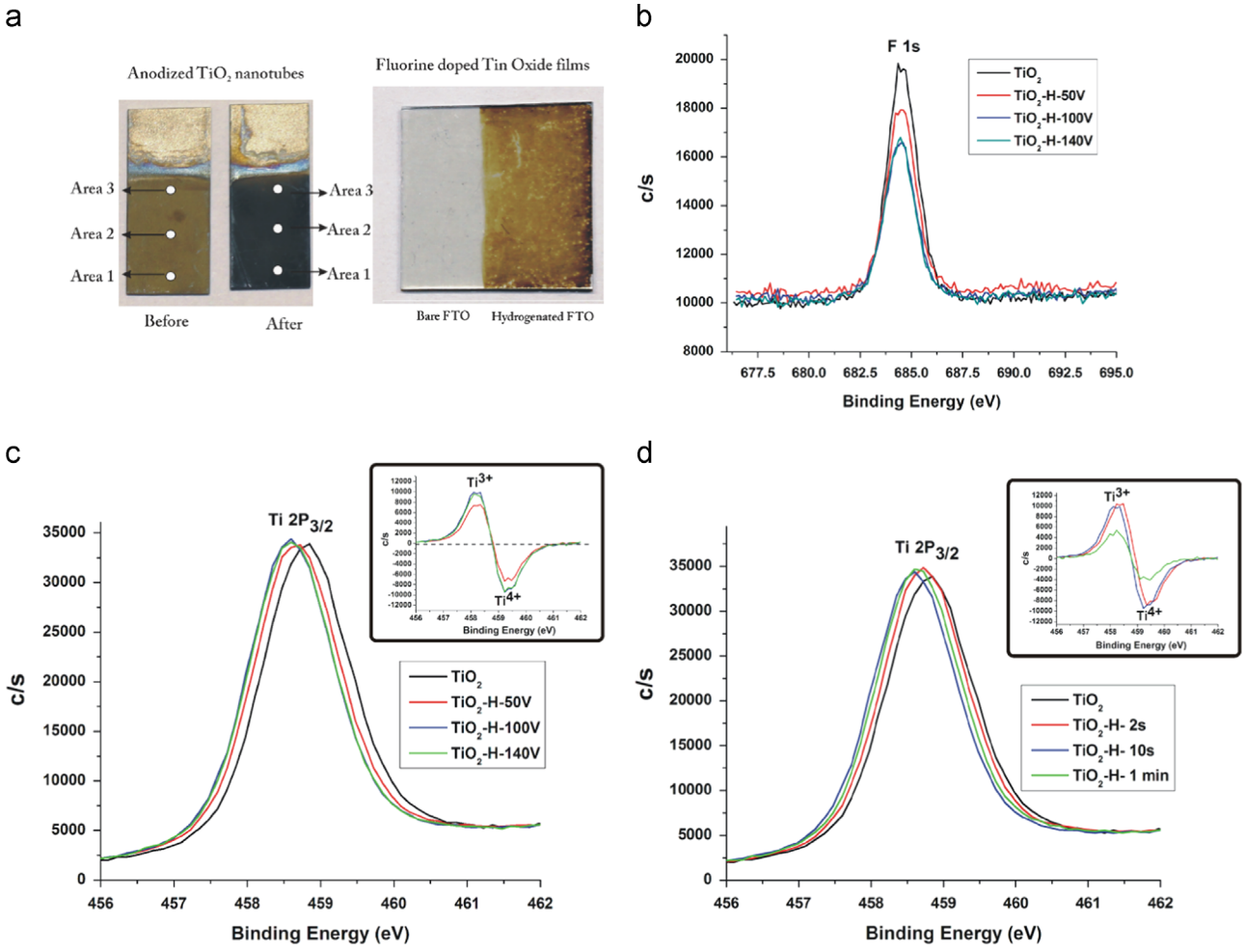

Fig. 1. (a) TiO_2 nanotubes and FTO film before and after electrochemical process, (b–d) XPS spectra of TiO_2 nanotubes hydrogenated at different voltages (for 10 s) and durations (at 100 V) (inset of c and d – difference spectrum).