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High surface area Ag-TiO_2 nanotubes for solar/visible-light photocatalytic degradation of ceftiofur sodium

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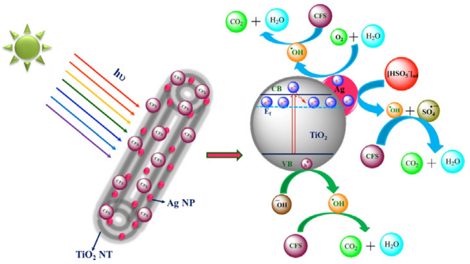
HIGHLIGHTS

- Large surface area TiO_2 nanotubes have been synthesized and modified with Ag NPs.
- Ag-TiO_2 NTs show very good charge separation due to 1D charge delocalization.
- They exhibit excellent photocatalytic degradation of CFS under UV–vis light.
- It photocatalytically activates $HSO_5{}^-$ to produce $^{\bullet}$OH and $SO4^{\bullet -}$ simultaneously.
- Ag-TiO_2 NTs retain their photocatalytic activity at least up to 4 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium dioxide nanotubes (TiO_2 NTs) with very high surface area (469 m^2/g) have been synthesized through a simple hydrothermal method and their surface has been modified using silver nanoparticles (Ag NPs). The Ag NPs deposited TiO_2 NTs (Ag-TiO_2 NTs) show an extended optical response from UV to visible region coupled with a surface plasmon resonance band and thus can be utilized as a plasmonic photocatalyst. The photoluminescence intensity of TiO_2 NTs is lower than that of TiO_2 nanoparticles due to the delocalization of photogenerated electrons along the one dimensional nanotubes which reduces the rate of charge recombination. The Langmuir adsorption constant of Ag-TiO_2 NTs (for ceftiofur sodium adsorption) is twice that of P25 TiO_2. The Ag-TiO_2 NTs exhibit excellent photocatalytic activity toward the degradation of ceftiofur sodium (CFS) due to high surface area and mesoporosity of TiO_2 NTs. The addition of peroxomonosulfate in the photocatalytic system greatly amplifies the CFS degradation owing to the simultaneous generation of both •OH and $SO_4{}^{\bullet -}$. The catalyst retains its photocatalytic activity at least up to four consecutive cycles.

1. Introduction

The application of nanostructured materials toward the photocatalytic degradation of environmentally harmful organic pollutants has recently gained much attention [1,2]. Among the various semiconductor photocatalysts available, TiO_2 is the most widely employed material because of its superior photo-reactivity, non-toxicity, long-term stability and low-cost [3]. However, in recent years, much dedication has been paid to one dimensional (1D) TiO_2 nanomaterials, such as, nanorods (NRs) [4,5], nanotubes (NTs) [2,6] and nanofibers (NFs) [7,8], owing to their superior physical and opto-electronic properties. The surface modification of these 1D TiO_2 nanostructures by adopting appropriate synthetic techniques has opened-up wide range of possibilities for obtaining increased photocatalytic activity. The distinct physical properties of 1D nanomaterials, such as, high surface area and mesoporous

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nature of nanotubes [6,9], superior charge transport property of nanofibers [8] and large surface area and enhanced surface defects of nanorods [4,10], make these 1D nanomaterials as potential competitors to zero dimensional (0D) nanomaterials (i.e., nanoparticles (NPs)). The quantum confinement of electrons at nanoscale level assists the rapid and unidirectional transport of photogenerated charge carriers to target pollutants [11,12]. However, the photocatalytic efficiency of TiO_2 nanomaterials including the 1D TiO_2 nanostructures is still not up to the mark to meet out the practical needs under direct sunlight irradiation due to wide band-gap energy ($\sim$3.2 eV), poor quantum yield and occurrence of rapid charge recombination reactions. Much research efforts have been focused toward the modification of TiO_2 with an aim to overcome the above limitations [12–15].

Generally the deposition of noble metal nanoparticles on a semiconductor surface extends the absorption of semiconductor from UV to visible-light region of the solar spectrum, owing to the unique surface plasmon resonance absorbance feature, and enhances the electron–hole pair separation and as a consequence, the rate of photocatalytic reaction increases. Noble metal nanoparticles show strong and broad surface plasmon resonance (SPR) absorption in the visible region of the solar spectrum due to the collective oscillations of their conduction band electrons by absorbing visible light. The frequency of the SPR band can be tuned by altering the size and shape of the noble metal nanoparticles, which can dramatically amplify the visible-light absorption and therefore employed to develop efficient visible-light-driven plasmonic photocatalysts [16]. In the plasmonic photocatalysts, in which noble metal nanoparticles are deposited on the surface of semiconductor, the metal nanoparticles act as a component for harvesting visible light due to their surface plasmon resonance while the metal–semiconductor interface efficiently separates the photogenerated electrons and holes. Hence, several works pertaining to surface modification of TiO_2 nanoparticles (TiO_2 NPs) with noble metal NPs such as gold (Au) and silver (Ag) and their application as photocatalysts have been carried out with considerable success [17–19]. The photocatalytic activity of noble metal NPs loaded TiO_2 toward the degradation of various environmental pollutants, such as, methylene blue [20], methyl orange [21], rhodamine blue [22,23] and 4-cholorophenol [24], have been well documented. However, their photocatalytic efficiency is not up to the level needed for practical applicability. Therefore, it is essential to develop new plasmonic photocatalysts with high specific surface area, low charge recombination, superior photocatalytic activity and good stability.

Among the different 1D TiO_2 nanomaterials, the TiO_2 nanotube (TiO_2 NT) is regarded as a most promising material owing to its fascinating properties [25]. Recent studies demonstrate that the TiO_2 NTs with high specific surface area prepared through anodization technique exhibit outstanding photocatalytic properties [26,27]. But, it has not been possible to rely on expensive anodization techniques for the large-scale preparation of TiO_2 NTs and hence researchers are concentrating on low-cost hydrothermal methods. In view of the above facts, in the present work, TiO_2 NTs with very high surface area were synthesized through a simple hydrothermal method and their surface was modified with silver nanoparticles (Ag NPs). Their photocatalytic activity toward the degradation of ceftiofur sodium (CFS), a third-generation cephalosporin antibiotic, was studied. The CFS is generally administered through intramuscular injection for the treatment of certain respiratory diseases in beef cattle, swine and day-old chicks and also in the treatment of inter-digital dermatitis of cattle [28]. Thus, CFS is usually discharged from animal farms and regarded as a major persistent organic pollutant to both soil and water environment [29,30].

2. Experimental

2.1. Materials

Titanium(IV) chloride (Merck, 99.6%) was used as a starting material for the preparation of TiO_2 nanoparticles (TiO_2 NPs). Silver nitrate (Sigma–Aldrich, 99.9%) was used as a precursor for the preparation of silver nanoparticles. Potassium peroxomonosulfate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and potassium peroxodisulfate ($K_2S_2O_8$) purchased from Sigma Aldrich, and hydrogen peroxide purchased from Merck were used as such. Ceftiofur sodium ($C_{19}H_{16}N_5O_7S_3Na$) obtained from Fluka was employed as a target organic pollutant.

2.2. Synthesis of TiO_2 nanoparticles (TiO_2 NPs)

$TiCl_4$ (3 mL) was slowly introduced into double distilled water in an ice bath (0 °C) under constant stirring until it was completely dissolved and then 6 mL of 30% NH_4OH was added to this suspension [31]. The generated white titanium hydroxide ($Ti(OH)_4$) was allowed to stand for 1 h. Then, the obtained TiO_2 NPs were filtered, washed with double distilled water and dried at 100 °C in a vacuum oven for 3 h.

2.3. Synthesis of TiO_2 nanotubes (TiO_2 NTs)

TiO_2 NTs were synthesized by employing a slightly modified hydrothermal method reported already [32]. Briefly, TiO_2 NPs (1 g) were dispersed in 50 mL of 10 M aqueous NaOH solution in a 250 mL round bottom flask under constant stirring for 30 min. The milky white suspension was then heated in an oil bath at 120 °C for 48 h and filtered after cooling. The precipitate was re-dispersed in 250 mL of 0.025 M HCl and stirred for 30 min. The TiO_2 NTs formed were separated through filtration followed by washing with double distilled water, dried at 100 °C for 3 h and calcined at 400 °C for 3 h in a muffle furnace.

2.4. Preparation of Ag-TiO_2 nanotubes (Ag-TiO_2 NTs)

The silver nanoparticles (Ag NPs) were deposited on the surface of TiO_2 NTs through photo-reduction method [33] in which Ag^+ ions were converted to Ag NPs under UV irradiation. 1 g of the preformed TiO_2 NTs were dispersed in 250 mL of double distilled water and irradiated with UV light for 10 min to remove the impurities present on their surface. About 2.5% (w/w) of Ag^+ (i.e., 40 mg of $AgNO_3$) was added into the TiO_2 NTs suspension and the pH was adjusted to 3.5 using perchloric acid, followed by UV irradiation for 40 min with continuous stirring under N_2 atmosphere. Then, the suspension was filtered, washed thoroughly with double distilled water, dried at 100 °C for 3 h and finally calcined at 400 °C for 3 h to obtain the Ag-TiO_2 NTs.

2.5. Characterization studies

Diffuse reflectance spectra (DRS) of the samples were recorded on a Shimadzu UV-vis spectrophotometer (UV-2550) fitted with ISR-2200 DRS accessory. Solid-state photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 spectrofluorophotometer. Material phase analysis was carried out by powder X-ray diffraction (XRD) technique (Rigaku diffractometer, CuKα radiation, $\lambda = 1.5406$ Å). Morphological analysis of the TiO_2 NTs and Ag-TiO_2 NTs were carried out using a transmission electron microscope (TECNAI G^2). Flowsorb II 2300 Micrometrics surface area analyzer was employed for measuring the surface area, pore volume and pore diameter of the samples. The extent of degradation