Supplemantary information

Robust synthesis of bismuth titanate pyrochlore nanorods and its photocatalytic applications

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1 Synthesis of Bismuth titanate pyrochlore

The oil-in-water micro-emulsion was prepared by using the surfactant sodium bis(2-ethylhexyl) sulphosuccinate **(**AOT) in iso-octane. The water to surfactant ratio was kept at 15. An acid stabilized equimolar solution of bismuth and titanium precursors was prepared separately and added drop wise to AOT-iso-octane. Ultrasonication of the solution initiates the formation of a white colloid solution of the reverse micelle. Ultrasound was used for vigorous mixing and to ensure the transport of the materials across the reverse micelles. Ammonium hydroxide in AOT-iso-octane was later added to swing the pH from acidic to alkaline (pH = 9.5) causing the white mixture to precipitate. The precipitate was washed with DI water and dried to form a white powder by heating overnight in air at 100 °C. This was followed by carbonization in nitrogen at 350 °C and further followed by calcination of the powder in oxygen at various temperatures. A step-by-step procedure is given in the flow chart shown in **Figure 1** below.

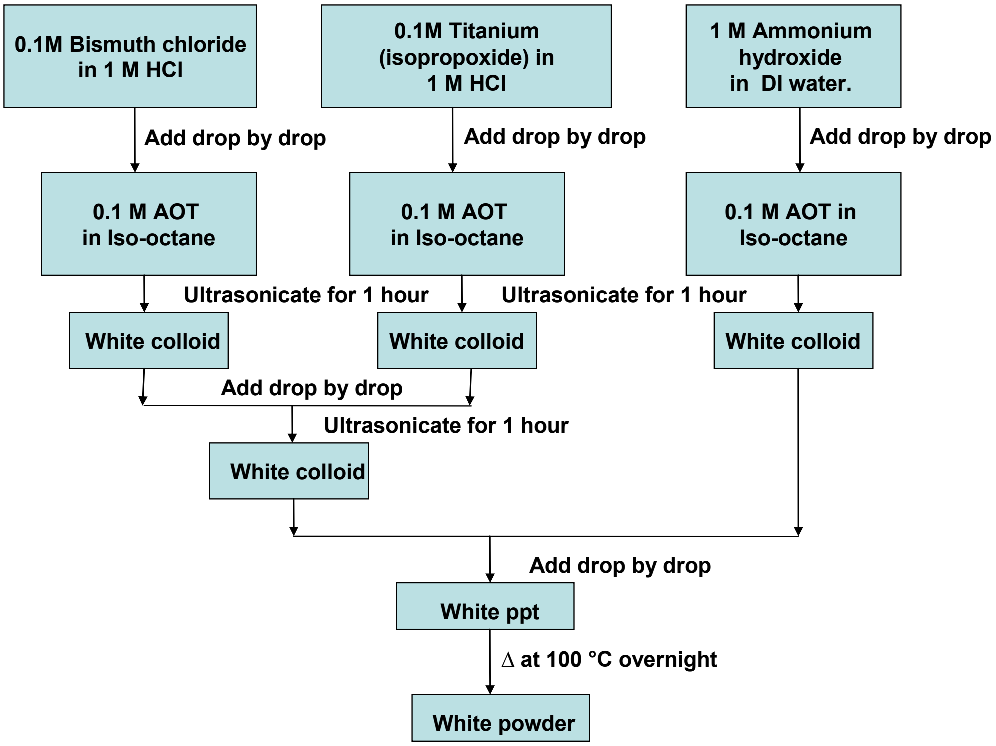
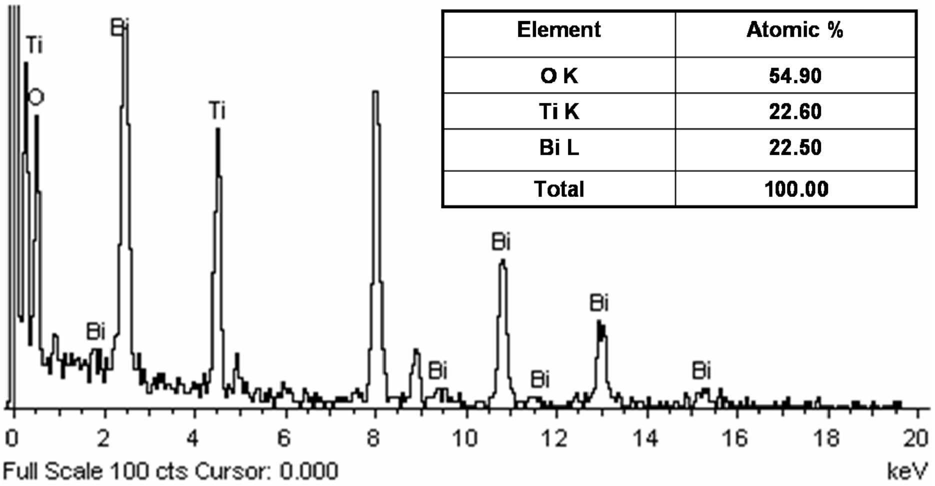


Figure 1: Schematic representation of a reverse micellar method for bismuth titanate pyrochlore synthesis.

2 Characterization of bismuth titanate pyrochlore

X-ray diffraction (XRD) was performed using a Philips APD 1740 system equipped with a graphite crystal monochromator and CuKα radiation (λ=1.54Å) between the ranges of 20° to 80° = 2θ. XRD was carried out using specially obtained polished quartz cut 6° from (0001) crystal plane with a cavity of dimension 3mm diameter and 1 mm depth (Gem Dugout X-ray Diffraction Products). A field emission-scanning electron microscope (FESEM, Hitachi, S-4700) was used to analyze the morphology of BTO with an accelerating voltage of 20 kV. High resolution transmission electron microscopic studies (HRTEM, JEOL 2100F) with selected area electron diffraction (SAED) and Fast Fourier Transformation (FFT) were performed at 200 kV to determine the morphology and the crystal phase. Parts of the results are shown below in **Figure 2** and **3.**



Element	Atomic %
O K	54.90
Ti K	22.60
Bi L	22.50
Total	100.00

Figure 2. HRTEM-EDS spectrum of BTO pyrochlore nanorods formed after calcination at 650 °C in oxygen.

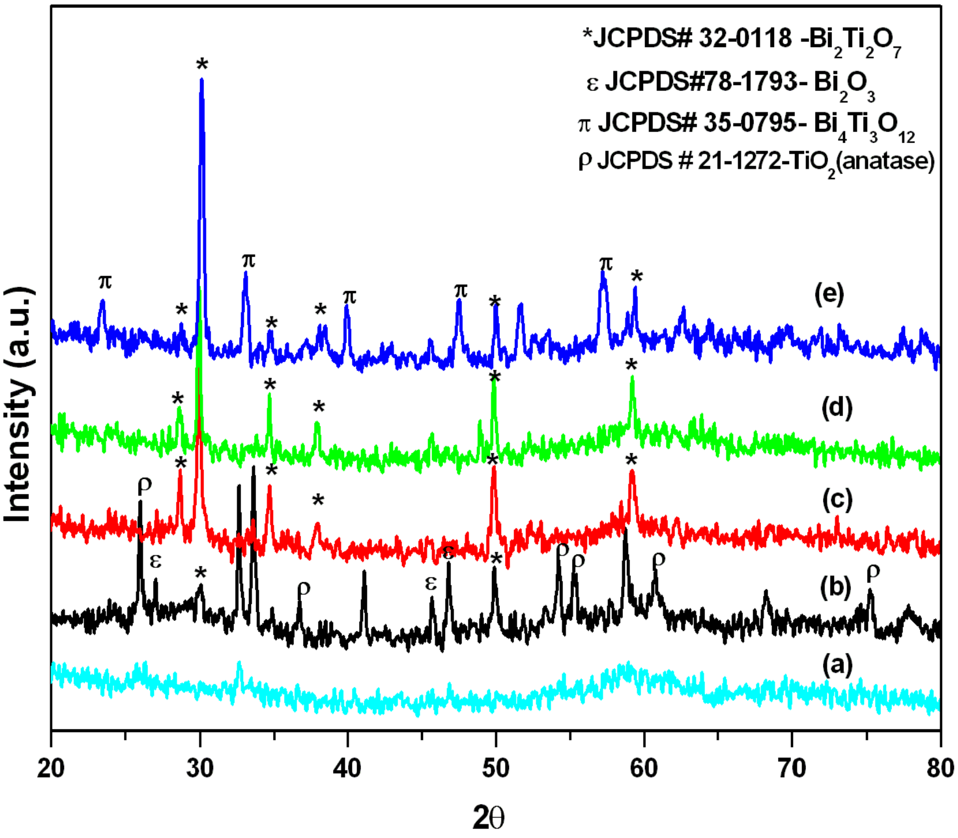


Figure 3. XRD of the heat treated material after different calcination temperature (a) uncalcined sample, (b) calcined at 500 °C (c) calcined at 650 °C (d) calcined at 750 °C and (e) calcined at 900 °C in oxygen atmosphere.

3 Computational model and methodology

The analysis of the electronic property of the BTO has been performed by using a plane wave based Density Functional Theory (DFT) calculations. CASTEP program present in the Materials Studio® package supplied by Accelrys® was used for modeling. Plane wave functionalized ultrasoft pseudopotentials were used with a kinetic energy cutoff of 300 eV. The Generalized Gradient Approximation (GGA) with Perdew-Wang exchange and correlation functional (PW91) has been adopted. BTO with a pyrochlore crystal structure has been obtained from ICSD (ICSD# 413013). All the BTO properties have been calculated by utilizing a primitive unit cell of the BTO pyrochlore crystal structure. To compare the properties of BTO, anatase TiO_2 (ISCD#. 82080) has been considered as a standard. The model estimates are shown in **Figure 4** below.

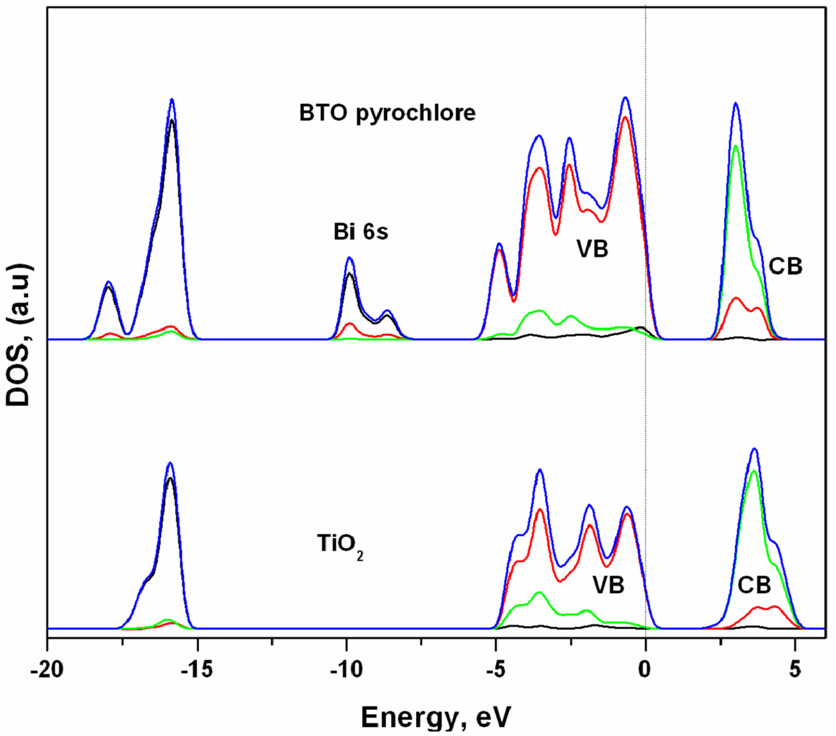


Figure 4. Partial density of states (PDOS) determined from the DFT calculation of BTO pyrochlore and TiO_2 anatase.

4 Photocatalysis:-Water splitting

Light source

The following is the general information about the light source used for photocatalytic water splitting reactions.

- Light source: Commercial immersion-type medium pressure quartz mercury vapor UV-vis lamp
- Company: Ace glass
- Contact info of lamp vendor: Phone: 1-800-223-4524, website: aceglass.com
    - The website has a .pdf of the brochure that contains the details of the light source.

Light type	**Wavelength range (nm)**	**Energy output (W)**	**% of energy output**
Far UV	220-280	27	15.4
Middle UV	280-320	28.7	16.3
Near UV	320-400	28	15.9
Visible	400-600	75.7	43.1
Infrared	1000-1400	16.4	9.3
Total		**175.8**	**100**

- Part number for the lamp: 7825-34

Details of the light output from the lamp

It is to be noted that the lamp emits both UV as well as visible light.

Experiment details

This section includes the details of the reactor, experimental procedure, and the measurement technique.

Reactor: Photo catalytic hydrogen generation experiments were performed in a slurry type photochemical reactor supplied by Ace Glass, Vineland, NJ as shown in the **figure 5**. The part number of the complete reactor setup is 7840-340. The major parts of the setup include a reactor, a concentric quartz tube (part # 7854) that fits inside the reactor and is designed to circulate water for maintaining the temperature of the reaction mixture, and a power source. The cooling water flows between the lamp and the contents of the reactor. Other parts are labeled in **figure** 5.

Experiment procedure: 150 mg of the photocatalyst (BTO as well as TiO_2) was weighed and introduced into the reactor. 300 ml of methanol-water mixture was prepared in the ratio of 1:5. Similar mixtures of water and methanol have been used earlier to examine the water splitting ability of a photocatalyst.[1] The reaction mixture was bubbled with nitrogen for 30 min to remove dissolved oxygen before illuminating the system. The lamp (details given above) was introduced into the annulus of the reactor at the location shown in **figure 5**. Cold tap water was circulated around the lamp between to maintain the temperature of the reaction.

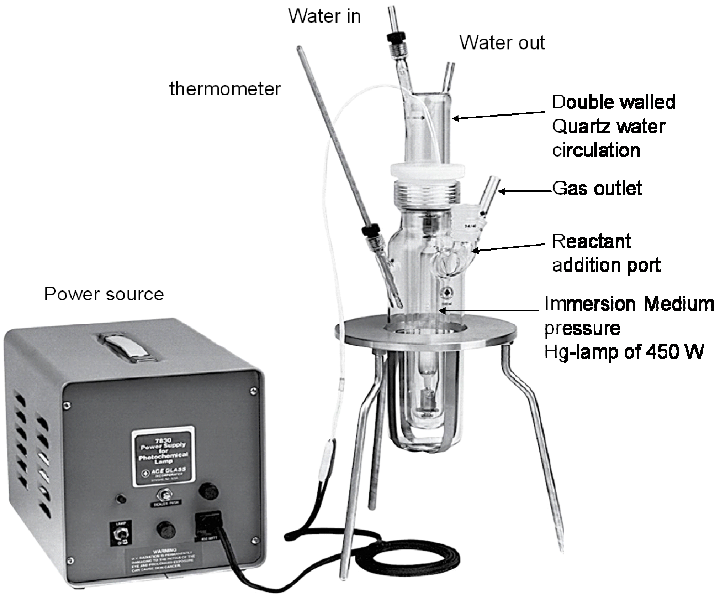


Figure 5. Photochemical reactor set up used to study the hydrogen evolution reaction. (Source: Ace Glass, Vineland, NJ)

Measurement details: The gases evolved were collected through the outlet of the reactor. A gas sampling tube with a rubber cork was used to collect gas from the outlet. A gas chromatograph (GC) was used to identify the gases evolved. The GC was calibrated using high purity (>99.995) hydrogen. The collected gas was analyzed using a HP 6890 GC system with a TCD detector. A precision Hamilton® needle was used to remove representative sample of the gas from the sampling tube and injected into the GC.

A molecular sieve capillary column HP-PLOT 5A, 30m, 0.32mm, 25µm was used to determine the concentration of hydrogen.

5 Photocatalysis: - Environmental remediation

Photodegradation experiments were performed by coating the photocatalysts (BTO power or Degussa P 25 TiO_2) on an indium tin oxide (ITO) covered glass slide. Before coating, the ITO glass slides were washed thoroughly with DI water followed by ultrasonication in iso-propyl alcohol for 15 min. Conducting side of the cleaned ITO glass slides were coated with a solution prepared by mixing ethylene glycol (10 mL), ethanol (5 mL), polyvinylpyrrolidone (5 mg), and 10 mg of photocatalyst. The photocatalyst coated ITO glass slides were dried and annealing in oxygen for 3 h at 500 °C to remove any organic molecules. This makes a uniform film coating of the photocatalyst on ITO. A similar procedure was adopted to coat Degussa-P25 in an earlier report.[2] The photoactivity of the Degussa P25 film was compared with the photo degradation activity of BTO films using 20µM methyl orange in DI water as a test compound. The use of MO as a test compound has been reported in other literature [3] including our past work as well.[4] The setup used for performing the photodegradation experiments in described in detail in an earlier work (reference 2a and 4). A 405 nm cutoff filter purchased from Newport Corporation was used to examine the effects of visible light illumination. Photocatalytic degradation of MO as a function of time is shown in **Figure 6** below.

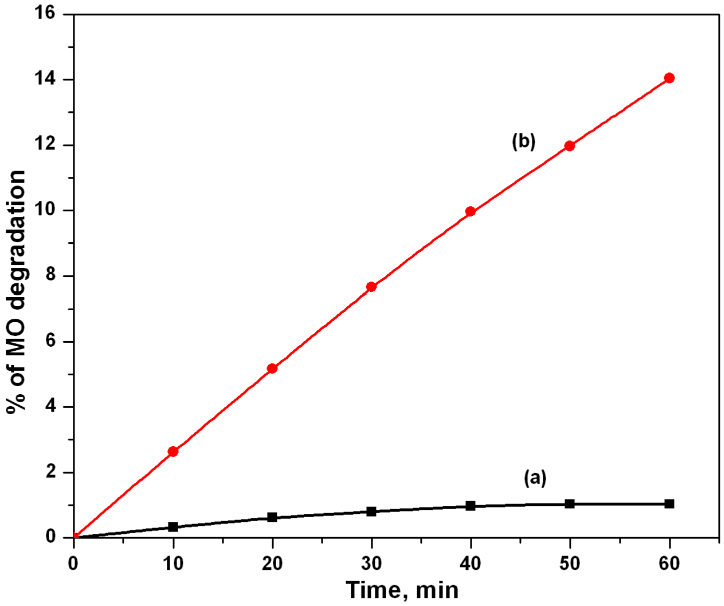


Figure 6. Photodegradation of MO in the presence of visible light (λ≥ 405 nm) illumination and photocatalyst films prepared on ITO using (a) Degussa P25 TiO_2 and (b) BTO nanorods.

Additional references:

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