Photocatalytic Behavior of Ferroelectric Materials: Comparative Study of BaTiO\(_3\) and Ag-loaded BaTiO\(_3\) for Wastewater Treatment

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Abstract. This work investigated the photocatalytic-induced degradation of organic dyes in the wastewater using barium titanate (BaTiO\(_3\)) supported silver (Ag) metal particles. BaTiO\(_3\) ceramics were synthesized using a solid-state reaction route. Ag metal was loaded on BaTiO\(_3\) particles using silver nitrate and polyethylene glycol reagents at room temperature without heat and light source. Ag-loaded BaTiO\(_3\) powder was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Ag-loaded BaTiO\(_3\) powder showed more degradation of Rhodamine B (RB) dye as compared to BaTiO\(_3\) powder. Around 95.05, 94.75, and 94.5% of RB dye degradation were observed within 180 min under visible light during the first, second, and third photocatalytic cycles. The photon-induced strong surface plasmon resonance (SPR) effect of Ag metal has played a critical role in the induction of visible light photocatalysis in Ag-loaded BaTiO\(_3\) powder.

Keywords: Photocatalysis, Rhodamine B, Ferroelectric, Silver, BaTiO3

1. Introduction

Water utilities worldwide are struggling with deteriorating water quality and quantity in the face of tightening regulation and heightened demand [1]. Water quality (pollution) is currently a major environmental issue in India [2]. One of India’s primary reasons for water pollution is untreated sewage, the largest water pollution source [3]. The second primary reason most rivers, lakes, and surface water pollution is due to industries and agricultural run-off [4]. Researchers have found that untreated sewage discharge is the most critical source of surface and groundwater pollution [5]. There is a considerable gap between the generation and subsequent treatment of wastewater. Thus, worldwide wastewater generated is approximately 80% of water supplied by various different sources. India accounts for 18% of the world population and 4% of world water resources. The country’s only 30% water is recycled remaining water is taken from the surface or the ground [6, 7]. However, the population’s dependence on water is not regularly circulated. For this, we must develop cost-effective and environment-friendly techniques [7, 8].

Dyes are produced and used in the textile, printing, paper industries, and coloring many other materials. It chemically bonds on the substrate surface [9]. They can be defined as substances...
that generate color when applied to these substrates. It also temporarily changes the crystal structure of elements. They stick to the well-matched surface by using a water solution. They create covalent bonds with salts or metals. Uses techniques are either physical adsorption or mechanical retention techniques [10]. Dyes are categorized based on their chemical structure, uses, and the groups of atoms (chromophores) present in the dye. The chromophores are diverse functional groups determining the color and defining the dyes’ behavior, such as aril methane, azo, methane, nitro, and anthraquinone. Nowadays, many practical solutions are available to this severe problem, but photocatalysis is a very effective technique because this is non-toxic, economical, and renewable [11]. This catalyst has one more capability: the catalyst used can be reused just by cleaning it again. In this method, the visible rays of solar light energy are employed on the solution as an energy source that is green and clean, and this is also safe to use; these are abundant in the amount [12]. Now the big question that comes to mind that how we can exploit these solar energies. These are freely available energy, so the synthesis of natural and artificial photocatalysts comes into the picture. Because it attracted the world with tremendous and cost-effective activities, it has fascinated significant scientific interests in the world as a whole [13, 14]

Recently it has been observed that ferroelectric materials have shown photocatalytic performance due to the presence of an internal field, which restricts the recombination of electron-hole pair [15]. BaTiO$_3$ is one of the promising ferroelectric materials [16]. The photocatalytic performance of BaTiO$_3$ can be observed in the presence of UV light [17]. UV light has a drawback limiting its use in water cleaning [18, 19]. UV light can ensure cancer; thus, it can be avoided for water cleaning applications [20]. Therefore the photocatalytic activity in visible light can also be improved by morphology change deposition of noble metals, heterostructures construction, and doping of transition metal, composite, etc. [21–23].

Photocatalysis is visible light obtained by using noble metal (Au, Ag, etc.) [24]. Due to the significant broadening of the light absorption range, Noble metals display SPR [25, 26]. This further load to photocatalysis and the deposition of noble metal restricts the electron/hole pair’s recombination, enhancing the photocatalytic performance [27]. However, the low cost and ease of availability, and simple method to load on catalyst bring silver (Ag) one of the most satisfactory photocatalysis candidates [28, 29].

The various methods have been generally used to load Ag NPs, such as photoreduction [30, 31], conventional calcination, and impregnation chemical reduction methods, which act as external energy for heating. Luo et al. [32], proposed a novel way of loading Ag NPs on BaTiO$_3$ ceramic particles at room-temperature without imposing light or heat. The authors mentioned that BaTiO$_3$ particles exhibit a catalytic reduction of Ag$^+$ ethylene glycol solution from this research point of view. We have adopted this method of loading Ag$^+$ nanoparticles.

2. Methods

BaTiO$_3$ powder was synthesized through the solid-state reaction process [33]. In this process, the oxide powder of BaCO$_3$ and TiO$_2$ were weighed according to stoichiometric molar ratios. These powders were mixed and well-grounded in an agate mortar using acetone medium for 30 min. After this, the dried homogenous powder was calcined at 1100°C for four h in the Nabertherm furnace. Ag-loaded BaTiO$_3$ was synthesized using the method mentioned in reference [32]. In this method, 2g of each BaTiO$_3$ and AgNO$_3$ were added into 100 ml of polyvinyl glycol. The suspension was stirred using a magnetic stirrer for 12 h to obtain Ag loading on BaTiO$_3$. After this, Ag-loaded BaTiO$_3$ powder was filtered out using filter paper. The powder was thoroughly washed at least ten times and then dried in an oven at 150 C for two hours.

The phase of the sample was examined by the X-ray diffraction (XRD) technique using the Rigaku diffractometer (Rigaku Smart Lab, Japan) by which the pattern was collected for $2\theta$ range from 20° to 80° with the scanning rate of 2°/min. The microstructure was observed with
a scanning electron microscope (SEM; model JSM 7800F, JEOL, Tokyo, Japan). During the photocatalysis experiment, Rhodamine B (RB) dye solution was prepared in deionized water. RB dye was used as a model dye. The initial dye concentration was taken five mg/L. 10 ml dye solution was taken in a beaker, and a sample of 0.2g of sample was added to the dye solution. The beaker was irradiated with visible light during photocatalytic experiments under constant stirring at 500 rpm. Before performing the photocatalysis experiment, the adsorption equilibrium was achieved between dye solution and sample by placing the sample under dark for 24 h. During photocatalysis, the test samples were collected every 30 min. These samples were tested under the UV visible spectrophotometer to record the dye solution’s corresponding absorbance value. The percentage of degradation was found by using the following formula [34].

\[ \text{Degradation \%} = \left( 1 - \frac{A}{A_0} \right) \times 100 = \left( 1 - \frac{C}{C_0} \right) \times 100 \]

Where \( A_0 = \text{Initial Absorbance} \), \( A = \text{Absorbance at time } t' \)
\( C_0 = \text{Initial Concentration} \), \( C = \text{Unknown Concentration} \)

### 3. Results

XRD patterns of both samples (BaTiO\(_3\) and Ag loaded BaTiO\(_3\)) are provided in Figure 1. XRD peak positions observed in both samples are precisely matched to the perovskite structure of BaTiO\(_3\) according to JCPDS File No. 01-087-0719. In Figure 1, no other addition peak in the XRD pattern revealed the non-existence of any impurity phases. Ag’s peaks were also not observed in the XRD of Ag loaded BaTiO\(_3\) powder, which may be due to Ag metal’s low loading content on BaTiO\(_3\) particles.

![Figure 1. XRD of BaTiO\(_3\) and Ag-loaded BaTiO\(_3\)](image)

The morphology of BaTiO\(_3\) powder and Ag-loaded BaTiO\(_3\) powder is shown in Figure 2(a–b). The grain morphology of BaTiO\(_3\) was random, as shown in Figure 2(a); however, the loaded Ag particles can be observed on BaTiO\(_3\) particles as shown in Figure 2(b).
Figure 2. SEM image of BaTiO$_3$ and Ag-loaded BaTiO$_3$

The visible light was used for the photocatalysis experiment to photoexcite the BaTiO$_3$ and Ag-loaded BaTiO$_3$ powder samples. Figure 3(a) showed the decrease in absorbance peak intensity of RB dye with an increase in irradiation time using Ag loaded BaTiO$_3$ powder sample, which indicated the promising dye degradation capability of Ag loaded BaTiO$_3$ powder sample. For the same irradiation time, the dye degradation with BaTiO$_3$ powder and without any sample cases is shown in Figure 3(b).

Figure 3. (a)(b) Photocatalysis performance of BaTiO$_3$ and Ag/BaTiO$_3$ ceramics

This indicated that Ag loaded BaTiO$_3$ sample possessed significantly higher dye degradation capability than two other control samples. Thus, it can be concluded that the loading of Ag metal particles has a critical role in increasing dye degradation capability. Maximum 95.5% dye degradation was recorded with Ag loaded BaTiO$_3$ sample under 180 min of visible light irradiation. A slight drop was recorded in the repeatability test of Ag loaded BaTiO$_3$ powder sample (maximum of 2%) after five photocatalysis cycles, as shown in Figure 4. Even after the 5$^{th}$ cycle, Ag loaded BaTiO$_3$ sample powder gave 93% of dye degradation. This showed that the dye degradation performance of the Ag-loaded BaTiO$_3$ sample is repeatable.
4. Discussion
The transfer of an electron from the valence band to the conduction band of BaTiO$_3$ is not possible, as the bandgap of BaTiO$_3$ lies in the ultraviolet (UV) region, and here the visible is provided.

![Figure 4](image_url)  
**Figure 4.** Repeatability graph of photocatalysis of Ag/BaTiO$_3$

The surface plasmon resonance (SPR) effect has been widely reported in the case of Ag metal, due to which hot electrons are produced from Ag metal. These electrons can directly transfer from Ag metal to the conduction band of BaTiO$_3$ ceramic and subsequently can reduce adsorbed oxygen (O$_2$) to superoxide (•) radical. Similarly, the holes present in the valence band of BaTiO$_3$ and/or Ag metal can oxidize adsorbed water (H$_2$O) to hydroxyl (• OH) radicals. These and • OH subsequently decomposed the RB dye into degradation products.

To further study, photocatalysis effects were explored by using the RB dye.

5. Conclusion
In this work, ferroelectric barium titanate ceramic was fabricated via a solid-state reaction route and loaded with Ag metal particles. Ag-loaded BaTiO$_3$ sample gave remarkable dye degradation performance under visible light irradiation, and the dye degradation performance of Ag-loaded BaTiO$_3$ was found to be repeatable.

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