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Phase stability and photoactivity of CuO modified titania nanotube prepared by hydrothermal method

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ABSTRACT

Titania nanotubes prepared through a modified hydrothermal method were functionalized with CuO in order to create a composite photocatalyst with enhanced reactivity. Their structural and morphological stability was monitored using X-ray diffraction and scanning and transmission electron microscopy. The X-ray photoelectron spectroscopy analysis indicated the presence of CuO in the titania matrix, which enhanced the anatase to rutile phase transformation. The morphological stability and photoactivity of titania nanotubes depend on the amount of CuO incorporated into the material matrix. The photocatalytic activity of the materials displays two maxima and a minimum and is the result of complex structural and electronic interactions and competing mechanisms.

1. Introduction

Heterogeneous photocatalysis using titania nanostrucutures has numerous applications in pollution control and environmental purification systems [1]. The low toxicity, chemical inertness, and wide availability of titania make it a highly attractive photocatalyst for these applications [2]. The applicability of titania; however, will be expanded when it is modified to absorb visible light more strongly and to better match the solar spectrum and when its photoefficiency is improved [3]. The life times of the photogenerated holes and electrons play an important role in determining the photocatalytic efficiency of the system. Titania nanocomposites containing mixed phases (e.g., anatase and rutile) or mixed oxides (e.g., WO_3/TiO_2) often improve light harvesting, reduce charge recombination, and enhance photoactivity [4–6]. The solid–solid interfaces of mixed phase TiO_2 are critical for electron transfer, charge trapping and defect stabilization [7–9]. In anatase and rutile mixed phase it is reported that at the interface electrons migrate from rutile to anatase and holes from anatase to rutile [10–12]. Other oxides also show enhanced charge transfer and increased photoactivity at heterojunctions [13–15].

Coupling titania with small band gap semiconductors is a widely accepted strategy for visible light sensitization and enhanced charge separation [16]. Cu_2O, for instance, has been shown to enhance the visible light photoactivity of titania by sensitization and improved charge separation [17]. The mixed oxide, TiO_2–Cu_2O, boosted the photocatalytic degradation of dodecylbenzenesulfonate under visible light irradiation and the authors observed that a 5% TiO_2–Cu_2O composite showed better activity than the other samples [18]. Cu_2O/TiO_2 nano-hetrostructures prepared through chemical precipitation method improved the photoactivity for the degradation of acid orange II in water under UV and visible light irradiation. An 70:30 composition of Cu_2O and titania exhibit maximum photocatalytic efficiency [19]. Anodized titania nanotube arrays decorated with Cu metal improve the photoelectrocatalytic reduction reaction of Cr^{6+} ion [20]. Hydrothermally synthesized titania nanotubes were effectively used for the removal Cu(II) ions from the solution to create a material that in turn showed enhanced photocatalytic degradation of bisphenol A [21]. Cu^{2+} ion grafted on titania and WO_3 also

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effectively produced the photocatalytic degradation of 2-proponol under visible light. The interfacial charge transfer from the titania valence band to Cu(II) ion provides visible light phtotoacivity to the system [22,23]. Cu_2O doped titania nanotubes prepared by a sonochemical electrochemical deposition technique showed improved photocurrent in the solar spectrum [24]. Cu doped titania was effective for the photoreduction of CO_2 to methanol [25–27]. The detrimental effect of Cu loading beyond 3 wt.% in photocatalytic activity was noted by Slamet et al. [25]. The optimum loading of CuO on rutile titania was found to be 0.1 wt.% by Li et al. [28]. They established the existence of two type of Cu^{2+} species in the titania matrix through EPR spectroscopy and observed the trapping of excited electron by Cu^{2+} centers reduces the photoactivity at a Cu concentration above 0.1 wt.%. In the present work we synthesize a material that combines high surface area titania nanotubes with CuO, a narrower band gap semiconductor, to increase the photocatalytic activity of the system, and specifically, to determine if the composite shows visible light activity. We also investigate in detail the effect of CuO loading on the morphological and phase stability of the anatase titania nanotubes.

2. Experimental

2.1. Preparation of CuO functionalized titania nanotubes

Titania nanotubes were prepared by a modified hydrothermal method described previously [29–33]. In a typical experiment, 2 g of anatase titania powder (assay 99%, Sigma Aldrich Chemicals, USA) was stirred with 50 ml of 10 M NaOH solution (assay 97%, BDH Chemicals, USA) in a 125 mL Teflon lined pressure digestion vessel. The digestion vessel was kept in an oven for 48 h maintained at 120 °C and the resultant precipitate was washed with 1 M HCl (assay 38%, EMD Chemicals, USA) followed by several washings using deionized water to attain a pH between 6 and 7. The titania nanotube powder thus formed was dried in an oven at 110 °C over night. The doping was carried out by ultrasonically dispersing titania nanotube with a calculated amount of cupric sulphate and ammonium hydroxide solution, stirring for 30 min at 293 K, and then mixing 2% hydrogen peroxide solution as reported in our earlier publication [28]. Different concentrations of $CuSO_4$ (corresponding to 0.1, 0.5, 1, 2 and 4 mol% Cu) were added to the titania matrix. The resulting powders were further calcined under hydrogen atmosphere (80 ml min^{-1}) at 400 °C for 3 h. The undoped and Cu doped samples are denoted as NT, 0.1CuNT, 0.5CuNT, 1CuNT, 2CuNT and 4CuNT.

2.2. Characterization

XRD patterns of the samples were taken in a Rigaku X-ray diffractometer in the diffraction angle 2θ range 5–80° using Cu Kα radiation. The anatase to rutile ratio was calculated using Spurr equation [34].

$$\%\text{Rutile} = \frac{1}{1 + 0.8[I_A(101)/I_R(110)]}$$

X-ray photoelectron spectra (XPS) were obtained with an Omicron ESCA-2000-125 spectrometer using an Al Kα radiation source. The optical spectra of the samples were recorded with a diffuse reflectance attachment on a Cary 1E UV–vis light spectrophotometer. The morphology of titania nanotubes was observed by a scanning electron microscope (SEM, Hitachi S-4800-II, Japan) and a Hitachi HD-2300A dedicated scanning transmission electron microscope with three image detectors (secondary electron detector, bright-field detector, and high-angle annular dark-field detector) at 200 kV. BET surface area measurements and pore size analysis were carried out by nitrogen adsorption using a micromeritics gemini 2010 surface area analyzer after degassing the sample at 120 °C for 24 h.

2.3. Photocatalytic activity measurement

The photocatalytic activity of samples was studied using acetaldehyde photodegradation as previously described in detail [35,36]. For photocatalytic measurements, 10 mg of TiO_2 nanotube and CuO doped TiO_2 nanotube powders were placed in a photocatalytic system consisting of a closed square Teflon container with a quartz window. Into the closed dark chamber, 1 ml of saturated vapor of acetaldehyde was introduced and kept for 1 h for equilibration. Photocatalytic reactions were carried out by irradiation with a Xenon arc lamp. For the UV–vis light experiments, no filter was used. For visible light experiments, a 400 nm long pass filter was installed. The energy density and irradiance spectra for the lamp with and without the 400 nm filter are included in Fig. S1 of the Supplementary information. As the photo catalytic reaction proceeded, the degradation of acetaldehyde was monitored at different time intervals using an HP 5890 gas chromatograph equipped with a flame ionization detector (GC–FID).

3. Results and discussion

3.1. Characterization of CuO functionalized titania nanotubes

The X-ray diffraction patterns of the samples are provided in the Fig. 1 and indicate that up to 0.5 mol% Cu loading only the tetragonal phase of anatase is present. When the concentration of Cu is increased above 0.5 mol% anatase to rutile phase transformation occurs. Cu is reported to enhance the anatase to rutile phase transformation [37–39]. It is proposed that the lower valence Cu cation accelerates this phase transformation by creating oxygen vacancy defects in titania [40]. It is worth noting that although XRD may not indicate the presence of rutile in materials with Cu loading of 0.5 mol% and lower, there may be small domains

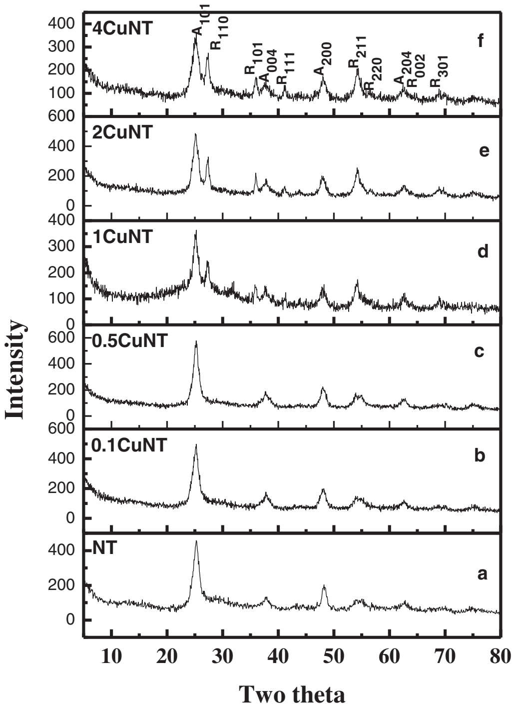

Fig. 1. X-ray diffraction pattern of samples (a) NT (b) 0.1CuNT (c) 0.5CuNT (d) 1CuNT, (e) 2CuNT and (f) 4CuNT; anatase (1 0 1) and rutile (1 1 0) main peaks are marked.