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In situ sol-gel synthesis of anatase TiO_2-MWCNTs nanocomposites and their photocatalytic applications

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ABSTRACT

Visible light photoactive titania-multiwalled carbon nanotubes (TiO_2-MWCNTs) nanocomposites were synthesized by *in situ* sol-gel method, in this TiO_2 nanoparticles were decorated on the surface of MWCNTs. The XRD analysis shows good crystalline nature of synthesized nanocomposite. UV–vis DRS study confirms the red shift of nanocmposites with respect to the increasing content of MWCNTs. The photocatalytic activity has investigated by degradation of methyl orange dye under ultraviolet as well as sunlight irradiation and photo-inactivation of *Bacillus subtilis* under visible light irradiation. The MWCNTs exist in the nanocomposite was able to absorb a high amount of photon energy in the sunlight, driving effectively photochemical degradation reactions. In the photodegradation of methyl orange dye under sunlight as well as photo-inactivation of *Bacillus substilis* under visible light, significant enhancement in the degradation/inactivation reaction rate was observed with the TiO_2-MWCNTs (0.5 wt.%), nanocomposite as compared to TiO_2 NPs. The COD study confirms the environmentally benign nature of photodegraded dye solution. This work provides new insight for the fabrication of sunlight/visible active TiO_2-MWCNTs nanocomposite photocatalyst for degradation of organic compounds and photo-inactivation of bacteria.

1. Introduction

The organic pollutant like dyes are one of the most hazardous chemical compounds present in industrial effluents and need to be treated since their presence in water bodies [1]. They are esthetically objectionable for drinking and other purposes [2]. The dyes from, paper, rubber plastic and textiles industries are released in the effluent water [3]. They are readily mixed with environmental water bodies on a large scale, during dyeing process, about 1 to 15% of the dye is lost and released in wastewater [4]. These dyes are the common pollutants and the major source of environmental contamination [5,6]. Numerous approaches are available for removal of organic pollutants and to treat the wastewater but these are very costly and ineffective.

Semiconductor titanium dioxide (TiO_2) is a benchmark photocatalyst for the successful removal of organic pollutants in both liquid and gas phases because of its efficiency, photo-stability, reusability and nontoxicity [7]. Even if TiO_2 NPs has several advantages, but it has two limitations, a large-scale technical applications, and electron-hole recombination which limit its efficiency [8]. TiO_2 NPs absorbs only 4–5% of the solar light impinging on the earth's surfaces because it active under only UV light irradiation with wavelength shorter than 400 nm with the optical band gap 3.2 eV [9,10]. To overcome these limitations several approaches have been applied to enhance photocatalytic activity of TiO_2 NPs by increasing active sites of reaction, retardation of electron–hole recombination and visible light catalysis by modifying optical properties of TiO_2 NPs. The most used strategies to modify the optical properties of TiO_2 NPs are metal doping [11], non-metal doping [12], and formation of nanocomposite with metal NPs [13], metal oxide NPs [14], polymer [15], and nanostructures of carbon material like carbon nanotube, graphene, fullerene etc. [16].

Nowadays MWCNTs have attracted great attention in photocatalytic studies due to their remarkable electrical [17], mechanical [18] and thermal [19] properties. The hetero-junction nanocomposite (NCs) of TiO_2-MWCNTs NCs show great ability to conduct electrons and adsorb organic pollutants [20,21]. The role of MWCNTs in photocatalytic activity can be explained as it acts as

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adsorbent and dispersing agent [22]. Additionally, the unique morphology of MWCNTs consists of multiple layers of graphite overlaid and rolled them to form tubular shape conductive structure might facilitate the separation of electron-hole pairs on the surface of TiO_2-MWCNTs NCs [21]. This help for increasing the rates of photocatalytic oxidation and enhancement in the photocatalytic efficiency of TiO_2 NPs. The various methods have been employed for the decoration of TiO_2 NPs on the surface of MWCNTs, impregnation, electro-spinning [17], electrophoretic deposition [23], chemical vapor deposition [24] and hydrothermal method [25].

Recently many researchers have investigated the preparation of TiO_2/CNTs NCs using various methods. Kuo et al. [26] prepared TiO_2/CNTs NCs film by chemical vapor deposition (CVD) method. This method requires highly expensive devices with high temperature for fabricating the nanocomposites. There are very few reports available on environmental non-benign organic precursors for direct coating of TiO_2 NPs on the surface of MWCNTs and its photodegradation performance towards methylene blue dye in the presence of visible light [27,28]. The TiO_2/MWCNTs NCs; which was prepared by wet impregnation also used for both liquid and gas phase environmental cleanups, but this methodology ease suffering with improper composition of the NCs [29] Ashkarran et al. synthesized solar photo and bioactive CNT-TiO_2 nanocatalyst by using electrical arc discharge method and applied for photo degradation of dye and inactivation of bacteria in present of UV light [30]. In earlier reports, we have synthesized TiO_2/MWCNTs NCs by ex-situ sol gel method and tested for photo-inactivation of bacteria under visible light irradiation [31]. Now researchers concentrated on the use of visible-light for photo degradation of pollutants using TiO_2-MWCNT nanocomposite as a photocatalyst [32]. Also TiO_2 based NPs has widely used for photo-inactivation of bacteria [33]. The removal of organic pollutant from the environment by using sunlight attracts the greatest attention due to its abundance on earth. Therefore, there is a need to fabricate photocatalyst material which shows higher efficiency under sunlight.

In the present work, we have synthesized TiO_2-MWCNTs NCs with different concentration of MWCNTs (0.1 to 0.5 wt.%) by a simple *in situ* sol-gel method. The aim of the present work is to enhance the photocatalytic efficiency of TiO_2 NPs under sunlight. The photocatalytic performance of TiO_2-MWCNTs NCs towards methyl orange (MO) dye under UV and sunlight irradiation and photo-inactivation of *Bacillus subtilis* under visible light irradiation was examined. The superior photocatalytic activity of TiO_2-MWCNTs NCs was observed compared to pure TiO_2 NPs under sunlight irradiation.

2. Materials and methods

2.1. Materials

Titanium (IV) isopropoxide (97% sigma Aldrich), glacial acetic acid (99% sigma Aldrich) and sodium dodecyl sulphate (sigma Aldrich) are of AR grade. MWCNTs were purchased from applied science innovations Pvt. Ltd Pune (synthesized with (CVD) method, diameter: 10–20 nm, length: 10–40 μm and surface area: >500 m^2/g).

2.2. Functionalization of MWCNTs

Acid treatment was carried out for the functionalization of MWCNTs as described in previous reports [34]. The MWCNTs were refluxed in a mixture of H_2SO_4: HNO was (3:1 vol ratio) at 100 °C for 5 h. Then, the content was cooled, centrifuged, and washed with distilled water several times to maintain its neutralization. Further, it was dried at 80 °C in the electric oven for obtaining its functionalized form. To further use, these functionalized MWCNTs (FMWCNTs) were dispersed in distilled water with ultra-sonication for a long time.

2.3. Synthesis of TiO_2-MWCNTs nanocomposites

The TiO_2-MWCNTs (TC) NCs were synthesized by *in situ* sol-gel methods. Stoichiometric (1:1) amounts of 5 mL titanium (IV) isopropoxide and 5 mL glacial acetic acid were mixed in aqueous solution, and then 5 mL aqueous sodium dodecyl sulphate (5 wt.%) was added. Afterword, a stoichiometric amount of FMWCNTs suspension was added; later 100 mL distilled water was added and stirred magnetically for 2 h. Then, 40 mL ammonia solution was added and in the mixture to maintain the pH 10 of whole mixture and stirred for 2 h at 60 °C. The precipitate was centrifuged and washed with deionized water and ethanol several times. The product was dried at 110 °C, calcinated in air at 450 °C for 4 h nanocomposite with different concentration of FMWCNTs (0.1, 0.3 and 0.5 wt.%) and these are denoted as TC 0.1, TC 0.3 and TC 0.5. Pure TiO_2 NPs were synthesized with same method without FMWCNTs suspension and denoted as TiO_2 NPs.

2.4. Photocatalytic degradation of methyl orange dye

The photocatalytic activity of TiO_2 NPs and TC NCs was evaluated for the degradation of an aqueous solution of methyl orange (MO) dye. Firstly, the MO degradation was carried out under UV light irradiation by using (365 W) medium pressure mercury lamp. The lamp was placed inside a cylindrical vessel and this vessel was surrounded by a circulating water jacket for cooling. The 100 mg of photocatalyst and 200 mL of aqueous solution of MO (20 ppm) was investigated for UV and sunlight activity. To ensure the adsorption-desorption equilibrium, the whole suspension was magnetically stirred in the dark for 30 min at room temperature. Then the solution was irradiated using medium pressure mercury lamp. The continuous stirring was maintained to keep the mixture in suspension. After a specific time interval, aliquots were withdrawn from the suspension and centrifuged immediately, in order to separate the NPs. The change in the concentration of MO dye in solution was monitored on UV–vis spectrophotometer by measuring the absorbance in the wavelength range 200–800 nm while distilled water is used as a reference. To study the degradation under the sunlight the same experimental procedure was followed under sunlight irradiation. The numbers of experiment were performed at 11 am to 4 pm in the month of May. During the photo degradation MO dye, the intensity of sunlight irradiation was measured with light meter (model Agonic Lx-101, Agrawal Electronics, India,) and this was 1120 W/m^2. All the experiments of photo degradation were performed at ambient temperature and average experimental data is reported here.

2.5. Chemical oxygen demand (COD) analysis

The chemical oxygen demand (COD) test is commonly used as a promising technique to measure the organic strength of waste water. This test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water [35]. The COD of dye solution was estimated under dark and light condition, as well as before and after the photocatalytic treatment with a standard dichromate method using COD digester. The test samples are MOS = MO dye stock solution (20 ppm), MOD = dye solution stirred under dark and MOL = dye solution after light treatment with catalyst TC 0.5 NCs.