

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

Abdullah M Al-Hamdi¹, Mika Sillanpää¹, Joydeep Dutta^{2,3,*}

(1. Laboratory of Green Chemistry, Lappeenranta University of Technology, Sammonkatu 12, 50130 Mikkeli, Finland; 2. Chair in Nanotechnology, Water Research Center, Sultan Qaboos University, P.O. Box 17, 123 Al-Khoudh, Sultanate of Oman; 3. Functional Materials Division, School of Information and Communication Technology, KTH Royal Institute of Technology, Isafjordsgatan 22, SE-16440 Kista, Stockholm, Sweden)

Received 31 March 2015; revised 20 July 2015

Abstract: Photocatalytic degradation of phenol with sol-gel prepared rare earth doped tin dioxide (SnO₂) nanoparticles was reported. Gadolinium doped tin dioxide (SnO₂: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 SnO₂: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 SnO₂:Gd nanoparticles are efficient visible light photocatalysts.

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

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 (TiO₂), zinc oxide (ZnO) and tin dioxide (SnO₂) are active catalysts capable of degrading dyes, phenols and pesticides^[7–10]. Furthermore, these semiconductors have been recognized

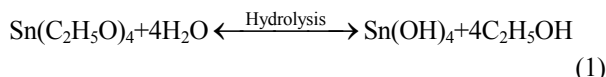
as preferable materials for photocatalytic processes because of their high photosensitivity, nontoxic nature, low cost of production^[11] and chemical stability^[10,12–15]. In the photocatalytic oxidation process, organic pollutants are decomposed in the presence of a wide-band gap semiconductor that promote reactions in the presence of UV light without being consumed in the overall reaction^[16]. Though the band gap of SnO₂ (3.6 eV), ZnO (3.3 eV) and TiO₂ (3.2 eV) are quite comparable^[17–19], SnO₂ is not used very frequently compared to the other two photocatalysts^[18]. Photocatalytic degradation of organic compounds is 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 SnO₂ 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 TiO₂ with nitrogen^[25], ZnO with transition metals^[15] or with rare earth metals among others^[24]. Incorporation of rare earth metal ions into the SnO₂ matrix introduces defects lowering the optical gap and hence leading to a better

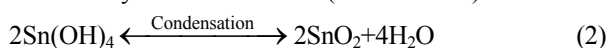
* Corresponding author: Joydeep Dutta (E-mail: dutta@squ.edu.om, joydeep@kth.se; Tel.: +46737652186)

photoactivity in the visible region^[24,26,27]. Several studies of SnO₂ doping with different metals to produce nanocrystals have been reported in recent years^[28–30]. On SnO₂ stoichiometric surfaces, Sn⁴⁺ is easily reduced to Sn²⁺ 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 SnO₂ (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 SnO₂. It is well known that the influence of rare earth (RE) cations on the catalytic properties of SnO₂ is associated with acid/base characteristics of the oxides involved^[32–35]. SnO₂ 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 TiO₂ have shown potential in red shifting absorption and thus improving the photocatalytic activity of TiO₂ more than undoped TiO₂ under visible light irradiation^[40].

The most widely used solution for the synthesis of SnO₂ nanoparticle is sol-gel processes, based on hydrolysis of a reaction of metal alkoxides in water:



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:



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 SnO₂ nanoparticles with phenol in water as a test contaminant.

1 Experimental

1 Materials

Analytical-grade tin (IV) chloride (SnCl₄, Sigma Aldrich,

purity: 99.99%), sodium tetraborate (Na₂B₄O₇, Merck, 99.99%), sodium dihydrogen phosphate (NaH₂PO₄, Merck, 99.99%), lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, Fluka), cerium (III) chloride anhydrous (CeCl₃ Sigma Aldrich, 99%), (ammonium cerium (IV) nitrate (NH₄)₂Ce(NO₃)₆, Sigma Aldrich, 99%), (neodymium (III) nitrate hexahydrate (Nd(NO₃)₃·6H₂O, Sigma Aldrich, 99%), gadolinium (III) chloride (GdCl₃, Sigma Aldrich, 99.9%), ethanol, (C₂H₅OH, ETAX Aa Merck Absolute), phenol (C₆H₅OH Sigma Aldrich, purity: 99.99%), *p*-benzoquinone (O: C₆H₄:O, BDH, AnalaR 99.99%), resorcinol (C₆H₄(OH)₂, BDH, AnalaR 99%), acetic acid (C₂H₄O₂, Sigma Aldrich, purity: 99.99%), catechol (C₆H₆O₂, Sigma Aldrich, purity: 99.99%), hydroquinone (Sigma Aldrich, purity: 99.99%), (sulfuric acid (H₂SO₄, Sigma Aldrich, 99.99%), hydrochloric acid (HCl, Sigma Aldrich, 99%), sodium hydroxide pellets (NaOH, SigmaAldrich, 99%), and methanol (CH₄O, 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-SnO₂ nanoparticles

SnO₂ 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 SnCl₄ 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 SnO₂) 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

Download English Version:

<https://daneshyari.com/en/article/1259793>

Download Persian Version:

<https://daneshyari.com/article/1259793>

[Daneshyari.com](https://daneshyari.com)