DEFECT ENGINEERING FOR IMPROVED PHOTOCATALYTIC PERFORMANCE OF REDUCED LEAD TITANATE (PbTiO$_3$) UNDER SOLAR LIGHT IRRADIATION

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ABSTRACT. Lead titanate (PbTiO$_3$) nanoparticles were prepared successfully by template free hydrothermal method. Size, crystallinity, morphology and phase determination of the nanoparticles were made by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and field-emission scanning electron microscopy (FESEM). FESEM results had shown that all nanoparticles were in the range between 20 to 40 nm size and found in the form of agglomerates. The average crystallite size of PbTiO$_3$ nanoparticles was calculated to be nearly 35 nm. PbTiO$_3$ nanoparticles were reduced by hydrogenation at high temperature to make the material active for visible light. Furthermore, optical absorbance of PbTiO$_3$ nanoparticles was determined by applying ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy. By using Davis-Mott model, the direct optical band gap of 2.65 eV was acquired. Methyl orange (MO) was used as pollutant to check the photocatalytic activity of reduced PbTiO$_3$ nanoparticles under solar light irradiation. Photocatalytic activity of reduced PbTiO$_3$ nanoparticles increased 2.6 times more than that of pure PbTiO$_3$ nanoparticles for methyl orange (MO) under solar light irradiation.

KEY WORDS: Lead titanate (PbTiO$_3$), Photocatalytic performance, Hydrothermal growth, Solar light, Irradiation

INTRODUCTION

Recently, efforts have been made for the progress of functional nanomaterials, which can introduce new opportunities for the development of functional nanostructures. Oxide based functional materials such as zinc oxide (ZnO) and titanium dioxide (TiO$_2$) has been investigated intensively for its various applications in chemical sensors, photocatalytic reactions, and energy conversion fields [1-4] because of their low cost advantages and non-toxicity. During the past few decades, TiO$_2$ has been considered as a photocatalyst for the degradation of organic pollutants for environmental applications after the discovery of decomposition of water into oxygen and hydrogen by Fujishma and Honda in 1972 for the first time [5].

A critical drawback of titania, however, is that it has a large band gap (3.2 eV), which limits its activity under UV light. UV light is only the 3-5% of solar light. Efforts have been made to tune the band gap of titania to make it responsive for visible light spectrum which is 50% of the solar light. Doping of metal and non-metal ions are considered as a strong tool for reducing the band gap of TiO$_2$ [6-10]. Metal ions with oxidation state less than Ti$^{4+}$ such as B, Al, Sb, etc causes to produce the acceptor levels just above the valance band while doping of some non-metal ions such as carbon and nitrogen also causes to introduce the acceptor energy levels above the valance band. Doping of transition metal ions produces the energy levels just below the conduction band such as V$^{5+}$, F$^{-1}$, etc [11, 12]. New energy states in the form of acceptor levels...
or donor levels causes to reduce the band gap which extends the activity of TiO$_2$ for visible region. Another, technique for reducing the band gap of TiO$_2$ is to reduce the T$^{+4}$ to Ti$^{+3}$. Reduction of T$^{+4}$ to Ti$^{+3}$ produces a donor level just below the conduction band. To get complete control over the reduction of T$^{+4}$ to Ti$^{+3}$ is a great challenge for researchers. Mainly, hydrogenation of TiO$_2$ nanoparticles plays a key role for the reduction of T$^{+4}$ to Ti$^{+3}$ and produces black TiO$_2$ with band gap of nearly 1.54 eV [13] which is responsive under visible region of electromagnetic spectrum. Hydrogenation of TiO$_2$ is done under high temperature and pressure while hydrogen is highly flammable gas and it has limitations for industrial application of TiO$_2$.

More recently, composites of TiO$_2$ with low band gap materials were prepared and used for photocatalytic performance. Composites of TiO$_2$ with low band gap materials such as CdS, CdSe, CuO, CuS causes to improve the photocatalytic response under visible light irradiation and UV light [14-18]. Composites of such materials were prepared with different morphologies, core-shell structures, nano wires, nano tube, nano rods etc.

Another challenge, which reduces the performance of TiO$_2$, is its high electron-hole recombination rate which limits its activity. In order to inhibit the electron-hole recombination, TiO$_2$ is coated with p-type materials such as CuO, NiO, SnO [19-22], etc. These composites inhibit the electron-hole recombination rate and improve the photocatalytic performance of TiO$_2$ nanoparticles.

Titanates have been neglected for investigation of its photocatalytic performance because of its complex structure and large band gap. However, these have been studied for electrical, optical and piezoelectric properties [23, 24]. According to our knowledge, few reports have been published on SrTiO$_3$, ZnTiO$_3$, and FeTiO$_3$ for their photocatalytic properties [25, 26]. Meidan et al., have reported the garden like superstructure of SrTiO$_3$ synthesized by hydrothermal method and showed super photocatalytic behavior for degradation of pollutant such as methyl blue (MB) [27]. Kong et al., have reported the preparation of ZnTiO$_3$ powder and investigated the photocatalytic performance of the material [25]. We prepared PbTiO$_3$ by hydrothermal synthesis and tuned its band gap (2.65 eV) as low as responsive for visible light region by hydrogenation. In literature band gap of PbTiO$_3$ is reported from 3 eV to 4.5 eV [28, 29] experimentally while theoretically it is calculated upto 1.7 eV [30]. To the best of our knowledge, no single report has been published on photocatalytic performance of PbTiO$_3$ yet [27]. Moreover, we investigated the photocatalytic performance of PbTiO$_3$ nanoparticles for methyl orange (MO) under solar light.

**EXPERIMENTAL**

**Sample preparation**

Pure PbTiO$_3$ nanoparticles were prepared by template free hydrothermal method. Pb(OH)$_2$, Titanium tetra isoproxide (TTIP), diethanol amine (DEA) and distilled water H$_2$O were used as preliminary materials. 40 mL of 0.45 M solution of Pb(OH)$_2$ was obtained by dissolving 4.3417 g Pb(OH)$_2$ under constant stirring for 10 min at 60 $^\circ$C. Similarly, another 0.45 M solution of TTIP was prepared. The solution concentration is maintained at 0.5 M and the molar ratio is kept at 1.0 for diethanolamine (DEA) to titanium tetra isoproxide (TTIP). Homogeneous mixture of these solutions was obtained by mixing and stirring these two solutions for two hours at room temperature. The Teflon lined stainless autoclave is used for the template free hydrothermal method by transferring the homogeneous solution inside the autoclave which is heated at 180 $^\circ$C in oven for 24 hours. After the completion of reaction, the obtained precipitates were washed several times with the deionized water and ethanol through centrifuge, and then dried at 80 $^\circ$C for 12 hours in oven. The prepared lead titanate nanoparticles were reduced by hydrogenation. White lead titanate powder was heated at 500 $^\circ$C for three hours under the constant flow of hydrogen gas to get black colored powder.

*Bull. Chem. Soc. Ethiop. 2019, 33(2)*
Photocatalytic performance of reduced lead titanate (PbTiO$_3$) 375

Characterization

X-ray powder diffraction analysis was conducted on a Rigaku D/MAX-RB X-ray diffractometer (XRD), using CuKα radiation (λ = 1.54056 Å) to investigate the crystal structure of synthesized material. Morphological details of prepared samples were investigated by using field emission scanning electron microscopy (FE-SEM) (Zeiss-SUPRA55). Energy dispersive X-Ray Spectroscopy (EDX) equipped with FESEM was used to measure the elemental compositions of the synthesized material. Band gap of pure PbTiO$_3$ and reduced PbTiO$_3$ was measured by using UV-Vis spectro-photometer (Jasco V-570).

Photocatalytic activity

Photocatalytic performance of PbTiO$_3$ and reduced PbTiO$_3$ was measured by the degradation efficiency of methyl orange (MO) under solar light irradiation. For performing the photodegradation experiments, 50 mg samples of powder was suspended in 200 mL of 10 mg/L solution of MO in 250 mL reactor. A 500 Watt Xenon lamp was used as a source of solar light. Spectrophotometer is used to measure the UV-Visible absorption spectrum of the filtered solution. Area of adsorption band in the range of 200 to 800 nm was integrated to monitor the reaction process. Degradation of the pollutant at any time was analyzed and measured by C/Co where Co gives the maximum absorption intensity at zero time and C shows the absorption intensity at time “t”.

RESULTS AND DISCUSSION

Figure 1(a) depicts the XRD pattern of PbTiO$_3$ and reduced PbTiO$_3$ nano particles prepared by hydrothermal method. All the diffraction peaks of XRD graph, shown in Figure 1(a), are well matched to the tetragonal structure of PbTiO$_3$ (JCPD file # 06-0452). Good crystallinity of prepared material can be observed from the sharpness of the diffraction peaks. Furthermore, absence of any characteristic peak corresponding to the impurity ensures the purity of synthesized material. Debye-Sherrer formula [31] was used to measure the crystallite sizes of PbTiO$_3$ structure. The average crystallite size of synthesized materials is estimated to be 35nm.

Figure 1. (a) XRD pattern of PbTiO$_3$ nanoparticles and (b) EDX spectra of PbTiO$_3$ nanoparticles.

Bull. Chem. Soc. Ethiop. 2019, 33(2)
Figure 1(b) shows the EDX pattern of PbTiO$_3$ nanoparticles. EDX graph confirms the presence of Pb, Ti and O elements. Absence of any impurity peak in the EDS patterns confirms the purity of synthesized material. Atomic weight percentage of Pb, Ti and O atoms confirms the formation of PbTiO$_3$. Atomic weight ratio between Pb to Ti and O atoms is 1:1.02 and 1:3.4 respectively. As oxygen ratio is not taken accurate by EDX analysis due to experimental limitations.

Morphology of the nanoparticles is studied by field FESEM. Figure 2 represents the FESEM images of the PbTiO$_3$ and reduced PbTiO$_3$ nanoparticles synthesized by hydrothermal method. It can be observed that all the nanoparticles are in the size ranging from 20 to 40 nm. Figure 2(a-b) represent that all PbTiO$_3$ nanoparticles are in the form of agglomerates. Figure 2(c-d) represents the FESEM images of hydrogenated PbTiO$_3$ nanoparticles which are also in the form of agglomerates but little dispersed as compared to PbTiO$_3$ prepared by template free hydrothermal method and in the range of 20 to 40 nm.

![Figure 2. FESEM images of PbTiO$_3$ nanoparticles.](image)

Figure 3(a) shows the UV-visible absorption spectrum for reduced PbTiO$_3$ nanoparticles. It can be observed from the UV-graph that PbTiO$_3$ nanoparticles shows absorption in the visible light region. Absorption in the visible region indicates that PbTiO$_3$ nanoparticles have become...
visible light active material. It confirms the reduced form of PbTiO$_3$ on annealing at high temperature in hydrogen atmosphere. Optical band gap of the PbTiO$_3$ nanoparticles was investigated at room temperature by UV- vis-NIR- spectroscopy. Tauc and Davis Mott model is used to measure the band gap of reduced PbTiO$_3$ nanoparticles [32].

![Figure 3](image1.png)

Figure 3. (a) UV-visible spectra for reduced PbTiO$_3$ nanoparticles, (b) Band gap calculations for reduced PbTiO$_3$ nanoparticles.

Normally, PbTiO$_3$ has large band gap (3-4.5 eV) which is active in the UV-light region. Reduced PbTiO$_3$ induces oxygen vacancies. Each oxygen vacancy provides two free electrons [33]. These free electrons reduce the nearest Ti$^{4+}$ to Ti$^{3+}$. Reduction of Ti$^{4+}$ to Ti$^{3+}$ induces donor levels just below the conduction band. Formation of these new energy levels inside the band gap causes to reduce the active band gap of PbTiO$_3$ to 2.65 eV which is active in the visible light region. Figure 3(b) shows the band gap calculation for PbTiO$_3$ nanoparticles which is estimated to 2.65 eV. In literature band gap of paraelectric cubic PbTiO$_3$ is reported from 3 to 4.5 eV [23, 24] experimentally while Piskunov et al. have reported best calculated band gap 1.7 eV [25]. The band gap value calculated in this work is quite near to the ever best theoretically calculated band gap value, 1.7 eV. Figure 4 represents the schematic diagram for the formation of new energy levels just below the conduction band due to the reduction of Ti$^{4+}$ to Ti$^{3+}$.

![Figure 4](image2.png)

Figure 4. Schematic diagram for PbTiO$_3$ and reduced PbTiO$_3$. 
Low band gap value of prepared PbTiO$_3$ nanoparticles makes the material suitable for photocatalytic applications. PbTiO$_3$ nanoparticles are mostly studied for their piezoelectric effect. Very few reports have been presented for the study of its photocatalytic activity. It has been neglected for a long period of time for its photocatalytic performance because of its large band gap of 3 to 4.5 eV [23, 24].

Figure 5(a-c) represents the photocatalytic degradation of methyl orange (MO) without catalyst, with PbTiO$_3$ nanoparticles and reduced PbTiO$_3$ nanoparticles under solar light irradiation. Figure 5(d) shows the curve of C/Co versus time which indicates that methyl orange degraded to 80% within 75 min under solar light irradiation for reduced PbTiO$_3$ and photocatalytic performance of hydrogenated PbTiO$_3$ increased due to the formation of new energy levels inside the band gap of PbTiO$_3$ under solar light irradiation. Photocatalytic performance has improved up to 2.6 time more than that of pure PbTiO$_3$ nanoparticles.

**CONCLUSION**

PbTiO$_3$ nanoparticles are prepared by template free hydrothermal method. Nanoparticles are characterized by XRD, FESEM and EDX. Calculated band gap of PbTiO$_3$ nanoparticles is nearly 2.65 eV which correspond to the visible region. Low band gap of PbTiO$_3$ nanoparticles make the material photoactive under visible light which degraded the methyl orange to 80% within 75 min under solar light irradiation and photocatalytic performance of reduced PbTiO$_3$ improves 2.6 times more than that of pure PbTiO$_3$ nanoparticles. Such materials can be synthesized and used for photocatalysis as well as water splitting for hydrogen production.

Bull. Chem. Soc. Ethiop. **2019**, *33*(2)
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