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Gadolinium doped tin dioxide nanoparticles: an efficient visible light active photocatalyst

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Abstract: Photocatalytic degradation of phenol with sol-gel prepared rare earth doped tin dioxide (SnO_2) nanoparticles was reported. Gadolinium doped tin dioxide (SnO_2:Gd) nanoparticles were found to absorb higher visible light compared to lanthanum, neodymium and cerium doped materials that were studied in detail. Photocatalytic degradation of phenol under artificial white light and sunlight in the presence of SnO_2:Gd nanoparticles was studied with high performance liquid chromatography (HPLC), capillary electrophoresis (CE), total organic carbon (TOC) measurements and the determination of chemical oxygen demand (COD). Clear correlations between the results obtained from these multiple measurements were found, and a kinetic pathway for the degradation process was proposed. Within 150 min of solar irradiation, the TOC of a 10 ppm phenol solution in water was reduced by 95%–99%, thus demonstrating that SnO_2:Gd nanoparticles are efficient visible light photocatalysts.

Keywords: rare earth dopants; solar irradiation; phenol photo-degradation; tin dioxide nanoparticles; organic by-products

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Increased water pollution across the world, has drawn considerable attention for the need of environmentally friendly, clean chemical technologies to remove the contaminants. Natural water sources today are threatened by the high concentration of hazardous chemical substances, such as phenol, bisphenol A, phthalates, azo dyes, herbicides, pesticides among others, most being the contribution from oil refining and industrial discharges[1,2]. Excess use of fertilizers and pesticides[3], pharmaceutical residues[4], land filling of domestic wastes[5] from rotting of vegetation[6] contribute to pollute water resources. Phenol is a hazardous and a recalcitrant water pollutant, difficult to be completely degraded through common waste water treatment methods, leading to toxicity towards microorganisms, causing serious environmental concerns. It is a necessity to remove these toxic compounds from natural water prior to its use.

Advanced oxidation processes (AOPs) are the best technologies for the treatment of persistent organic pollutants to harmless end products. These techniques are based on the generation of reactive species such as hydroxyl radicals. Semiconductor photocatalysts are increasingly applied technology for the reduction of organic and inorganic compounds in water. Many researchers have reported that titanium dioxide (TiO_2), zinc oxide (ZnO) and tin dioxide (SnO_2) are active catalysts capable of degrading dyes, phenols and pesticides[7–10]. Furthermore, these semiconductors have been recognized as preferable materials for photocatalytic processes because of their high photosensitivity, nontoxic nature, low cost of production 11and chemical stability[10,12–15]. In the photocatalytic oxidation process, organic pollutantsare decomposed in the presence of a wide-band gap semiconductor that promote reactions in the presence of UV light without being consumed in the overall reaction[16]. Though the band gap of SnO_2 (3.6 eV), ZnO (3.3 eV) and TiO_2 (3.2 eV) are quite comparable[17–19], SnO_2 is not used very frequently compared to the other two photocatalysts[18]. Photocatalytic degradation of organic compoundsis mainly achieved through irradiation with ultraviolet lamps, whose sources are mainly mercury vapor lamps that require relatively high energy to run, contain hazardous mercury, and needs cooling, leading to a short life time. An option to replace Hg lamps is the use of light emitting diodes (LED)[20–22]. Another alternative is the utilization of solar light, which is abundant free source of energy for providing environmentally friendly, green chemical processes. Recent interest has developed in the synthesis of SnO_2 nanoparticles of different sizes[23,24].

In order to render the large band gap metal oxide semiconductors photoactive in the visible region, several attempts have been reported like doping TiO_2 with nitrogen[25], ZnO with transition metals[15] or with rare earth metals among others[24]. Incorporation of rare earth metal ions into the SnO_2 matrix introduces defects lowering the optical gap and hence leading to a better

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photoactivity in the visible region[24,26,27]. Several studies of SnO_2 doping with different metals to produce nanocrystals have been reported in recent years[28–30]. On SnO_2 stoichiometric surfaces, Sn^{4+} is easily reduced to Sn^{2+} changing the surface electronic structure of the material, leading to the formation of Sn5S. Also, oxygen atoms residing on the nanoparticle surface lead to energetically favorable reconstructions of the SnO_2 (110) and (101) surfaces[31]. The oxygen vacancies thus produced, easily bind with electrons to form an excitation energy level below the conduction band of SnO_2. It is well known that the influence of rare earth (RE) cations on the catalytic properties of SnO_2 is associated with acid/base characteristics of the oxides involved[32–35]. SnO_2 is an oxide (isoelectronic point, iep ~4–7), whereby (RE) basic characters favor some catalytic aspects[36]. Also (RE) metals incompletely occupy 4f and empty 5d orbitals, imbibing the formation of labile oxygen vacancies with relatively high mobility of bulk oxygen species[25]. Doping with (RE) cations influences the material's electronic distribution, causing the absorption of oxygen species and producing high surface area and smaller sized particles[37–39]. Rare earth metals co-doped TiO_2 have shown potential in red shifting absorption and thus improving the photocatalytic activity of TiO_2 more than undoped TiO_2 under visible light irradiation[40].

The most widely used solution for the synthesis of SnO_2 nanoparticle is sol-gel processes, based on hydrolysis of a reaction of metal alkoxidesin water:

$$Sn(C_2H_5O)_4+4H_2O \xleftrightarrow{\text{Hydrolysis}} Sn(OH)_4+4C_2H_5OH \quad (1)$$

The alkoxy groups are substituted by hydroxide groups with the evolution of an inorganic network (sol) that is followed by a second reaction (condensation) as follows:

$$2Sn(OH)_4 \xleftrightarrow{\text{Condensation}} 2SnO_2+4H_2O \quad (2)$$

Two hydrolyzed molecules liberate water (gel), upon linking together that occurs through the destruction of the gel with the subsequent formation of nanoparticulate materials[24,26,27]. Sol-gel method offers several advantages, such as high purity, better homogeneity, precise control over the stoichiometry, and capability in controlling the powder size and surface of metal oxide at lower temperatures. In this work, visible light active tin dioxide nanoparticles doped with rare earth metals were synthesized and detailed studies of photocatalytic activity studies under visible light irradiation were presented for gadolinium doped SnO_2 nanoparticles with phenol in water as a test contaminant.

1 Experimental

1 Materials

Analytical-grade tin (IV) chloride ($SnCl_4$, Sigma Aldrich, purity: 99.99%), sodium tetraborate ($Na_2B_4O_7$, Merck, 99.99%), sodium dihydrogen phosphate (NaH_2PO_4, Merck, 99.99%), lanthanum nitrate hexahydrate ($La(NO_3)_3·6H_2O$, Fluka), cerium (III) chloride anhydrous ($CeCl_3$ Sigma Aldrich, 99%), (ammonium cerium (IV) nitrate $(NH_4)_2Ce(NO_3)_6$, Sigma Aldrich, 99%), (neodymium (III) nitrate hexahydrate ($Nd(NO_3)·6H_2O$, Sigma. Aldrich, 99%), gadolinium (III) chloride ($GdCl_3$, Sigma Aldrich, 99.9%), ethanol, (C_2H_5OH, ETAX Aa Merck Absolute), phenol (C_6H_5OH Sigma Aldrich, purity: 99.99%), *p*-benzoquinone (O: C_6H_4:O, BDH, AnalaR 99.99%), resorcinol ($C_6H_4(OH)_2$, BDH, AnalaR 99.%), acetic acid ($C_2H_4O_2$, Sigma Aldrich, purity: 99.99%), catechol ($C_6H_6O_2$, Sigma Aldrich, purity: 99.99%), hydroquinone (Sigma Aldrich, purity: 99.99%), (sulfuric acid (H_2SO_4, Sigma Aldrich, 99.99%), hydrochloric acid (HCl, Sigma. Aldrich, 99%), sodium hydroxide pellets (NaOH, SigmaAldrich, 99%), and methanol (CH_4O, Sigma Aldrich, 99% HPLC grade), sodium chloride (NaCl, BDH 99% AnalaR grade) were used in the experimental studies. Double deionized water with a high purity from Ultra Clear Water SG was used for the preparation of all solutions.

1.2 Photocatalyst preparation

1.2.1 Synthesis of pure and doped-SnO_2 nanoparticles

SnO_2 nanoparticles containing different mass percentages of rare earth metal (gadolinium, lanthanum, cerium and neodymium) ions in the starting solution were synthesized by sol-gel process, according to the following procedure: 3.80825 mL of $SnCl_4$ mixed in 50 mL absolute alcohol (ethanol) and 50 mL ultra-pure water in a round bottom flask and used as precursor for synthesizing control (undoped SnO_2) nanoparticles. The mixture was subjected to vigorous stirring for 3 h at room temperature, until a colourless solution was obtained. For the synthesis of rare earth metals doped tin oxide nanoparticles, different concentrations of rare earth metals (0.2 wt.%, 0.4 wt.%, and 0.6 wt.%) were mixed and dissolved separately in ethanol and added to the precursor solution. A turbid colloidal solution of tin alkoxide started to appear after adding 25% aqueous ammonia drop by drop into the solution with continuous stirring until a pH value of 8 was reached. The sol was left for 48 h for aging in air until the gel was formed. Filtration and successive washing with ultra-pure water was repeated several times to remove both ammonia and chloride ions until all chloride ions had been removed (determined by examining the filtrate solution using aqueous silver nitrate solution). Later a series of samples were synthesized in the same way by changing the concentration of tin tetrachloride and the mass percentage amount of the required dopant. Each dopant was added carefully and under vigorous stirring to the total solution containing pure tin tetrachloride. They were then subjected to dissolution in ethanol