Original Article

Ionic liquid assisted hydrothermal synthesis of TiO$_2$ nanoparticles: photocatalytic and antibacterial activity

Kristappagari Manjunath$^a$, Lakshmi Sagar Reddy Yadav$^{b,c}$, Thummala Jayalakshmi$^b$, Viswanath Reddy$^d$, Hanumanthappa Rajanaika$^e$, Ganganagappa Nagaraju$^{b,*}$

$^a$ Centre for Nano and Material Sciences, Jain University, Kanakapura, Karnataka 562112, India
$^b$ Department of Chemistry, Siddaganga Institute of Technology, Tumkur 572103, India
$^c$ Department of Chemistry, BMS Institute of Technology, Bangalore 560064, India
$^d$ Department of General Education, Gulf Medical University, Ajman, UAE
$^e$ Department of Biotechnology, Tumkur University, Tumkur 572101, India

ABSTRACT

In this work, anatase phase TiO$_2$ nanoparticles have been successfully synthesized at 130 °C for 2 days via ionic liquid-assisted hydrothermal method. The obtained products were characterized using various analytical techniques. X-ray diffraction data reveals that sample has anatase TiO$_2$ nanoparticles. FTIR spectrum shows that the presence of ionic liquid and indicates Ti-O-Ti peak at around 456 nm and the bands at 1410 and 1581 cm$^{-1}$ indicates C–H in-plane vibrations and stretching of imidazolium ring. UV–Vis spectrum shows maximum band at 272 nm due to TiO$_2$ nanoparticles. SEM images show the TiO$_2$ nanoparticles are almost spherical in shape. TEM images reveal that the average diameters of TiO$_2$ nanoparticles are in the range of 35 nm. TiO$_2$ nanoparticles exhibited excellent photocatalytic activity for the degradation of methylene blue organic dye. Furthermore, the antibacterial properties of TiO$_2$ nanoparticles were investigated against four bacterial strains using the agar well diffusion method.

© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Nanostructured TiO$_2$ as a promising catalyst in the photodegradation of most pollutants in water and air have been extensively studied mainly due to its superior ability of destruction of organic contaminants [1]. It is well known that the properties of nanomaterials majorly depend on their structure and morphology. Now-a-days, synthesis of nanostructures with novel morphologies and functional properties have recently been attracted tremendous attention [2–4]. Generally, nanomaterials are synthesized using molecular solvents such as organic solvents and water. Amongst, only a limited number of molecular solvents can be used and some

* Corresponding author.
E-mail: nagarajuyn@rediffmail.com (G. Nagaraju).
https://doi.org/10.1016/j.jmrt.2017.02.001
2238-7854/© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
organic solvents cause environmental pollution [5]. Various methods are available to prepare TiO$_2$ based nanoparticles, such as sol–gel, solvothermal, sonochemical, hydrothermal, chemical vapor deposition, electro-deposition, physical vapor deposition, combustion etc. [6–11]. Here, a different trial has been used which is one of the soft solution method compared to other methods using ionic liquids (ILs) as solvents via hydrothermally.

Over the past two decades, ILs have attracted tremendous attention due to their physical and chemical properties such as low boiling point, large electrochemical window, high thermal stability, negligible vapour pressure, non-volatile and high ionic conductivity [12]. An important aspect of the interaction of ILs with nanoparticle precursors involves the nucleation and growth of nanoparticles. Literature says that, ILs have been successfully used as a reaction media for the synthesis of TiO$_2$ nanomaterials. The most attractive property of ILs for the synthesis of TiO$_2$ nanoparticles is the surfactant-like nature, which inhibits the aggregation of the resultant nanoparticles [13]. Furthermore, the fine-tuning ability of the reactants composition benefits the shape and size controlling over the TiO$_2$ nanoparticles. The above mentioned unique properties of IL make the reactions to conduct in open reactor. The term ‘ionothermal’ has been used to describe reactions that are conducted in ILs at high temperature with ambient pressures. As a result, ionothermal reactions avoid high pressure of hydrothermal or solvothermal reactions and eliminate safety problems related to high pressure [14]. Zhou et al. fabricated macroporous TiO$_2$ architectures via the spontaneous self-assembly of mixture of octadecene and 1-alkyl-3-methyl imidazolium-based ionic liquid as the reaction medium [15]. Nagaraju et al. synthesized ionic liquid-assisted hydrothermal synthesis of TiO$_2$ nanoparticles and its application in photocatalysis [16]. Nakashima et al. reported the synthesis of hollow TiO$_2$ micropores by subjecting a mixture of [BMMI] [PF$_6$], toluene and Ti (OBu)$_4$ to vigorous stirring [17]. Dionysiou et al. [18] prepared mesoporous TiO$_2$ using aqueous solution of titanium tetra isopropoxide and [BMim] [PF$_6$]. Prasad et al. have synthesized TiO$_2$ nanoparticles via sol–gel process and tested for antibacterial activity against gram positive bacteria (Staphylococcus aureus) using Disk diffusion method. They have observed highest activity against Ampicillin and Amikacin which signifies that TiO$_2$ nanoparticles are capable of the antimicrobial action on cephalosporins, beta lactams, macrolids, amino glycosides, lincosamides and glycopeptides [19]. Devi et al. prepared Mn doped TiO$_2$ via sol–gel process and studied the photocatalytic activity of degradation of oxo-fused polycyclic aromatic dye [20]. Thoma et al. have highlighted the comprehensive, multi-disciplinary access for the exploitation of low-cost water remediation methods. Chimie douce and green chemical principles thought to be crucial for making such kind of technologies which are economically viable and socially relevant [21].

Here, we have synthesized TiO$_2$ nanoparticles using ionic liquid assisted hydrothermal method. The obtained product was characterized by various techniques and used for photocatalytic degradation of methylene blue organic dye under solar as well as UV irradiations. We have also examined for antibacterial activities against four bacterial strains using the agar well diffusion method.

2. Experimental procedures


The ionic liquid 1-n-butyl-3-methyl imidazolium chloride [BMMI]Cl was prepared using previously described report [12]. 151.5 g [1.85 mol, 1 eq] of freshly distilled N-methyl imidazole, 100 mL of acetonitrile and 220 g [2.4 mol, 1.3 eq] of 1-chlorobutane were mixed in three-necked, round-bottomed flask and reflux it to 60 $^\circ$C for 48 h. The solution was then cooled to room temperature. The volatile material was removed from the resulting yellow solution under reduced pressure. The remaining light-yellow oil was re-dissolved in dry acetonitrile [250 mL] and added dropwise via cannula to a well-stirred solution of 1000 mL of dry ethyl acetate and one seed crystal of 1-butyl-3-methylimidazolium chloride, placed in 2000 mL round-bottomed flask, equipped with a nitrogen inlet adapter and an overhead mechanical stirrer. The imidazolium salt begins to crystallize exothermically almost immediately, and after the addition of the acetonitrile solution was completed, the flask was cooled at –30 $^\circ$C for 2 h.

The supernatant solution was removed via filtration through a filter cannula and the resulting white solid was dried under reduced pressure [0.1 mbar, 0.001 mm] at 30 $^\circ$C for 6 h to afford 1-butyl-3-methylimidazolium chloride. The structure of ionic liquid was as shown in Scheme 1.

2.2. Synthesis of TiO$_2$ nanoparticles:

In a typical synthesis, 0.4 g TiO$_2$ P25 was added to 5 mL H$_2$O taken in Teflon tube. The mixed solution was then gently stirred and then 35 mL H$_2$O was added slowly in to the Teflon tube followed by 2 mL HNO$_3$ and 0.5 g butyl-methyl imidazolium chloride BMI. Cl with constant stirring. Then the whole mixture was subjected to hydrothermal treatment at 130 $^\circ$C for 2 days. After the reaction was complete, the autoclave was cooled to room temperature naturally. The product obtained from centrifugation was washed several times with water followed by ethanol. The obtained product was mixed with acetonitrile and stirred overnight to remove ILs. The final product obtained from centrifugation was dried in an oven at 80 $^\circ$C overnight.

Scheme 1 – Structure of 1-butyl-3-methyl imidazolium chloride – [BMMI] Cl.
2.3. Procedure for photocatalytic degradation of dye

Photocatalytic experiments were carried out in a 150 mm × 75 mm batch reactor. An aqueous suspension was prepared by dispersing 100 mg of TiO₂ nanoparticles in 100 mL of 10 ppm methylene blue dye solution. During the photocatalytic experiments the slurry composed of dye solution and catalyst were placed in the reactor and stirred magnetically for agitation with simultaneous exposure to sunlight and UV light. The known volume (10 mL) of the exposed solution was withdrawn at specific interval of time (30 min). TiO₂ nanoparticles were removed from the solution by centrifugation to assess the extent of degradation. The dye concentration was measured using a spectrophotometer at 664 nm. The % of degradation can be determined using the following formula.

\[
\% \text{ of degradation} = \frac{C_i - C_f}{C_i} \times 100
\]

where \( X \) is the % of degradation where \( C_i \) and \( C_f \) are the initial and final dye concentrations respectively. The experiment was carried out by varying various parameters like sunlight/UV light irradiation time.

2.4. Procedure for antibacterial activity

Antibacterial activity was screened by agar well diffusion method [22] against four bacterial strains namely Gram-ve Klebsiella aerogenes NCIM-2098, Escherichia coli NCIM-5051, Pseudomonas desmolyticum NCIM-2028 and Gram+ve bacteria Staphylococcus aureus NCIM-5022. Nutrient agar plates were prepared and swabbed using sterile L-shaped glass rod with 100 μL of 24 h mature broth culture of individual bacterial strains. The wells were made by using sterile cork borer (6 mm). Wells were created into each petri-plates. Different concentrations of TiO₂ nanoparticles (1000 and 1500 μg/well) were used to assess the activity of the nanoparticles. The TiO₂ nanoparticles were dispersed in sterile water and it was used as negative control and simultaneously the standard antibiotics Ciprofloxacin (5 μg/50 μL) (Hi Media, Mumbai, India) as positive control were tested against the bacterial pathogens. Then the plates were incubated at 37 °C for 24–36 h. The zone inhibition of every well measured was in millimeter. Triplicates were maintained in every concentration and the average values were calculated for the ultimate antibacterial activity. The bacterial rate (K) could be calculated by the following equation.

\[
K = \frac{A - B}{B} \times 100
\]

where A and B are the number of bacterial colonies corresponding to the positive control group and the sample group, respectively.

2.5. Characterization

The crystal structure and composition of TiO₂ nanoparticles were determined by Powder X-ray diffraction (PXRD), data were recorded on Philips Xpert PRO PANalytical X ray diffractometer with graphite monochromatized Cu-Kα (1.5418 Å) radiation. The Fourier transform infrared (FTIR) spectrum of the sample is collected using Bruker Alpha-P spectrometer. The absorption spectrum of the sample is measured on a UV-1800 UV-Vis spectrometer (UV-Vis). The surface morphology was examined by Carl Zeiss ultra 55 scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed using JEOl JEM 1200 Ex operating at 100 kV.

3. Results and discussion

Fig. 1 shows the XRD pattern of TiO₂ nanoparticles prepared at 130 °C for 2 days. All the diffraction peaks of the product can be indexed to anatase form of TiO₂ nanoparticles (JCPDS no. 021–1272), \( a = b = 3.785 \text{ Å}, c = 9.513 \text{ Å}, 141/\text{amd} \). The average diameter of NPs was found to be 40 nm and was calculated from Debye-Scherrer’s equation:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where \( D \) is the crystal size and \( \lambda \) is the wavelength of X-ray radiation (1.5418 Å), \( \beta \) is the full width half maximum of diffraction peak and \( \theta \) is the scattering angle.

The FTIR spectrum of the as-prepared sample is shown in Fig. 2. The bands at 1581 and 1410 cm⁻¹ can be assigned to C–H stretching and in-plane vibrations of the imidazolium ring [23]. The bands at 616 and 644 cm⁻¹ can be attributed to aliphatic (organic compounds) in-plane vibrations. The bands at 924 and 1010 cm⁻¹ are due to the respective out of plane vibrations of the organic cations, respectively. The band at 456 cm⁻¹ is due to the presence of Ti–O–Ti.

The UV–Vis spectrum of the TiO₂ nanoparticles in Fig. 3, shows a maximum absorbance band at 272 nm. The band at around 272 nm can be assigned to the TiO₂ nanoparticles (Eg = 3.7 eV) which shows the shift of the band toward lower wavelength which is called blue shift when compared to that of bulk TiO₂ (Eg = 3.2 eV). Observation of blue shift is due to reduction of size (quantum size) and confinement effects [16,24].

Fig. 1 – XRD pattern of TiO₂ nanoparticles.
The SEM images of the as-prepared sample are shown in Fig. 4. It shows the TiO$_2$ nanoparticles are almost spherical in shape. The morphology is further confirmed by TEM and is shown in Fig. 5. It shows of TiO$_2$ nanoparticles are almost oval in shape and the average size of the TiO$_2$ nanoparticles are found to be 35 nm.

4. Effect of different nature of light source on photocatalytic activity

Fig. 6 shows the effect of different light source on photocatalytic degradation of methylene blue dye. Two different light sources are used namely sunlight and UV-light. The experiment was carried out by dispersing 100 mg of TiO$_2$ nanoparticles in 100 mL of 10 ppm methylene blue dye solution. From Fig. 6, it is clearly shown that photocatalytic degradation of the dye was more in UV-light than in sunlight. This is due to the fact that the absorbance band of TiO$_2$ nanoparticles appeared in UV region.

The photocatalytic degradation of methylene blue organic dye has been studied by several researchers [25,26] and the mechanistic scheme leading to the photocatalytic degradation of the methylene blue organic dye is shown below.

\[
\text{TiO}_2 + h\nu(\text{UV}) \rightarrow \text{TiO}_2(e^-_{\text{CB}} + h\nu_{\text{VB}}) \\
\text{TiO}_2(h\nu_{\text{VB}}) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^-
\]
where \( h_v \) is the photon energy required to Ti excite the semiconductor electron from the valence band (VB) region to conduction band (CB) region. From the above characterization results high crystallinity, small size provides sufficient number of active sites to adsorb dye molecules on the surface of the sample for degradation which enhances the degradation. Absorbance spectra play a crucial role in selecting the suitable catalyst for photocatalysis based on absorbance band.

5. **Antibacterial activity studies**

The antibacterial properties of the TiO\(_2\) nanoparticles is evaluated against Gram-ve *K. aerogenes*, E. coli, *P. desmolyticum*. Gram+ve bacteria *S. aureus* using agar well diffusion method. In this method, the TiO\(_2\) nanoparticles showed significant antibacterial activity on all the four bacterial strains. The bacterial strains of Gram-ve *K. aerogenes*, E. coli, *P. desmolyticum*. Gram+ve bacteria *S. aureus* with 500 and 1000 \( \mu \)g concentration of TiO\(_2\) nanoparticles show the zone of inhibition as shown in Fig. 7. The data is shown in Table 1. The mechanism is as follows “The antibacterial activity of TiO\(_2\) NPs shows the maximum inhibition zone was observed in the presence of nano-TiO\(_2\). Nanomaterials are known to inactivate cellular enzymes and DNA by binding to electron-donating groups such as Carboxylates, Amides, Indoles, Hydroxyls, Thiols, etc. They cause little pores in bacterial cell walls, leading to increased permeability and cell death. Based on this study, nano-TiO\(_2\) has an efficient antibacterial effect and can be used as an antibacterial agent”.

![Fig. 5 - TEM images of TiO\(_2\) nanoparticles.](image1)

![Fig. 6 - Photocatalytic photo degradation of Methylene blue using TiO\(_2\) nanoparticles.](image2)
Fig. 7 – Zone of inhibition of (a) *Klebsiella aerogenes*, (b) *Escherichia coli*, (c) *Staphylococcus aureus* and (d) *Pseudomonas desmolyticum*.

<table>
<thead>
<tr>
<th>Sl. no</th>
<th>Treatment</th>
<th><em>Klebsiella aerogenes</em> (B1) (Mean ± SE)</th>
<th><em>Escherichia coli</em> (B2) (Mean ± SE)</th>
<th><em>Staphylococcus aureus</em> (B4) (Mean ± SE)</th>
<th><em>Pseudomonas desmolyticum</em> (B5) (Mean ± SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Standard (5 μg/50 μL)</td>
<td>8.33 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.00 ± 0.00</td>
<td>9.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>II</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; (500 μg/50 μL)</td>
<td>2.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.33 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.00 ± 0.00</td>
</tr>
<tr>
<td>III</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; (1000 μg/100 μL)</td>
<td>3.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.67 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.00 ± 0.00</td>
<td>2.33 ± 0.33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Values are the mean ± SE of inhibition zone in mm. (a) and (b) represent statistical significance.

<sup>a</sup>P < 0.05 as compared with the control group.

<sup>b</sup>P < 0.01 as compared with the control group.
6. Conclusions

We have successfully synthesized TiO$_2$ nanoparticles using functionalized ionic liquid via hydrothermal method. PXRD confirmed the existence of anatase phase TiO$_2$ nanoparticles. The average size of the TiO$_2$ nanoparticles from TEM were found to be 35 nm. TiO$_2$ nanoparticles exhibited excellent photocatalysis for the degradation of methylene blue organic dye. The antibacterial properties of TiO$_2$ nanoparticles were investigated by their bactericidal activities against four bacterial strains using the agar well diffusion method.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

One of the author Nagaraju thanks BRNS-BARC, DAE, Bombay, Govt. of India for financial support to carry out the research work (37/2/14/25/2015/BRNS dated 03/12/2015). Dr. K. Manjunath and Dr. G. Nagaraju thank CNPq-TWAS and UFRGS for providing the fellowships and facilities. L. S. Reddy Yadav acknowledges BMSIT for providing financial support and encouragement for the research work.

REFERENCES