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Synthesis and characterization of carbon nanotubes/titanium molybdate nanocomposite and assessment of its photocatalytic activity

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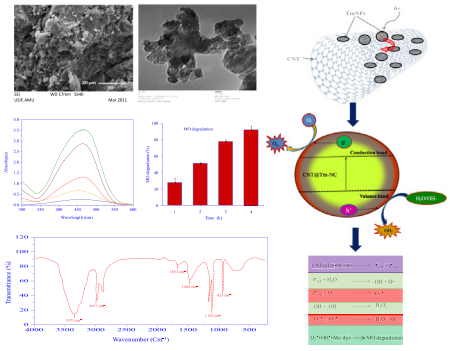
HIGHLIGHTS

- Carbon nanotubes/titanium molybdate nanocomposite (CNT@Tm-NC) was successfully synthesized.
- The structural, optical, thermal and dielectric properties of synthesized CNT@Tm-NC were studied.
- CNT@Tm-NC showed the photocatalysis of MO dye via production of ROS.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we have synthesized carbon nanotubes/titanium molybdate nanocomposite (CNT@Tm-NC), the structural, optical, thermal and dielectric properties of the as synthesized CNT@Tm-NC were studied. The XRD analysis ensures that CNT@Tm-NC has the nanostructure structure and confirmed that the titanium molybdate nanoparticles (NPs) were successfully incorporated in the CNT matrix. The thermal analysis (TGA) exhibited an enhanced thermal stability of the CNT@Tm-NC as compare with CNT owing to the strong interaction between the titanium molybdate NPs and CNT matrix. The energy band gaps as calculated through the Tauc relation were found to be higher in the CNT@Tm-NC. The impedance, dielectric constants (ε', ε''), dielectric loss ($\tan\delta$) and AC conductivity (σ_{ac}) were studied as the function of frequency, which have been explained by 'Maxwell Wagner Model'. Moreover, CNT@Tm-NC exhibited the promising photocatalytic activity for the photo-decoloration of the methyl orange (MO) dye under UV light irradiation. Results also showed protection of photo-decoloration of the MO dye by the disodium ethylenediaminetetraacetate dehydrate (EDTA-Na_2; $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) (hole scavenger) and tert-butyl alcohol ($C_4H_{10}O$) (radical scavenger) clearly suggested the implication of reactive oxygen species in the photocatalytic activity of CNT@Tm-NC. It is encouraging to conclude that CNT@Tm-NC bears the potential of it is applications in photocatalysis.

1. Introduction

The methyl orange (MO) dye belongs to the Azo group (—N=N—), which comprise about half of the total world dye market and during dyeing operation processes, about 15% of them end up in wastewaters [1]. Besides that, MO dye is also released by many industries such as paper, plastic, leather, food, cosmetic and pharmaceutical industries [2]. These effluents result in significant environmental pollution and recognized as potential carcinogens [3]. Thus, the search for new methods of photocatalysis beyond conventional methods has become a key aim of public health

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research [2,4]. Possible innovative strategies encompass the photocatalysis of MO dye through the use of novel class of NPs and nanomaterials [5].

Among them carbon nanotubes (CNTs) have attracted immense research interest in the last decade because of their unique optical, electronic, magnetic, mechanical, and adsorption properties [6]. The CNTs also exhibiting high electrical conductivity and high electron storage capacity and therefore act as extremely effective electron sinks. Hence, CNTs supported with metal oxide NPs have been reported to exhibit enhance physico-chemical properties from those of bare CNTs [7,8]. These modified properties of the CNTs/metal oxide NPs nanocomposites have been used to synergistically enhance the photocatalytic activity of metal oxide NPs through the retardation of electron–hole recombination [9,10].

There is, thus a need for identify a novel class of photocatalytic active CNTs based nanocomposites, could present us with new opportunities for the development of safe and effective nanomaterials for MO dye photocatalysis [11,12]. Therefore, in present study, we synthesized CNT@Tm-NC and investigated their photocatalytic activity against MO dye. Therefore, we tested the photocatalysis reaction driven by the CNT@Tm-NC or the ROS produced by the CNT@Tm-NC are responsible for degradation of MO dye. The photocatalysis enhancement of the MO dye is attributed to the excited state electrons in CNT which migrate to the conduction band (CB) of TmNPs.

2. Materials and methods

2.1. Materials

Titanium chloride and trisodium molybdate were purchased from E. Merck (India) Limited. Single-walled carbon nanotubes (SWNT), 2,7-dichlorofluorescin diacetate (DCFH-DA) and methyl orange (MO) dye were obtained from Sigma–Aldrich (St. Louis, Missouri, USA), other chemicals used in this study were purchased from SRL, India. All other chemicals used were of the highest purity available from commercial sources.

2.2. Synthesis of CNT@Tm-NC

For the *in situ* synthesis of CNT@Tm-NC, trisodium molybdate (1 mM) and titanium chloride (1 mM) were dissolved in 100 mL of MQ water using ultra-sonicator. The SWNTs (250 mg) was added into the 100 mL (trisodium molybdate/titanium chloride) solution and pH was increased to ~8.0 using ammonia solution. The reaction mixture was stirred for 1 h at 90 °C and synthesized CNT@Tm-NC was centrifuged. The synthesized CNT@Tm-NC was washed several time with water and dried in vacuum oven at 60 °C. The dried CNT@Tm-NC was converted into fine powder and stored in amber color sample container until further use.

2.3. Characterization of CNT@Tm-NC

The X-ray diffraction (XRD) patterns of powder sample of CNT@Tm-NC was recorded on MiniFlex™ II benchtop XRD system (Rigaku Corporation, Tokyo, Japan) operating at 40 kV and a current of 30 mA with Cu Kα radiation (λ = 1.54 Å). The diffracted intensities were recorded from 20° to 80° 2θ angles. The crystalline size (D) of the titanium molybdate (TM)-NPs in CNT@Tm-NC was calculated following the Debye–Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$; where λ is the wavelength of X-ray, β is the broadening of the diffraction line measured half of its maximum intensity in radians and θ is the Bragg's diffraction angle [13]. The crystalline size of the TM-NPs was determined by employing the full width at half maximum (FWHM) value of the most intense XRD peak present in the CNT@Tm-NC. For the FTIR spectroscopic measurements CNT@Tm-NC powder was mixed with spectroscopic grade potassium bromide (KBr) in the ratio of 1:100 and spectra recorded in the range of 400–4000 wavenumber (cm^{-1}) on Perkin Elmer FTIR Spectrum BX (PerkinElmer Life and Analytical Sciences, CT, USA) in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. The optical property of CNT@Tm-NC in the solution was monitored by measuring the absorbance (A) using UV–vis spectrophotometer (Perkin Elmer Life and Analytical Sciences, CT, USA) in the wavelength range of *A* 200–800 nm [13]. The morphological analysis scanning electron microscopy (SEM) was performed using the fine powder of the as synthesized CNT@Tm-NC on a carbon tape in a JSM-6510LV scanning electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV. The transmission electron microscopy (TEM) of aqueous solutions of CNT@Tm-NC was carried out on JEOL 100/120 kV transmission electron microscope (JEOL, Tokyo, Japan) with an accelerating voltage of ~150 kV. For TEM analysis, a drop of aqueous CNT@Tm-NC was placed on the carbon coated copper grid and air dried under dark. The obtained images were converted into an enhanced meta file format. The thermal stability of the CNT@Tm-NC was investigated by thermal gravimetric analysis (TGA)/differential scanning

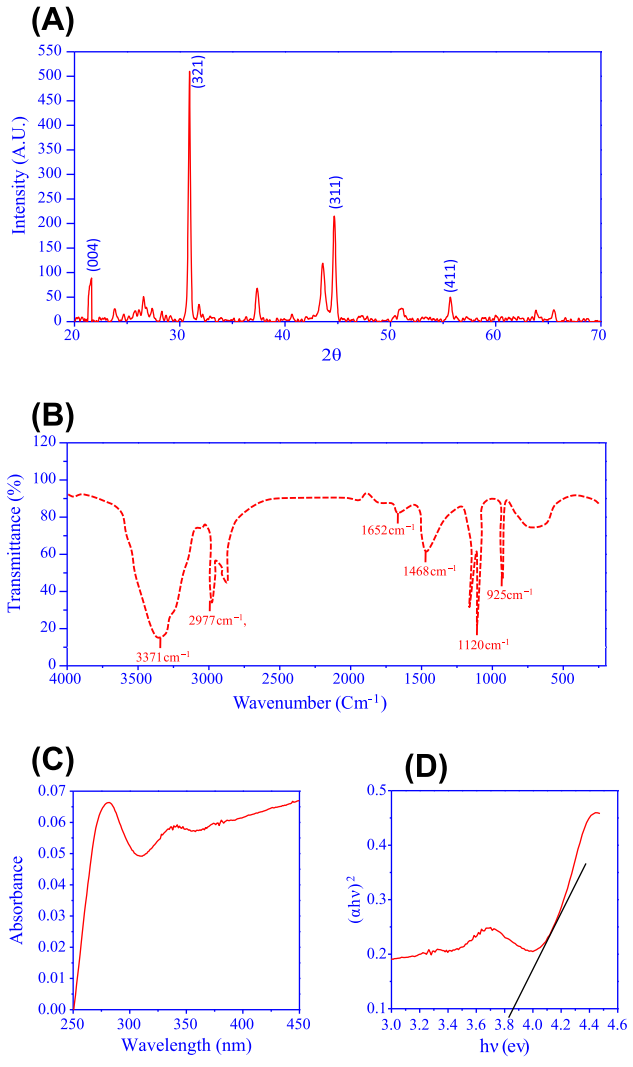

Fig. 1. Structural and optical characterizations of CNT@Tm-NC. (A) XRD pattern. (B) FTIR spectrum. (C) UV–visible absorbance spectrum and (D) energy band gap (E_g).