

PHOTOCATALYTIC AND MECHANICAL PROPERTIES OF CHITOSAN DOPED TITANIUM DIOXIDE NANOCOMPOSITE FILM

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Abstract

In the present study, we report newly fabricated Chitosan blended TiO₂ nanocomposite film by sol-gel and solution cast method. The synthesized nanocomposite films were characterized by XRD, FT-IR, TG-DTA and FESEM with EDAX. Further, the mechanical properties (Tensile strength and Elongation) were determined using Universal Testing Machine. From the obtained results, it was concluded that the Chitosan blended TiO₂ nanocomposite film exhibits higher photocatalytic, antibacterial and mechanical properties than TiO₂ film.

Keywords: Composites, Sol-gel method, Semiconductivity, Antibacterial activity, spectroscopical studies.

1. Introduction

Environmental remediation of hazardous wastes, contaminated ground and surface waters and the control of toxic air contaminants are the major tasks to be followed along with the industrial growth[1-6]. Advanced oxidation technology (AOT) is a solution to environmental remediation. AOT deals with the generation of highly reactive chemical species at ambient conditions, which degrade the pollutants. The most efficient AOTs are those that produce free hydroxyl radicals. These radicals have high oxidizing power and are superior to the other usual oxidants[7-11]. Semiconductor TiO₂ is widely used as photocatalyst for solar energy conversion and storage, abatement of organic pollutants,

inactivation of bacteria, etc. [1–4]. The widely reported band gap energy of anatase TiO₂ is about 3.2 eV and on illumination with light of energy not less than the band gap electron–hole pairs are created[12-16]; electrons in the conduction band (CB) and holes in the valence band (VB). The hole produces hydroxyl radical from the adsorbed water molecule or hydroxide ion and the hydroxyl radical is the predominant reactive oxidizing species (ROS) in the mineralization of organics. The adsorbed oxygen molecule picks up the CB electron to form superoxide radical ion ($O_2^{\cdot-}$) which through a series of reactions provides ROS. Modification TiO₂ to enhance the photocatalytic activity is of interest and doping TiO₂ with nonmetal or transition metal ion or with noble metal is widely adopted to shift the absorption edge to visible region and to improve the separation of photogenerated electron–hole pair[17-21].

Over the recent years, hybrid materials based on chitosan have been developed, including conducting polymers, metal nanoparticles and oxide agents due to excellent properties of individual components and outstanding synergistic effects simultaneously. In this regard, Chitosan, a linear cationic[22-26], pH sensitive, non-toxic, biodegradable and biocompatible polysaccharide prepared from the deacetylation of chitin seems to offer numerous distinct advantages. It is the second most abundant biopolymer widely present as the basic components of exoskeletons of crustaceans and insects. The structure of chitosan is similar to that of cellulose; it consists of β (1-4)-linked D-Glucosamine residue with 2-hydroxyl group being substituted by an amino or acetylated amino group. The structures of cellulose, chitin and chitosan are shown in the figure 1[27-35]. Chitosan is soluble in diverse acids and able to interact with polyanions to form complexes and gels. It has the adsorption capacity of 1000-1100 g Kg⁻¹ which is higher

than activated carbon, that is [36-39], it is a super high-capacity adsorbent for contaminant removal in water. This high adsorption capacity of chitosan gives rise to the binding ability of chitosan with contaminants in water through hydroxyl and amino groups present on the surface. Currently, researchers have been devoted to fabricate the combination of chitosan and metal oxide nanomaterials for the environmental remediation process [40-45].

This study is mainly focused on (i) fabrication of chitosan and Chitosan-doped TiO_2 nanocomposite film by sol-gel and solution cast method. Further the mechanical properties (Tensile strength and Elongation) were determined using Universal Testing Machine.

2. Materials and methods

2.1. Materials

Titanium Tetra IsoPropoxide (TTIP) and Tween-80 were purchased from Spectrochem. Crab shells were collected from Kasimedu Seafood Market, Sodium hydroxide, hydrochloric acid was purchased from Merck. Glacial acetic acid was obtained from Qualigens were purchased and used as received. Freshly prepared de-ionized water was used in all the experiments.

2.2. Synthesis of Chitosan from Crab shell

The Crab shells were collected from Kasimedu Seafood Market, Chennai, Tamil Nadu, India. The Crabs exoskeletons collected were placed in Ziploc bags and

refrigerated overnight. The synthesis of chitosan can be achieved by performing the following four steps;

(i) Coarse purification: Approximately 500 g of crab shells were coarsely cleaned with running water until sand and other impurities like soils were removed. The cleaned crab shells were dried overnight in the hot air oven at 110°C.

(ii) Deproteinization: The dried shell samples were grounded by using a mortar and transferred to a beaker. 2% of NaOH was added to the beaker containing the shell samples and heated under stirring at 60–70 °C for 30 minutes. The shell samples were filtered off with a strainer and the process was repeated for few times until the filtrate become clear and colorless. The samples were washed with demineralized water to remove the unreacted NaOH. For time-saving the shells samples may be soaked in NaOH solution for overnight after first NaOH treatment, again it was filtered and washed.

(iii) Demineralization: 7% of HCl was slowly added to the shells and the mixture was stirred at room temperature until the effervescence. The mixture was filtered off and washed with excess distilled water. The samples were dried overnight in a hot air oven at 60 °C to get around 100 g of chitin was obtained from crab shells. This step was known as demineralization.

(iv) Synthesis of chitosan from chitin by partial deacetylation: Chitin was loaded in a RB flask and 50% NaOH. The samples were heated at 125 °C for 2 h and then allowed to cool down followed by the addition of 250 mL of water. The next day the sample was filtered off and the residue was washed with excess water and dried in the hot air oven at 60 °C for 2 hr.

2.3. Casting of Chitosan film

Chitosan film was synthesized by solution cast method. 1 g of chitosan was dissolved in 100 mL of 1% (v/v) acetic acid solution and allowed to stirring for 24 hours. Later, it was sonicated for 15 min for well dispersion. Further, it was casted in a petri-dish and kept in an oven at 50-60 °C for overnight to get a homogeneous film.

2.5. Casting of Chitosan doped TiO₂ nanocomposite film

1 g of prepared TiO₂ composites was added into the chitosan solution (1 g of chitosan in 100 mL of 1% (v/v) acetic acid) and sonicated for 30 minutes and stirred continuously for 12 hrs until the clear solution was obtained. The mixture solution was cast onto the petri plates and dried at room temperature for 48 hrs to obtain the composite film.

2.6. Solar light intensity measurements

Solar light intensity was measured for every 30 min and the average light intensity over the period of an each experiment was calculated. The sensor was always set in the position of maximum intensity. The intensity of solar light was measured using New 200,000 Lux Digital Meter Light Luxmeter Meter Photometer with Footcandle FC. The intensity was $1200 \times 100 \pm 100$ lux and it was nearly constant in the course of the experiments.

2.7. Photocatalytic degradation of Methylene blue dye

The photocatalytic experiments were carried out under identical conditions on sunshiny days between 11 a.m. and 2 p.m. In all experiments, 50 ml of the reaction

mixture was irradiated under sunlight. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 20 mm diameter was used as the reaction vessel. The suspensions were magnetically stirred in the dark for 15 min to attain adsorption–desorption equilibrium between the dyes and TiO_2 chitosan and Chitosan doped TiO_2 nanocomposite film. Irradiation was carried out in the open-air condition. 50 mL of the dye solution with the synthesized catalysts were constantly aired by a pump to provide oxygen and for the thorough mixing of reaction solution. There is no volatility of the solvent was observed during the illumination time. After dark adsorption the first sample was taken. At specific time (15 min) intervals 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. 1 mL of the sample was properly diluted and its absorbance at 665 nm was measured immediately to monitor the degradation of the methylene blue.

2.8. Instrumentation and Analysis

The following physiochemical techniques have been used to characterize the prepared catalysts. To characterize the phase structure of the chitosan and Chitosan doped TiO_2 nanocomposite film; a Bruker D2 Phaser Desktop X-ray Diffractometer equipped with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.542 \text{ \AA}$) and operated at an accelerating voltage and emission current of 30 kV and 10 mA, respectively. Data were acquired over the range of 2θ from 0° to 70° with a step size of 0.0017 and a scan rate of $7^\circ/\text{min}$. Field Emission Scanning Electron Microscopy (FESEM) was performed to examine the surface morphology of the prepared nanocomposites using DXS-10 ACKT scanning electron microscope equipped with EXS, which was used to study the elemental composition. For FT-IR analysis was performed using a spectrophotometer (Perkin Elmer RX1 instrument). Thermogravimetric-differential thermal analysis (TG-DTA) of the

nanocomposites was taken on WATERS SDT Q 600 TA model instrument. Mechanical properties (Tensile strength and Elongation) of the films were determined according to ASTM standard method with Universal Testing Machine (TNUM-5900). The film was cut into (7x3 cm) rectangular shapes and measured.

3. RESULTS AND DISCUSSIONS

3.1. Photocatalytic activity

For the efficient use of solar light or use of the visible region of the spectrum, the technologies expanding the absorption scope of TiO_2 may then give the impression as an attractive challenge for developing the future generation of photocatalysts. The visible light photocatalytic activity of the F- doped TiO_2 was achieved by creating the oxygen vacancies. The photocatalytic activity of the chitosan film and Chitosan blended TiO_2 nanocomposite film was investigated by the photodegradation of the methylene blue dye (model organic pollutant) over a period of 2 hour under solar light irradiation. Percentage removal was calculated by using the following equation (Eq. 3)

$$\% \text{ removal of model pollutant} = \frac{C_o - C_t}{C_o} \times 100 \quad (3)$$

Where, C_o = concentration of model pollutant at 0 min, C_t = concentration of model pollutant at experimental time, t.

The photocatalytic mechanism was as follows: when the synthesized nanoparticles were illuminated under solar light irradiation, the electron transition from the valence band (VB) to the conduction band (CB) resulting in the electron (e^-)- hole (h^+) pair in which the electron (e^-) was getting reductive, and the hole (h^+) was oxidative and the general

photocatalytic mechanism is shown in the figure 7. The hole (h^+) reacted with OH^- on the surface of the nanomaterials, generating hydroxyl radicals ($\bullet OH$), superoxide anion (O_2^-) and perhydroxyl radicals ($HO_2^\cdot$). The $\bullet OH$ radicals are extraordinarily reactive species and attack most of the organic molecules with rate constants usually in the order of $10^6 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Figure 8 displays the photodegradation profiles of methyl orange dye by the synthesized nanocomposites. It can be seen from the figure 8, that all of the samples were capable of degrading methyl orange as indicated by the decrease in the methyl orange solution concentration throughout the period of the photocatalytic study but the TiO_2 has almost no photocatalytic activity under identical conditions. Besides, the photocatalytic activity increased in the order Chitosan film < Chitosan doped blended TiO_2 composite film. Hence, Chitosan doped blended TiO_2 exhibits highest photocatalytic activity than the chitosan film in the photodegradation of methylene blue.

3.2. Mechanical property

Mechanical studies of the synthesized chitosan film and chitosan doped blended TiO_2 films were carried out, through which their tensile strength and elongation were measured and shown in the figure 12. Pure chitosan film has low tensile strength of 65 MPa when compared to chitosan blended TiO_2 film whose strength was found to be 76 MPa. Nanoparticle doped chitosan film has higher strength due to the strong interaction of nanoparticles and the NH_2 group present in the chitosan molecules. Elongation of the

films were found in which chitosan film has low elongation of 10% while chitosan doped TiO_2 film has high elongation of 28 % because of the well dispersion of metal oxide into the polymer film.

4. Conclusions

In summary, a chitosan film and chitosan doped blended TiO_2 nanocomposite films were fabricated by a simple method. The synthesized nanocomposite films were characterized by XRD, FT-IR, TG-DTA and FESEM with EDAX. Among the synthesized materials, Chitosan blended TiO_2 nanocomposite film exhibits higher photocatalytic and mechanical properties. It is cost effective and environment-friendly materials for engineering applications for the removal of contaminants in water from the textile industries.

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