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SiO_2-coated pure anatase TiO_2 catalysts for enhanced photo-oxidation of naphthalene and anthracene

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ABSTRACT

Our current efforts reveal the preparation of SiO_2@TiO_2 nanocomposites having different thicknesses of silica shell and the relationship to photocatalytic activity (PCA) for the photo-oxidation of naphthalene and anthracene. The presence of SiO_2 coating over TiO_2 surface was demonstrated by FT-IR analysis, with peaks corresponding to Si—O—Si (1081 cm^{-1}) and Si—O—Ti (950 cm^{-1}) bonds observed. High-resolution transmission electron microscopy analysis confirmed the presence of SiO_2 in the as-prepared nanocomposites and the amount of Si, Ti, and O was determined by energy dispersive X-ray spectroscopy analysis. Increasing the SiO_2 shell thickness increases the surface area of the nanocomposites (69–235 m^2/g), which enhances naphthalene/anthracene adsorption. However, the observed PCA trend presents an inverse correlation to the adsorption studies, where the as-prepared samples possessing the highest surface areas exhibited the least PCA, while catalysts having lower surface areas (among silica coated samples) displayed the highest PCA in the degradation of naphthalene and anthracene to CO_2. Despite complete degradation of naphthalene and anthracene, incomplete mineralization occurred, ascribed to the formation of various intermediates, identified by GC–MS analysis.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of environmental pollutants that form largely by the incomplete combustion of crop residue, of which soil is a major source. PAHs are found primarily in soil, sediments, oil, and air. Among the variety of 16-PAHs there are toxicological concerns, as some are found to be carcinogens (Deng et al., 2006; Lo & Zhang, 2005). Studies have shown that 90% of human exposure to PAHs derive from food intake, thereby classifying them as an environmental pollutant; hence, PAHs should be minimized (Boström et al., 2002; O'Neill et al., 2003; Rengarajan et al., 2015). Human health risks of exposure to 16-PAHs by way of inhalation during autumn and winter seasons, for both children and adults living in the urban area of Amritsar and Punjab, India, is increasing and also affects roadside soil in the developing cities. Indeed, there are a number of PAHs; however, two PAHs, namely naphthalene (2 rings) and anthracene (3 rings), are initially formed during the combustion of agriculture waste and therefore are considered in the present study.

Heterogeneous photocatalysis using TiO_2 as a photocatalyst has shown great potential (Chen & Mao, 2007; Grover, Singh, & Pal, 2013, 2014; Nakata & Fujishima, 2012) for the degradation of numerous organic contaminants because of their low cost, low toxicity, high stability, and high photo efficiency compared with other photocatalysts. Typically however, lower specific surface areas of TiO_2 result in fewer reacting molecules adsorbing on the surface, which is disadvantageous for its photocatalytic activity (PCA). Within this context, modification of TiO_2 through coating with inert compounds, specifically with SiO_2, has drawn increasing research interest (Anderson & Bard, 1995; Hilonga, Kim, Sarawade, & Kim, 2010; Nussbaum & Paz, 2012; Ren, Chen, Zhang, & Wu, 2010; Wang, Wang, Chen, & Hori, 2008; Wilhelm & Stephan, 2007; Zhang et al., 2011) to increase the Brunauer–Emmett–Teller specific surface area (S_{BET}) and PCA. The larger band gap and relative location of the Fermi level of SiO_2 to that of TiO_2 suggests that the SiO_2 coating of TiO_2 hinders photo-produced charge carrier (e^-/h^+) transportation from the TiO_2 core to the surface, thus enhancing their recombination and blocking photoactivity (Lee, Koo, & Yoo, 2012; Nur, 2006; Nussbaum & Paz, 2012).

Interestingly, the presence of SiO_2 in the SiO_2@TiO_2 nanocomposite does not necessarily result in any deleterious effect to the PCA. Conversely, the silica shell can promote significant enhance-

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ment to the TiO_2 PCA. Such cases include the photooxidation of: β-naphthol (Qourzal et al., 2009), methylene blue, rhodamine-6G (Anderson & Bard, 1995), propyzamide (Torimoto, Ito, Kuwabata, & Yoneyama, 1996), and propionaldehyde (Takeda, Torimoto, Sampath, Kuwabata, & Yoneyama, 1995). However, most literature report the use of commercially available Degussa P25 TiO_2 as the titania source (Anderson & Bard, 1995; Hu, Li, & Fan, 2012; Lee et al., 2012; Nur, 2006; Ren et al., 2010; Zhang et al., 2011), whereas few have demonstrated other TiO_2 shapes and crystal structures (Hilonga et al., 2010; Nussbaum & Paz, 2012; Wang et al., 2008; Wilhelm & Stephan, 2007). Manipulating both the titania shape and crystal structure can yield limitless photoexcited charge carriers and concomitantly their PCA can be remarkably improved (Chen & Mao, 2007; Grover et al., 2013, 2014; Nakata & Fujishima, 2012). Therefore, by selecting the appropriate TiO_2 nanoparticle phase and shape, and thereafter applying a SiO_2 coating, the PCA can be enhanced and applied to the degradation of pollutants such as PAHs (Caruso, Susha, & Caruso, 2001; Lee, Omolade, Cohen, & Rubner, 2007; Lei et al., 2007; Rasalingam, Peng, & Koodali, 2014). Towards this end, TiO_2 nanoparticles comprising a nearly pure anatase phase and mixed morphologies (nanorods and nanopolygons) were modified with SiO_2 and comparatively studied against the commercial P25 TiO_2 source for the degradation of naphthalene and anthracene to CO_2 as well as determining their photo-produced intermediates.

Experimental

Preparation, characterization and photocatalytic activity of silica-coated TiO_2 nanoparticles

Titanium dioxide nanorods were synthesized *via* a hydrothermal route using P25 TiO_2 (Degussa Corporation, Germany, 99.9%) as a precursor, as reported previously (Grover et al., 2013). The obtained TiO_2 nanorods were calcined at different temperatures (200–800 °C) and among the as-prepared samples, TiO_2 nanorods calcined at 500 °C (C-5) were selected for the SiO_2 coating, as their properties have previously been reported to deliver enhanced PCA (Grover et al., 2014). Prior to silica coating, 50 mg of the as-prepared C-5 TiO_2 nanorods were sonicated (ultrasonicator Branson-1610, USA) in a mixture of ethanol (12 mL, Loba Chemicals, India 99.9%) and acetic acid (18.4 mL Loba Chemicals, India, 99.9%) for 30 min to fully disperse the titania in the media. Thereafter, a mixture of ethanol (6.2 mL) and tetraethyl orthosilicate (TEOS, Sigma–Aldrich, 99.9%) (1, 2, and 4 wt%,with respect to C-5) was added drop-wise to the above suspension under vigorous stirring followed by slow addition of concentrated H_2SO_4 (50–100 μL, Sigma–Aldrich, 99.9%). The system was refluxed at 80–90 °C for 1 h, washed with successive quantities of ethanol and dried. The catalysts are abbreviated as: S-C-5(1), S-C-5(2), and S-C-5(4), thereafter.

All samples were characterized using an absorption spectrophotometer (4000USB, Ocean Optics, USA). The FT-IR spectra of the samples were recorded using a Carry-600 FT-IR spectrometer (Agilent, USA) by placing pelletized samples (~1–2 mg) mixed with 100 mg KBr (dried at 90–100 °C for 3 h). Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) analysis was performed using a JSM 7600F microscope (JEOL, Japan), while high-resolution transmission electron microscopy (HR-TEM) images were recorded on a Hitachi 7500 electron microscope (Hitachi, Japan), using 120 kV accelerating voltage. S_{BET} were measured using a Smart Sorb 91/92 analyzer (Smart Instruments, India) using 150 mg of sample preheated at 150 °C for 1 h.

The photocatalytic activity of these catalysts was evaluated by irradiating 5 mL (20 ppm) aqueous solution of naphthalene and anthracene (Loba Chemie, India, 99.7% and 96% respectively) in a rubber-capped air-tight test tube under UV light

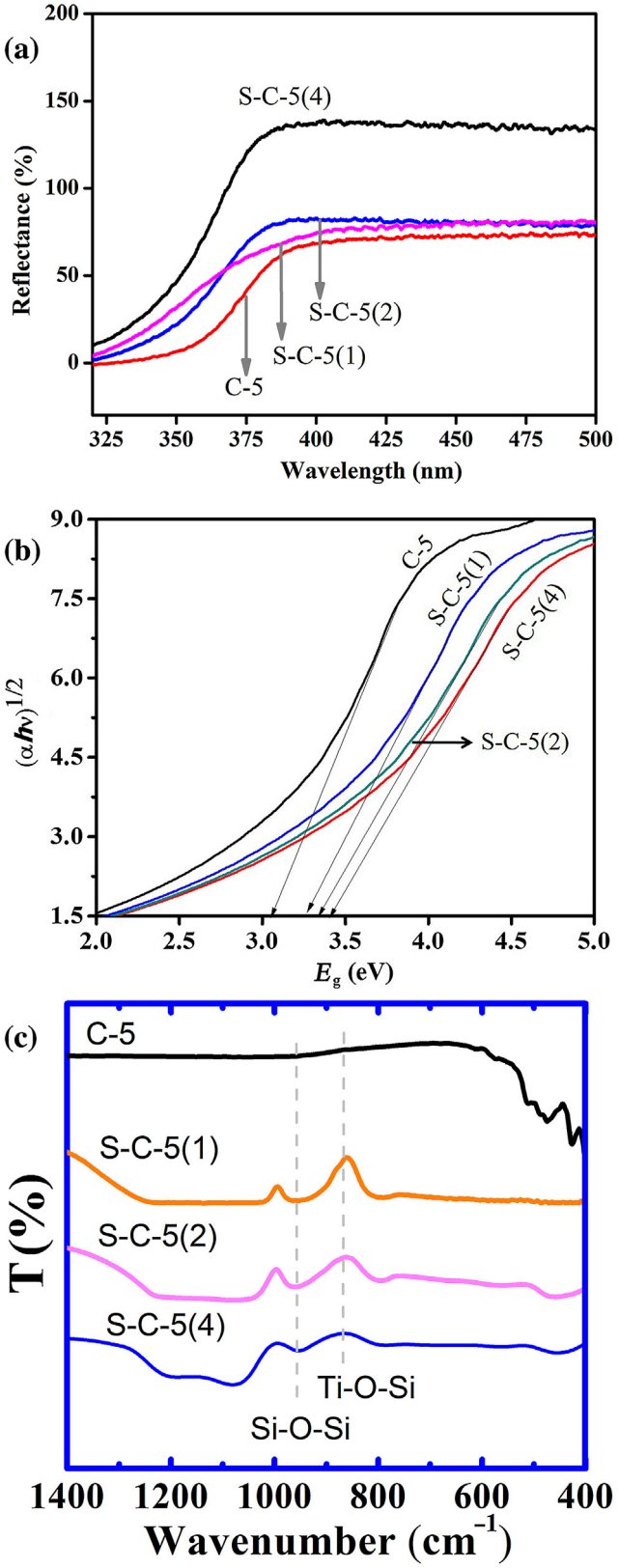

Fig 1. (a) Diffuse reflectance spectra, (b) bandgap energies, and (c) FT-IR spectra of as-prepared catalysts.

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