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PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE-CONJUGATED POLYMER COMPOSITE NANOPARTICLES SYNTHESIZED BY CHEMICAL OXIDATIVE POLYMERIZATION

Kakarla Raghava Reddy[1], S.B. Benaka Prasad[2], Han Mo Jeong[3], Anjanapura V. Raghu[*4]
[1]School of Chemical and Biomolecular Engineering, The University of Sydney, NSW2006, Australia
[2]Department of Chemistry, School of Engineering Technology, Jain University 560 078, India
[3]Department of Chemistry, Energy Harvest-Storage Research Center, University of Ulsan, Ulsan 680-749, South Korea
[*4]Centre for Emerging Technologies, Jain Global Campus, Jain University, Jakkasandra, Ramanagara 562 112, India

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Abstract

An organo-inorganic photocatalytic nanocomposite material based on conjugated polymer, polyaniline (PANI) with TiO2 nanoparticles has been synthesized by performing in situ chemical oxidative polymerization of aniline with ammoniumpersulfate (APS) oxidant in the presence of TiO2 nanoparticles. Morphological and structural properties of TiO2-PANI nanocomposites were analyzed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), respectively. FT-IR spectra show that the nanocomposites are almost identical to the structure of PANI alone. The photocatalytic activities of the nanocomposites were evaluated by photocatalytic degradation of Rhodamine B (RhB) under UV-light. The composites exhibited higher photocatalytic activity for the degradation of RhB than unmodified TiO2 nanoparticles, which is due to sensitizing effect of PANI.

Keywords: TiO_2; Conjugated Polymer; Nanocomposites; Photo Catalysts.

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1. Introduction

Polyaniline (PANI) is one of the most important conjugated polymers (CPs) due to its relatively easy processability, thermal/environmental stability, and reversible acid/base doping/de-doping characteristics [1-3]. The conjugation mechanism of PANI is unique among conjugated polymers, owing to a combination of benzenoid and quinoid rings that leads to three different oxidation states. PANI offers potential applications in the domains of composite materials, tissue engineering, actuators, robot manipulators, supercapacitors, molecular motors, and electronic and electro optic devices [4-6]. A current challenge of nanotechnology is to synthesize CP nanocomposites with metal nanoparticles that have multifunctional properties.

Encapsulation of metal nanoparticles into organic polymers leads to formation of functional nanocomposites that exhibit enhanced thermal stability, electrochemical, catalytic, magnetic, mechanical, optical and electro-rheological properties [7-10]. In addition, metal nanoparticles in polymeric matrixes allows for the development of materials suitable for applications in the fields of electrocatalysis, sensors, microelectronics, and magnetism. These composites can be prepared through different strategies. For example, Bose et al. [11] reported that Pt-PANI composites exhibit excellent catalytic activities because the conducting polymer acts as a nucleus to shuttle the electronic charge between catalytic sites. V_2O_5-PANI composite offers considerable promise for utilization as a cathode material for lithium secondary batteries [12]. Athawale and co-workers have synthesized a Cu-PANI composite that has been used as a catalyst for the conversion of alkenes to ketenes or aldehydes in a single step [13]. Given these numerous findings, the preparation of novel nanocomposites with metal nanoparticles and CPs is of great importance, as these advanced materials have interesting characteristics and features that may lend themselves to nano-technology applications.

In this article, we report preparation of TiO_2-PANI nanocomposites by in-situ chemical oxidative polymerization of aniline with oxidant in the presence of TiO_2 nanoparticles. TiO_2-PANI nanocomposites were characterized according to their structural and morphology by TEM, XRD, and FT-IR spectroscopy. Moreover, their photocatalytic activity was evaluated by the photocatalytic degradation of RhB under UV-light. TiO_2-PANI nanocomposites were found to have a higher photocatalytic activity than a pure TiO_2, which can be very useful for cleaning polluted water.

2. Experimental

The general procedure for synthesis of TiO_2-PANI nanocomposites is as follows. Initially, TiO_2 nanoparticles were synthesized through the sol-gel method and hydrothermal process at 550 °C, as per previous report with little modification [14]. Then, a various amount of TiO2 were dispersed in 15 mL of deionized water containing aniline (2.5 mmol) and were stirred for 10 min under ultrasonication. Then, 5 mL of aqueous ammonium persulfate (APS) (2.5 mmol) was added drop wise to the above solution and allowed to react for 12 h with constant stirring. A dark green precipitate was obtained and washed with methanol and distilled water several times until the filtrate was colorless. The precipitate was finally dried at 40°C under a vacuum for 24 h to obtain the nanocomposites as TiO_2-PANI nanocomposites. Nanocomposites were synthesized with different wt.% of TiO_2 with respect to the monomer. For comparative purposes, pristine PANI was synthesized under similar conditions and used for synthesis of the nanocomposites without using TiO_2. The prepared TiO_2/PANI nanocomposites were denoted as TiO_2/PANI-0, TiO_2/PANI-5, TiO_2/PANI-10, TiO_2/PANI-15 and TiO_2/PANI-20, respectively.

3. Results and Discussions

TiO_2-PANI nanocomposites were synthesized through an in-situ chemical polymerization of aniline monomers using APS as the oxidant in the presence of TiO_2 nanoparticles prepared through hydrothermal process. In this process, the reaction media of aqueous solution containing TiO_2 particles and aniline was sonicated for aniline monomer to be adsorbed onto the TiO_2 surface. After intruding oxidant solution, the polymerization of aniline monomer was takes place resulting in the final products of TiO_2-PANI nanocomposites. The fine dispersion of TiO_2 nanoparticles in polymer matrix is due to ultrasonication, which reduces the particles from aggregation and keeps the particles separately in the polymer matrix during polymerization process.

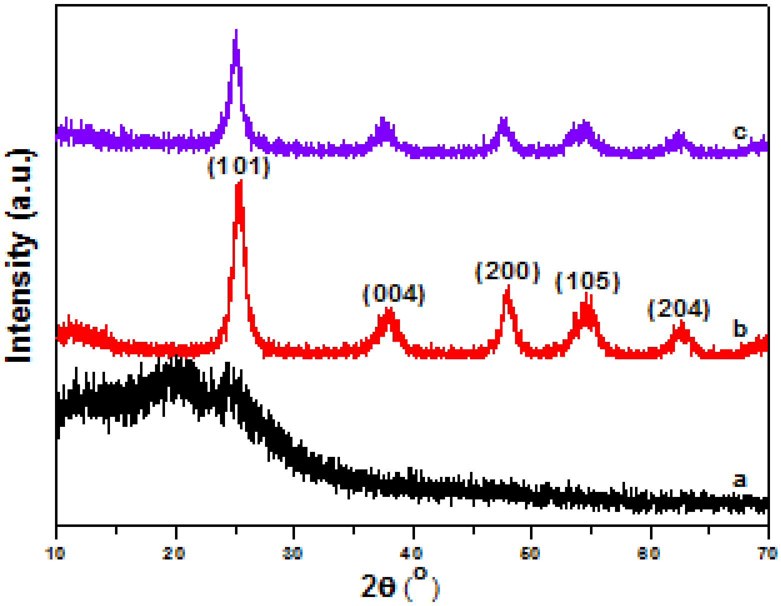

Figure 1: XRD patters of (a) pristine PANI, (b) TiO_2 NPs and (C) TiO_2-PANI nanocomposites.

The amorphous state of PANI is altered significantly by the introduction of TiO_2. The XRD diffraction patterns of TiO_2, pure PANI, and TiO_2-PANI nanocomposites are shown in Figure 2. The diffraction peaks at approximately $2\theta = 15°$, 21° and 25.8° of PANI (Figure 1a) indicates that pristine PANI is amorphous. TiO_2 nanoparticles show diffraction peaks at $2° = 25.4$, 37.9, 48.1, 54.2 and 62.8° and are marked with their indices as shown in Figure 1b, indicating that TiO_2 nanoparticles were successfully synthesized without any impurities. TiO_2-PANI nanocomposite (Figure 1c) has diffraction peaks corresponding to TiO_2. Polymer peak cannot be seen easily in the nanocomposite due to high crystalline nature of TiO_2. We conclude from the XRD results that nanocomposite have a more ordered arrangement and better crystallinity than that of pristine PANI.

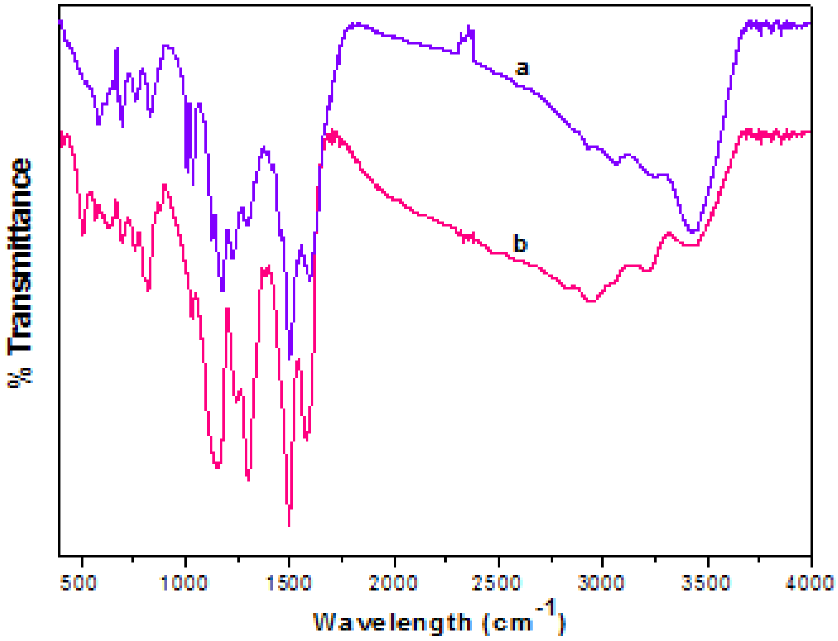

Figure 2: FT-IR spectra of (a) pristine PANI and (b) TiO_2-PANI nanocomposites

FT-IR spectra were used to confirm the presence of polymer in the nanocomposites, which are presented in Figure 3. For pristine PANI (Figure 2a), the absorption bands at 1495 and 1596 cm^{-1} are assigned to the stretching vibration of the benzenoid and quinoid rings. The bands at 1320 and 1215 cm^{-1} are assigned to the C-N vibration [15-17]. The three bands appearing between 800 and 900 cm^{-1} are attributed to an out-of-plane C-H vibration. The FT-IR spectra of the TiO_2-PANI nanocomposites (Figure 2b) are nearly identical to that of pure PANI, indicating that aniline was polymerized and present with TiO_2 in the nanocomposite.

The photocatalytic activity of the TiO_2 and TiO_2-PANI nanocomposites with different wt. % of TiO_2 was evaluated by measuring the decomposition rate of RhB under UV-light. Figure 3 shows the degradation of RhB in the presence of all the samples. Under UV-light, <5% of RhB molecules was decomposed without photocatalyst (Figure 3a), which can be ignored. Under UV-light, the photodegradation efficiency of RhB under in the presence of TiO_2 is ~40% (Figure 3b), which can be accounted for by the photosensitization capability of RhB molecules. After modification of TiO_2 with PANI, the photodegradation efficiency of TiO_2 was enhanced. All the composites higher photocatalytic activity than pure TiO_2, with nanocomposites of 20% TiO_2 having higher photocatalytic activity (Figure. 3f) (>80% under UV-light).

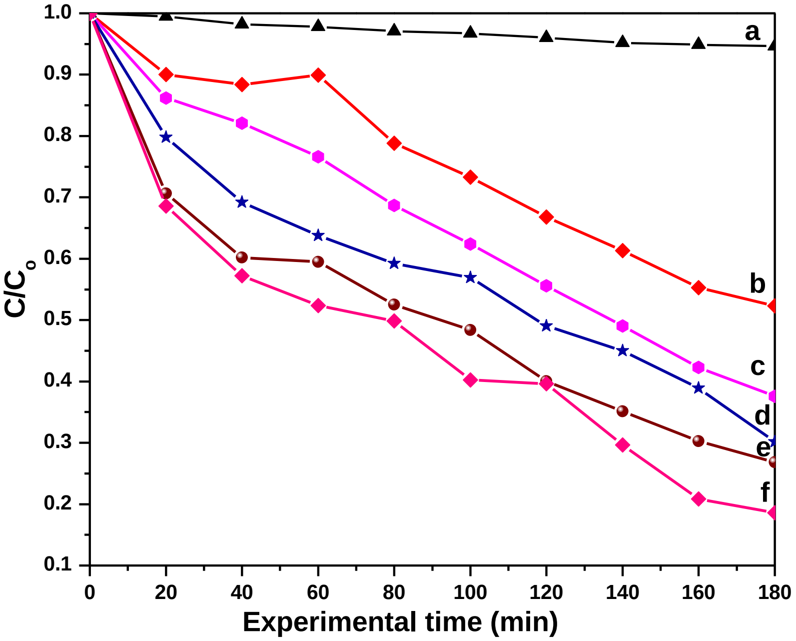

Figure 3: Relative concentration of RhB (C/Co) Vs time obtained for the photocatalytic degradation of RhB under UV light: (a) without catalyst (pure RhB), (b) TiO_2 particles and (c-f) TiO_2-PANI nanocomposites with different wt. % of TiO_2 (5, 10, 15 and 20%).

It is known that the conjugated polymer formed on TiO_2 may acts as a photosensitizer in the photocatalysis reaction. The conjugated polymer is an efficient electron donar and it can even be stimulated by natural light; the electrons generated from polymer can be easily transferred to the conduction band of TiO_2. If the electrons are trapped at the interface of polymer and TiO_2, the efficient charge separation of photo-created electron and hole pairs might occur. In this process, the reactive electrons can reduce O_2 adsorbed on the surface of nanocomposite to $.O_2$-, which can further transform into H_2O_2 and .OH, resulting finally in the oxidation of RhB. As a result, PANI modified TiO_2 have the enhanced the photocatalytic activity.

4. Conclusions

In summary, PANI-modified TiO_2 were prepared by an in-situ chemical oxidative polymerization method, and their structural, morphological and photocatalytic properties were characterized. These photocatalysts exhibit higher photocatalytic activity for the degradation of RhB than unmodified TiO_2 under UV-light. TiO_2-PANI nanocomposites with 20% of TiO_2 displayed the highest photocatalytic activity, which can degrade >80% RhB after 3 h irradiation. Hopefully, this work will open a new avenue to synthesize TiO_2 modified with other conjugated polymers or electron donating functional materials (e.g. graphene, quantum dots, carbon nitride, etc.) for efficient utilization of solar energy, and promote the wider application of TiO_2.

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*Corresponding author.
E-mail address: gsraghu2003@yahoo.co.in/reddy.chem@gmail.com