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Optical Properties of *in-situ* Chemically Synthesized PANI-TiO_2 Nanocomposites

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The present manuscript details on the synthesis of $(PANI)_{1-x}(TiO_2)_x$ nanocomposite ($x = 0$, 0.02, 0.04, 0.06, 0.08, 0.10) using an in-situ chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidant in presence of colloidal anatase TiO_2 nanoparticles at 0-5 °C in air. The X-ray diffraction of these specimens revealed amorphous nature of polyaniline which did not change with the addition of TiO_2 nanoparticles during polymerization process. The selected area electron diffraction (SAED) pattern obtained from TEM also indicated the amorphous nature of polyaniline. The TiO_2 nanoparticles exhibit diffraction from multiple lattice planes originating from polycrystalline nature of nanoparticles. The SAED pattern corresponding to the nanocomposite displays lattice planes showing inter planar spacing of 3.56 Å resulting from (101) lattice planes of TiO_2 nanoparticles. To study the vibration mode of PANI and PANI-TiO_2 nanocomposites, Raman spectra was observed. Absorption spectra of the nanocomposite samples have been taken using UV-VIS-NIR spectrophotometer (Varian Cary 5000). The band gap energy (E_g) of the nanocomposites was determined using Talc's relationship. As the content of TiO_2 was increased in the polymer matrix, the shift of the optical band gap was observed.

Keywords: X-ray spectra, UV-Vis spectra, Structure of nanoscale materials, Dielectric properties of solids and liquids.

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1. INTRODUCTION

The nanocomposites have been explored at great lengths in recent past due to their unique properties which were not available in their constituent materials. Conducting polymers are one such class of materials which exhibit unique electrical, optical and chemical properties, but their usage is limited due to their limited thermal stability. These conducting polymers find application in information storage, optical signal processing, batteries, and solar energy conversion [1-2]. Polyaniline (PANI) is one such conducting polymer, which is a candid photosensitizer due to its low band gap, π-*π transition in which the electron can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), high conductivity, good environmental stability, cheap monomer, and ease of preparation [3-5]. In line with other conducting polymers, PANI also suffers from lesser thermal stability which limits its applications. The synthesis of a composite material of PANI with any other component exhibiting superior thermal stability could present a new material with better characteristics for optoelectronic applications [6].

TiO_2 is one such material exhibiting excellent photocatalytic properties along with higher chemical stability, nontoxic and relatively low-price. Titanium (IV) oxide is found in rutile, anatase, brooked three polymorphic forms [7]. Among these forms, rutile and anatase phases are quite popular as a base for the use as pigments, catalysts and in the production of ceramic and electronic materials. On the other hand, the bottlenecks for TiO_2 usages such as wide band gap (3.2 eV) and low electrical conductance (1.1×10^{-5}-3.4×10^{-3} Ω/cm) could easily be addressed by mixing it with PANI [8-11]. The anatase TiO_2 is selected in this study which is more efficient as a photocatalyst than rutile form. Further, the clusters of TiO_2 formed during the composite formation can absorb UV energy which makes them suitable for photocatalytic application. The PANI in composite material can be decomposed by oxidation due to the presence of radicals released by irradiation and thus are useful as photocatalyst. Therefore, the contribution of higher conductivity from PANI and higher thermal stability of TiO_2 could complement each other in making new composite material with superior properties [12-14].

2. EXPERIMENTAL DETAILS

In-situ chemical oxidative polymerization method at lower temperature between 0-5 °C was used for synthesis of PANI, which has been reported earlier [15-16]. The $(PANI)_{1-x}(TiO_2)_x$ nanocomposite ($x = 0$, 0.02, 0.04, 0.08, 0.10) was prepared by an in-situ chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidant in the presence of an appropriate amount of colloidal TiO_2 nanoparticles at 0-5 °C in air. The obtained powder is washed multiple times and dried in vacuum before the structural, optical and dielectric measurements. The crystallinity of PANI, TiO_2 and PANI-TiO_2 nanocomposites is estimated by X-ray diffractometry (XRD, Bruker AXS D-8

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