Degradation of Organic and Toxic Pollutants by Embedding the Barium Titanate Nanoparticles in Polyaniline Matrix (BaTiO$_3$@PANI)

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Abstract. The embedment of barium titanate nanoparticles (BaTiO$_3$ NPs) in the polyaniline (PANI) matrix play a significant role in enhancing the properties of nanocomposites. In this research work BaTiO$_3$@PANI polymer nanocomposites were well synthesized by the in-situ polymerization by embedding different concentrations of BaTiO$_3$ NPs (1wt%, 3wt%, 5wt%, 7wt %) in the polyaniline matrix. The resulting nanocomposites were characterized for their structural, optical and photocatalytic properties. BaTiO$_3$@PANI nanocomposites exhibited higher photocatalytic activity than pure PANI and pure BaTiO$_3$ NPs towards the organic and toxic pollutants in liquid phase under visible light irradiation. The embedment of BaTiO$_3$ NPs in PANI have played an important role in affecting the photo reactivity and the increased weight ratio of BaTiO$_3$ NPs in PANI increased the photocatalytic efficiency of nanocomposites. The structural and optical properties were studied by XRD, FTIR and UV-Visible spectroscopy. The XRD confirmed the embedment of BaTiO$_3$ NPs in PANI matrix. The Fourier Transform Infra-Red (FTIR) spectroscopy identified the various functional groups and their respective vibrational and stretching modes. The results revealed that higher concentration of BaTiO$_3$ NPs in PANI proves to be a better photocatalyst. This work provides a comprehensive information to modify the polymers with nanoparticles.

Keyword: Photocatalysis, PANI, BaTiO$_3$ NPs, XRD, UV-Visible, FTIR

1. Introduction

Wastewater generated from the various industries like textiles is one of the main causes of water pollution which contain different dye stuffs [1]. Dyes generated from the textile industries have high toxicity which is very dangerous for aquatic life. Dyes can cause different chemical and biological changes and consume the dissolved oxygen in the water bodies. The various physical, biological, and chemical processes were used for the treatment of wastewater, containing organic toxic dyes [2]. Different innovative treatment techniques combining physical and chemical principles based on nano
filtration, advanced chemical oxidation (ACO), adsorption, ultrasonic decomposition, sedimentation, chemical coagulation, and electrocoagulation were employed. Most of these treatment methods have some deficiencies including high energy-waste, high cost, and production of secondary pollutants during the process of treatment [3].

Semiconductor materials were used as prominent photocatalysts and have been generally used in different areas extending from renewable energy to clean up environment fields [2,4,5]. In the recent years, large efforts have been made in order to develop a series of new organic and inorganic photocatalysts. However, some drawbacks of photocatalysts have weaken their applications to a great extent. The drawbacks and limitations include, the ineffective utilization of visible light, secondary pollution on the environment, the low quantum efficiency, high costs of rare elements, etc. [6]. In order to overcome these limitations and drawbacks many research experiments have been done to exploit effective visible light active photocatalysts with a slower recombination rate of charge carriers and higher stability. Researchers mainly focused on the modification of the surface or bulk properties of photocatalyst materials by doping with non-metal atoms, combining with noble metals, narrow band gap semiconductors and dye sensitization. Therefore, photocatalysis field has gripped keen interest because of their low cost, high efficiency, and lack of secondary pollution in the environment. In the last years, polyaniline (PANI) has been the most largely explored conducting polymer with good stability, corrosion protection, nontoxicity, facile and low cost synthesis [1,7]. PANI has shown excessive potential due to its high absorption coefficients in the visible light range and high mobility of charge carriers [2, 3, 8]. Moreover, after the irradiation of light, PANI is not only an electron donor but also itself is an excellent hole acceptor when irradiated with light. These distinctive characteristics of PANI make it a perfect material to attain higher charge separation efficiency in the Photocatalysis field [9–11]. In recent times, more and more attention has been focused on the combination of PANI and semiconductor photocatalysts [12–14]. Here In this research work, BaTiO$_3$@PANI polymer nanocomposites were well synthesized by the in-situ polymerization by embedding different concentrations of BaTiO$_3$ NPs (1wt%, 3wt%, 5wt%, 7wt %) in the polyaniline matrix. The embedment of BaTiO$_3$ NPs in PANI have played an important role in affecting the photo reactivity and the increased weight ratio of BaTiO$_3$ NPs in PANI increased the photocatalytic efficiency of nanocomposites [4, 15]. The resulting nanocomposites were characterized for their structural, optical and photocatalytic properties. The results revealed that higher concentration of BaTiO$_3$ NPs in PANI proves to be a better photocatalyst. This work provides a comprehensive information to modify the polymers with nanoparticles.

2. Materials and method

2.1. Synthesis of BaTiO$_3$ NPs

BaTiO$_3$ NPs were synthesized by co-precipitation method. The precursor materials used for synthesis in this present research work included Barium nitrate Ba(NO$_3$)$_2$, (purchased from Sigma Aldrich) Titanium dioxide TiO$_2$ (>99%, Sigma Aldrich) and oxalic acid (COOH)$_2$•2H$_2$O (>99.5%, Fisher Scientific India Pvt.Ltd.). First of all, 0.12 molar aqueous solution of Ba(NO$_3$)$_2$ was prepared using double distilled water. Then the required amount of TiO$_2$ powder in the ratio (Ba/Ti = 1:1) was added to the above prepared solution with continuous stirring. In order to break down the TiO$_2$ agglomerates in the solution the suspension was sonicated with ultrasonic waves for 10 minutes. Thereafter, 0.4 molar solution of Oxalic acid was prepared and was added drop wise into the mixture under continuous and vigorous stirring. Subsequently the ammonia solution was added dropwise to the above prepared mixture until the pH of the solution becomes 6-7[16]. In the solution, barium oxalate was precipitated on the surface of fine TiO$_2$ (seed) particles by heterogeneous nucleation. The precipitates obtained from the above mixture were then washed repeatedly using double distilled water, and then dried at 40$^\circ$C for 48 hours in vacuum oven. The as dried precursor was then calcinated
at 900°C for 5 hours and brought to the room temperature to obtain the BaTiO$_3$ NPs. The calcinated white powder was then characterized by using various techniques.

2.2. Synthesis of PANI
For the synthesis of polyaniline (PANI), 0.1M Potassium persulfate and 10% of aniline were first prepared in 1 M HCL. Polyaniline which is one of the most explored polymers is synthesized by using oxidative polymerization method. In this method, aniline was placed in an ice bath to maintain the temperature below 4°C. When the temperature was maintained, 0.1M potassium persulfate (oxidizing agent) was added dropwise to the aniline under constant stirring for 60 minutes. By addition of the oxidizing agent the monomer of aniline (10 %) was polymerized and a dark coloured green gel of polyaniline was obtained.

2.3. Synthesis of BaTiO$_3$/PANI nanocomposite
BaTiO$_3$-doped PANI polymer nanocomposites (BaTiO$_3$@PANI) were prepared with different wt% of BaTiO$_3$. The calculated amount of BaTiO$_3$ NPs were dispersed in 5 mL of deionized water and sonicated until a homogenous solution was obtained. The solution of BaTiO$_3$ was then added dropwise to aniline solution with vigorous stirring. The resulting mixture was sonicated for a few minutes until it became homogenous. After sonication oxidizing agent, Potassium persulfate, was added dropwise to the aniline/BaTiO$_3$ solution. By addition of the oxidizing agent the monomer of aniline (10 %) was polymerized and a dark coloured green gel of polyaniline/BaTiO$_3$ was obtained. The obtained BaTiO$_3$@PANI nanocomposites were washed, dried and used as photocatalysts.

3. Characterization
The phase composition and microstructure of the BaTiO$_3$ NPs, PANI and BaTiO$_3$/PANI nanocomposites were studied using X-ray diffraction pattern which was recorded on Miniflex II XRD system having voltage of about 30kV, using Cu-Kα radiations having wavelength $\lambda$-1.54 $\text{Å}$. The radiations diffracted by the synthesized materials were recorded by the detector from 20° to 80° 2θ angles. The crystallite size of the BaTiO$_3$ NPs was calculated using the Debye–Scherrer’s formula: $D = \frac{0.9\lambda}{\beta\cos\theta}$ whereas, D is the crystallite size of BaTiO$_3$ NPs, $\lambda$ is the wavelength of X-ray source used (1.541 $\text{Å}$), $\beta$ is the full-width-at-half-maximum (FWHM) of the diffraction peak. FTIR was used for determining the functional groups present in BaTiO$_3$ NPs, PANI and BaTiO$_3$/PANI nanocomposites. FTIR measurements were carried out on FT-IR spectrometer Spectrum Two (Perkin Elmer) in the diffuse reflectance mode at a resolution of 4 cm$^{-1}$ in KBr pellets. UV-visible spectroscopy was employed to characterize the optical properties of the various synthesized nano-composite materials. The optical absorption spectra of BaTiO$_3$ NPs, PANI and BaTiO$_3$ doped polyaniline nano-composites (BaTiO$_3$@PANI) was recorded at room temperature using UV-visible spectrophotometer (Shimadzu UV-1601). From these measurements optical constants such as optical band energy gap have been determined.

4. Results and Discussion
4.1. X-Ray Diffraction
The room temperature XRD pattern of PANI, BaTiO$_3$ NPs and 1wt%, 3wt%, 5wt% and 7wt% BaTiO$_3$/PANI nanocomposites are shown in Fig.1. XRD pattern of undoped BaTiO$_3$ and PANI shows their distinctive characteristic peaks indicating their polycrystalline nature [12]. The diffraction peaks at 2θ= 22.50, 34.0, 39.0, 46.0, 52.0, 57.0 and 66.0 corresponds to (100), (110), (111), (200), (210), (211) and (220) planes of BaTiO$_3$. For BaTiO$_3$/PANI nanocomposites intensity of the characteristic peak changes and many new peaks were observed due to the formation of polymer chains with BaTiO$_3$ which have influenced the growth of crystallinity. The result shows the increase in crystallinity which can be explained by the heterogeneous nucleation process of the polymers. No shift was observed in
the XRD peaks of the synthesized material with increased embedment of BaTiO$_3$ NPs in PANI matrix indicating formation of nanocomposite without any impurity.

![Figure 1](image)

**Figure 1** Showing the XRD pattern of BaTiO$_3$ NPs, PANI and 1wt%, 3wt%, 5wt% & 7wt% BaTiO$_3$/PANI nanocomposites

4.2. *Fourier transform infrared (FTIR) spectroscopy*

The FTIR spectra of 1wt%, 3wt%, 5wt% and 7wt% BaTiO$_3$/PANI nanocomposite are shown in Fig.2. The FTIR spectra shows clear infrared bands at 506 cm$^{-1}$ and 626 cm$^{-1}$ indicating distinctive peaks of metal Ti-O vibration and BaTiO$_3$ modes[7]. Peak at 791 cm$^{-1}$ indicates out of plane bending of aromatic C-H in the substituted benzene ring whereas band at 1129 cm$^{-1}$ attributes to C-N stretch of quinoid ring. Band at 1302 cm$^{-1}$ and 1497 cm$^{-1}$ ascribes to benzoid unit, C-N stretch of aromatic amine of PANI respectively. Characteristic broad band at 3442 cm$^{-1}$ attributes to N-H stretching mode of PANI. On the basis of these FTIR spectra we can confirm the formation of BaTiO$_3$/PANI nanocomposite [9,10].
4.3. UV-visible Spectroscopy

UV-visible spectroscopy was employed to characterize the optical properties of the synthesized nanocomposite of BaTiO$_3$/PANI. The absorbance varies depending on various factors like particle size, oxygen deficiencies and defects produced in the material. The absorbance spectra of BaTiO$_3$ and nanocomposites of 1wt%, 3wt%, 5wt% and 7wt% BaTiO$_3$/PANI shown in Fig. 3a We have observed a shift in absorption edge towards the higher wavelength indicating the red shift in the composites. In order to calculate the direct band gap of the samples Tauc’s relation is used

$$
\alpha h\nu = B (h\nu - E_g)^n
$$

Where B is constant, $\alpha$ is absorption coefficient and $n=1/2$ for direct band gap. An extrapolation of linear region of $(\alpha h\nu)^2$ versus $(h\nu)$ graph will give the band gap of the material. Band gap obtained from the graph for BaTiO$_3$ NPs, 1wt%, 3wt%, 5wt% and 7wt% BaTiO$_3$/PANI are 4.10eV, 4.02eV, 3.86eV 3.82eV and 3.92 eV respectively and shown in Fig.3b. This decrease in band gap is attributed to the formation of defective energy levels in the band gap of BaTiO$_3$ NPs and produces a new energy state located in the gap of the BaTiO$_3$ for electron hole pair recombination at lower energies. This band gap narrowing may have been credited due to creation of large no. of defects and polymer chains within the composite.
4.4. Photocatalysis Activity

The nanocomposites of BaTiO$_3$/PANI as a catalyst was tested for its photocatalytic activity for the degradation of model pollutant methylene blue (MB) dye under visible light source. Solution of MB dye was prepared in deionized water and stirred for 15 mins after adding catalyst for the adsorption equilibrium. Then experiment was carried out under the illumination of visible light [1,3] and absorbance of the samples was noted after the regular interval of time as shown in Fig.4a. From the absorption pattern of the samples it was observed that the degradation of the 7wt% BaTiO$_3$/PANI has shown the maximum reduction in the intensity of the absorption peak after 80 mins indicating the maximum degradation of pollutant. Fig.4b shows photo degradation of MB with addition of BaTiO$_3$ NPs, PANI and 1wt%, 3wt%, 5wt% & 7wt% BaTiO$_3$/PANI nanocomposites at different time intervals. The explanation for the increased photocatalytic activity is due to reduction in band gap of the material and secondly due to improved inhibition of recombination process of electron and hole pairs. Fig. shows the % degradation of 1wt%, 3wt%, 5wt% and 7wt% BaTiO$_3$/PANI with time. It shows that the embedment BaTiO$_3$ NPs into the PANI matrix have played an important role by injecting electrons in the conduction band of the PANI under the illumination of visible light which triggers the formation of radicals which are responsible for the degradation of organic dyes. However, fast photogenerated charge separation and comparatively slow charge recombination rate has enhanced the photocatalytic activity of BaTiO$_3$/PANI nanocomposite system. Fig.5 explains the %degradation rate of BaTiO$_3$ NPs, PANI and 1wt%, 3wt%, 5wt% & 7wt% BaTiO$_3$/PANI nanocomposites.
5. Conclusions

In summary, we present here a facile and unique route to synthesize BaTiO$_3$ NPs doped polyaniline nanocomposite through an in situ oxidative polymerization procedure. The XRD pattern confirmed the embedment of BaTiO$_3$ NPs into the matrix of PANI. FT-IR spectra measurements confirmed the presence of the conductive PANI in all prepared nanocomposites. The resulting nanocomposites were analysed for the photocatalytic properties. BaTiO$_3$@PANI nanocomposites exhibited higher photocatalytic activity than pure PANI and pure BaTiO$_3$ NPs towards the organic and toxic pollutants in liquid phase under visible light irradiation. The embedment of BaTiO$_3$ NPs in PANI have played an important role in affecting the photo reactivity and the increased weight ratio of BaTiO$_3$ NPs in PANI increased the photocatalytic efficiency of nanocomposites. It has been found from the above results that 7wt% of BaTiO$_3$ NPs into PANI matrix exhibited the higher photocatalytic activity as compared to other nanocomposite. In brief, this work provides a comprehensive information to modify the polymers with nanoparticles.
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