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Neodymium doped TiO_2 nanoparticles by sol-gel method for antibacterial and photocatalytic activity

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ABSTRACT

In the present study, TiO_2 and Nd doped TiO_2 nanoparticle was synthesized through Sol-gel method with different molar ratio and different starting material. The synthesized nanoparticle was characterized by XRD, UV-Vis, PL, FE-SEM, HR-TEM, and EDS analysis. The X-ray diffraction pattern confirms tetragonal anatase phase with average crystallite size of 14–10 nm. The influence of phase transition was identified by the addition of dopant Nd. The calculated band gap is in the range of 3.48–3.44 eV. Near UV and blue emission in PL spectrum indicate the presence of crystal defects in TiO_2 lattice. The structural morphology of the prepared sample was analyzed by FESEM. The average particle size of the sample was determined by TEM analysis. The elemental compositions and incorporation of Nd ions into the TiO_2 nanoparticles was detected by using energy dispersive spectra analysis. The antibacterial activity of pure TiO_2 and Nd doped TiO_2 nanoparticle was tested for different bacterial organisms like Escherichia coli (Gram-negative) and staphylococcus aureas (Gram-positive) bacteria. The photo catalytic activity of the prepared samples on degradation of Methylene Blue and Congo Red under ultraviolet irradiation were also studied.

1. Introduction

The environmental issues and industrialization increasingly attracted more attention for developing new ecofriendly water purification technologies. The release of dye-polluted wastewater by textile industries causes environmental problems. Synthetic organic dyes are mainly used in the textile industry; the removal of organic and inorganic dyes is a challenging one. The application of nanotechnology results in wastewater treatment owing to large surface area to volume ratio of nanomaterials [1]. The semiconductor photocatalysis has emanated as promising technology used for wastewater treatment, degradation of organic and inorganic pollutants in water. The application of photocatalysis is in the field of microbiology and agriculture because it is biologically inert and non- toxic. The antimicrobial agents are promising materials such as Nano sized metals and metal oxides. The metal oxide received more recognizing over past decade due to less toxicity, greater selectivity etc. antimicrobial agents are used in many industrial sectors including environmental, wastewater treatment, food packaging, textile and medical care [2]. In the metal oxide semiconductors, ZnO, TiO_2, Al_2O_3, CuO, SiO_2, Fe_2O_3 and CeO_2 are mostly used as a antimicrobial agents. Among these metal oxide semiconductors, TiO_2 is extensively used as an antimicrobial agents due to their photocatalytic activity under UV light [3].

There has been tremendous progress in the research of future nanoelectronic applications using TiO_2 nanoparticles in recent years. TiO_2 nanoparticles are highly investigated as a photo catalytic and photo electro chemical material [4]. It is also the most preferred semi conducting photocatalytic material due to its favorable properties like non-toxic, chemical inertness, stability, photosensitive etc. [5]. A growing interest in the development of well-structured, porous, high surface area, TiO_2 nanoparticles were used in many applications including building materials, medicaments production, pollutants destructions, solar energy conversion, photo catalyst, and antimicrobial activity. This application not only depends on the properties of TiO_2 but also on the crystalline structures of TiO_2 [6]. TiO_2 is usually in the forms of anatase, rutile, and brookite crystal phase. Anatase form of TiO_2 is more stable and more efficient in photo activity when compared with rutile and brookite [7].

Nowadays many studies have been devoted for the improvement of the antibacterial and photocatalytic properties of TiO_2 nanoparticles, the investigations suggests that these properties can be enhanced by doping with transition metals, non-metals,noble metals and rare earth metals [8]. The most important effects of doping are increasing the surface area, phase transformation, and particle size reduction [9].

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Doping with rare earth metals like La, Ce, Er, Pr, Gd, Nd, and Sm with TiO_2 nanoparticles is to enhance the photocatalytic and antibacterial properties. Several rare earth metals are used as a dopant for TiO_2 nanoparticles to improve the antibacterial and photocatalytic activities [10]. Neodymium is one of the element of lanthanide has obtained focus on several investigations because of its particular optical and magnetic properties and promising applications in the field of optoelectronic and magnetic devices [11]. Further, Nd doping with TiO_2 nanoparticles reduces the band gap and improves the possibilities of the photocatalytic degradation under visible light [12].

Several methods are available for the synthesis of TiO_2 nanoparticles such as hydrothermal method, solvothermal method, sol gel method, direct oxidation method, chemical vapour deposition, electro deposition, sonochemical method, and microwave method [13,14]. Among all these methods, the sol gel method is the best method because of its unique advantages including economic feasibility, simple lab equipment, less energetic conditions, possibilities of preparing powder, purity, and homogeneity [15].

Rui Tang et al., investigated the photocatalytic activity of N doped TiO_2 decorated N doped graphene composites by sol gel -method. N-RGO/N-TiO_2 composites effectively enhanced the photocatalytic activity than pure TiO_2 [16]. Previous reports on Nd doped TiO_2 nanoparticles focused on optical, structural, morphological and photocatalytic properties [17]. In this present work, pure TiO_2 and Nd doped TiO_2 nanoparticles were prepared by the sol gel method. The influence of various mole fractions of Nd^{3+} ions in TiO_2 nanoparticles, structural, optical, antibacterial, and photocatalytic properties were investigated in detail.

2. Experimental details

2.1. Materials

Synthesis of pure TiO_2 and Nd doped TiO_2 nanoparticles were carried out using analytical grade Titanium (IV) Isopropoxide (Merck, 97%), Neodymium (III) acetate dihydrate (Nd $(OOCCH_3)\cdot 2H_2O$) (Merck, 98%), Sodium Hydroxide (Merck, 99%), acetic acid (Merck, 99%) and ethanol (Merck, 99%) without any purification.

2.2. Preparation of pure and Nd doped TiO_2 nanoparticles

Pure TiO_2 and Nd doped TiO_2 nanoparticles were synthesized by sol-gel technique. Titanium (IV) isopropoxide (TTIP) was dissolved in 50 ml of isopropyl alcohol with vigorous stirring to avoid agglomeration. 2 ml of acetic acid were added to the above solution under constant stirring to complete the hydrolysis. A small amount of sodium hydroxide solution was added into the solution until it reaches pH 9. The transparent sols were allowed to aged for 24 h and washed 2–3 times with ethanol, distilled water and sodium hydroxide solution to remove metal ions present in the sols. Then the transparent sols were centrifuged at 8000 rpm for 15 min. Finally, the precipitate was dried at 120 °C for two hrs and annealed at 600 °C for 3hrs to obtain TiO_2 nanoparticles [18]. Nd doped TiO_2 nanoparticles were synthesized by same method as followed for the preparation of TiO_2 nanoparticles, except isopropyl alcohol was used as solvent for required amount of Neodymium(III) acetate dehydrate with different molar ratio (0.5 mM, 1.0 mM, 1.5 mM, 2.0 mM) and concentration of acetic acid was changed for hydrolyis.

3. Characterization techniques

Crystalline structure of the prepared samples were investigated using a powder X- ray diffractometer (PANa-lytical X′ Pert Pro) with Cu-Kα radiation source (wavelength: 1.5418 Å) and operating voltage and current was maintained at 45 kV and 30 mA respectively. The UV-Visible absorption spectra of prepared samples were recorded using JASCO (V-770, Japan) spectrophotometer. A PL spectrum was recorded at room temperature using JASCO spectroflurometer (Model FP8300, Japan) equipped with Xenon lamp. Field Emission Scanning Electron Microscope (ZEISS EIGMA) and High Resolution Transmission Electron Microscope (JOEL JEM- 2010) examined the size and morphology of the prepared samples. Energy Dispersion Spectrometer was used to carry out the elemental analysis using JOEL JEM- 2010.

3.1. Antibacterial assay

The pathogens Staphylococcus aureus and Escherichia coli were obtained from the Microbiology Laboratory, Kovai Medical Centre and Hospital, Coimbatore, South India. Kirby – Bauer disk diffusion method were performed against human pathogenic bacteria such as staphylococcus aureas (Gram positive) and Escherichia coli (Gram negative) for an antibacterial disk susceptibility tests. The standard inoculums is inoculated in the plates were prepared by dipping a sterile in the inoculums and poured on the petri dishes. After solidification, the petri dishes were spread with bacteria 2–3 times by rotating the plates at 60° to ensure homogenous distribution of inoculums. The inoculums were left to dry at room temperature with the closed lid. After inoculation, sterile discs stacked with prepared nanoparticles (100 μg of prepared samples) and standard ciprofloxacin (10 μg) were placed in the petri dish with the help of sterile forceps. Then the petri plates were incubated at 37 °C for 24 h. After incubation, the Zone of inhibition was measured in terms of diameter.

3.2. Measurement of photo catalytic activity

The photocatalytic activity of as prepared pure TiO_2 and Nd doped TiO_2 nanoparticles were analyzed by measuring the degradation rate of Methylene Blue(MB) and Congo Red(CR) dye solution using a photo reactor with two 20 W ultraviolet (UV) lamps which was used as the UV source for irradiation. In this experiment, 20 mg of pure TiO_2 and Nd doped TiO_2 nanoparticles were added to 100 ml of dye solution (40 mg/L) placed in a glass beaker. In each experiment, the solutions were stirred for 30 min under dark conditions to assure the formation of adsorption and desorption equilibrium of dyes on the pure TiO_2 and Nd doped TiO_2 nanoparticles, then the solution was irradiated under UV light. The pH of the solution was neutral. At 15 min interval, 10 ml of the solution was extracted from the solution and color removal of dye solution was determined by using UV- Vis spectrophotometer. UV-Vis spectroscopy was used to analyse the absorption changes, which is dependent to time between 400 and 800 nm. All these experiments were done at room temperature.

4. Results and discussion

4.1. Structural analysis

Fig. 1(A) shows the XRD pattern of as prepared TiO_2 nanoparticle. The determined characteristics 2Θ values are 25.37°, 37.87°, 48.13°, 54.22°, 55.10°, 62.85°, 68.80°, 70.25° and 75.22° and corresponding hkl plane values are (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0) and (2 1 5) respectively. All the diffraction peaks were well matched with JCPDS Card no. 89-4921. All the diffraction peaks are corresponding to tetragonal anatase phase of TiO_2 nanoparticle. Fig. 1(B-E) shows the XRD pattern of Nd doped TiO_2 nanoparticles with different concentration of dopant Nd. From the XRD pattern of Nd doped TiO_2 nanoparticle, the separate peak at 31.78 (1 2 1) indicates the presence of Brookite phase of TiO_2 and it is excellent agreement with the JCPDS Card no. 21-1272. The peaks at 45.48 (2 1 0) and 55.10 (1 1 0) correspond to rutile phase of TiO_2 nanoparticles. In TiO_2 and Nd doped TiO_2 nanoparticles, anatase phase is the prominent crystallite phase. The XRD pattern of TiO_2 nanoparticles has anatase crystalline phase. When Nd doped with TiO_2 nanoparticles, new peaks and shifts in