

Intermediate formation during photodegradation of phenol using lanthanum doped tin dioxide nanoparticles

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Received: 5 May 2015/Accepted: 24 July 2015 © Springer Science+Business Media Dordrecht 2015

Abstract Lanthanum (La)-doped tin dioxide (SnO_2) nanoparticles were synthesized by a modified sol–gel method at room temperature. The samples were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The photocatalytic activity of La:SnO₂ samples were investigated by studying the degradation profile of phenol and its by-products in water. The treated samples were analyzed by HPLC–UV and a UV–Vis spectrophotometer. Benzoquinone, catechol, resorcinol, hydroquinone, acetic acid, and 2-propanol were identified as phenol degradation intermediates. Maximum concentration acquired was in the order of catechol, resorcinol, hydroquinone, and benzoquinone, which was observed in the beginning stages while iso-propanol and acetic acid were observed in the final stages of phenol degradation. We achieved a complete photodegradation of a 10 ppm aqueous phenol solution and intermediates with 0.6 % of SnO₂:La nanoparticles in 120 min under artificial solar irradiation. A maximum degradation rate constant of 0.02228 min⁻¹ of propanol and a minimum of acetic acid 0.013412 min⁻¹ were recorded at 37 °C.

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Keywords Photocatalysis \cdot SnO₂ \cdot Rare earth metal \cdot Lanthanum \cdot By-product \cdot Phenol

Introduction

The overuse of pesticides, pharmaceuticals, and personal care products in modern society leads to many kinds of organics polluting the environment. Phenols or derivatives of phenols are commonly encountered organic pollutants in toxic waste discharged in industrial effluents [1, 2]. The accumulation of these toxic pollutants can adversely affect human life and derail sustainable development [3, 4] because of their toxicity, endocrine disrupting abilities, and carcinogenic behavior [5]. Phenol and its by-products are released into the air and water as a result of industrial activities [6]. Sources of phenol and its derivatives in water has been found in waste water discharged from refining activities of oil and coal tar industries [7], distillation of wood or coal [6], phenolic chemicals used in livestock dips [8], and discharges of domestic sewage or rotting vegetation [9]. The European Union and other countries have included some phenols in their list of priority pollutants [10], thus; it is important to develop new and effective treatment processes for the removal of organic and inorganic pollutants from water.

Advanced oxidation processes (AOP) are among the most effective technologies for the treatment of organic pollutants, because they can generate strong oxygenbased oxidizers (OH) [11], which can react non-selectively with different types of organics and can achieve complete oxidation [12]. AOP techniques can be built up using a combination of chemical and physical agents such as a catalyst and ultraviolet light [13].

Photocatalysis is a green technology for water treatment to remove recalcitrant organic compounds. Tin dioxide or stannic oxide (SnO₂) is one of the most promising metals oxide semiconductor photocatalysts, in which the inherent oxygen vacancies act as n-type dopants leading to effective charge separation in the presence of a pollutant [14]. SnO₂ has a rutile type tetragonal crystal structure, and its band gap is 3.6 eV at room temperature [15]. There are numerous applications of SnO₂, as gas sensors, pH sensors, and biosensors [16], in lithium ion batteries [17], transparent conductive electrodes, [18] etc. SnO₂ is, however, less studied compared to the other photocatalysts such as titanium oxide TiO_2 and ZnO [19]. Thus, it is of interest to investigate the influence of dopants on the enhancement of the photocatalytic activities of SnO_2 [20]. In addition, these semiconductors have been recognized as preferable materials for photocatalytic processes due to their high photosensitivity, nontoxic nature, low cost, and well-known chemical stability [21-25]. Apart from these properties, a good visible-light photocatalyst should have a high specific surface area and an adequate optical absorption band to be able to absorb sunlight. Incorporation of metal ions into the SnO₂ matrix could introduce defects lowering the effective optical gap and, hence, leading to a better photocatalytic activity [26, 27]. Renewed interest in the synthesis of SnO₂ nanoparticles of different sizes has probably arisen to address these problems [28-30].

Photocatalytic degradation of organic compounds is mainly achieved by ultraviolet light irradiation due to the wide metal oxide bandgap. A better alternative is to use visible light, or solar irradiation as it is an abundant free source of energy. Many ways have been developed for rendering the wide band gap metal oxide semiconductors photoactive in the visible region [31]. Of these, incorporation of defects in the metal oxides with transition metals is very popular [28]. For example, rare earth metal ions incorporated into the SnO₂ matrix introduces defects in the valence band tail states, effectively lowering the optical gap and, hence, leading to a better photoactivity in the visible region [32-34]. Several studies of SnO₂ doping with different metals to produce nanocrystals have been reported in recent years. [35–37] Sn^{4+} can be easily reduced to Sn^{2+} leading to a change in the surface electronic structure of SnO₂. Oxygen atoms on the surface of SnO₂ nanoparticles lead to energetically favorable reconstructions of the SnO₂ (110) and (101) surfaces [38]. These oxygen vacancies bind with electrons forming an excitation energy level below the conduction band of SnO₂. As rare earth metals incompletely occupy 4f and 5d orbital's, formation of labile oxygen vacancies with relatively high mobility of bulk oxygen species can occur very easily [39].

Sol-gel synthesis of SnO_2 nanoparticle is very popular as it is based on simple hydrolysis of metal alkoxides in aqueous media:

$$Sn(C_2H_5O)_4 + 4H_2O \xrightarrow{hydrolysis} Sn(OH)_4 + 4C_2H_5OH.$$

The alkoxy groups are replaced by hydroxide groups forming an inorganic network (sol) that is followed by a second reaction (condensation) as follows:

$$2\text{Sn(OH)}_4 \xleftarrow{\text{condensation}} 2\text{SnO}_2 + 4\text{H}_2\text{O}.$$

The sol-gel method offers several advantages, including the formation of homogeneous nanoparticles, precise control over the stoichiometry, and purity while the reaction takes place at lower temperatures.

In this work we describe the preparation of La doped tin dioxide nanoparticles at room temperature, using the sol–gel synthesis method. The photocatalytic properties SnO_2 :La nanoparticles were evaluated by studying the degradation profile of phenol and its intermediates that will contribute to a better understanding of the phenol degradation processes. This work provides a framework for studying degradation pathways in similar and for complex organic toxins.

Experimental

Materials

Analytical-grade tin (IV) chloride (SnCl₄₋, Sigma Aldrich, Purity: 99 %), lanthanum nitrate hexahydrate (La (NO₃)₃·6H₂O, Fluka), ethanol (C₂H₅OH, ETAX Aa Merck Absolute), phenol (C₆H₅OH, Sigma. Aldrich, 99 %), catechol (C₆H₆O₂, Sigma Aldrich, Purity: 99.99 %), hydroquinone (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 %), propan-2-ol ((CH₃)₂CHOH, Sigma Aldrich, Purity: 99.99 %), sulfuric acid (H₂SO₄, Sigma Aldrich, Purity: 99 %), hydrochloric acid (HCl, Sigma. Aldrich, 99 %), sodium hydroxide pellets (NaOH, Sigma. Aldrich, 99 %) and methanol (CH₄O, Sigma. Aldrich, 99 % HPLC 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.

Photocatalyst preparation

Synthesis of pure and doped-SnO₂ nanoparticles

Nanoparticles containing various molar compositions of SnO₂ were chemically synthesized by the sol-gel method, following the procedure described below: 3.80825 ml of SnCl₄ mixed in 50 ml absolute alcohol (ethanol) and 50 ml ultrapure water in a round bottom flask and used as a precursor for synthesizing 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 lanthanum metal doped tin oxide nanoparticles, a certain concentration of this metal was 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 %) of aqueous ammonia drop by drop into the solution upon continuous stirring until a pH value of 8 was reached. The sol was aged for 48 h in air until a 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). The dopant concentration studied in this work was kept up to 0.6 %, following our previously reported work [32].

Material characterization

Optical absorption spectra of colloidal suspension were recorded in a double beam spectrometer (Perkin Elmer, Lambda 45). To study the surface morphology of the SnO₂:La samples, scanning electron microscopy (SEM) was carried out with JEOL (JSM-5600LY) (Japan) working at 30 kV. High resolution transmission electron microscopy (HRTEM) was carried out with JEOL (JEM 2100F) (Japan) working at 200 kV. The crystalline phase of the synthesized SnO₂ nanoparticles were analyzed by X-ray powder diffraction (XRD) using a MiniFlex 600 diffractometer (Rikagu, Japan) with Cu K_{\alpha} radiation (wavelength = 1.54 Å). Diffractograms of powder was recorded in a 20 scan configuration, in the 10°–80° 20 range, with the data collected at steps of 0.02°. Then, 200–300 mg of sample was degassed at 300 °C for 3 h under nitrogen (N₂) flow, followed by a six point N₂ adsorption carried out at p/p_0 of 1–5 in a Nova[®] 2200 analyzer. The surface area was determined by a gas adsorption technique using the Nova[®] 2200 (Brunauer–Emmett–Teller (BET) method).

Photocatalytic experiments

UV photocatalytic reactor

The photoreactor was a cylindrical Pyrex-glass container of 50 mm internal diameter and 300 mm in height with 250 mL capacity. An 8 W medium pressure mercury lamp (Osaka, Japan) was used with an intensity of about 80 W/m² and the reaction temperature was kept at 25 °C by cooling with water.

Visible light photocatalytic reactor

The Pyrex-glass reactor was used with a cooling water jacket with a 250 ml capacity, 100 mm internal diameter, and 200 mm height. A 300 W xenon lamp simulating a solar light source (PLS-SXE300C, Beijing Perfect light Co. Ltd., China) was placed 71 mm above the surface of contaminant during the photocatalysis studies.

Experimental procedure

To investigate the effects of SnO₂:La, oxidative photodegradation of phenol and its intermediates were chosen to evaluate the photocatalytic activity of synthesized nanoparticles. The study of degradation of phenol and its by-products in water was carried out at 25 °C using the water-cooled cylindrical glass batch photoreactor of 250 mL volume. The experimental conditions were varied as follows: The amount of catalyst powder (photocatalyst) was kept at 0.065 g in 50.00 mL; the initial concentration of the pollutant was varied from 5-100 ppm and the pH of the solution was adjusted by the addition of 0.5 N NaOH to fix pH at 5.7. Then, 10 mg/ L phenol solution was used to carry out photocatalysis experiments. Before each test, the mixture was kept in the dark for 30 min under constant magnetic stirring to ensure that the adsorption-desorption equilibrium was reached before illumination. The sample was then taken out at the end of the dark adsorption period, prior to turning the light on or before exposure to sunlight. When the lamp was turned on, the irradiation time varied from 2 to 3 h; aliquots of the suspensions were collected and removed from the reactor every 15 or 30 min. At the given time intervals, the photocatalyst particles were removed from the samples first by centrifugation (4000 rpm, 5 min) using an Eppendorf Centrifuge (system model 5810R) and then filtered through 0.2 µm Millipore filters.

Analytical methods

Phenol photodegradation by-products were analyzed using high performance liquid chromatography (UHPLC focused), containing a P580 high-precision pump from Thermo Scientific (Germering, Germany), and fulfilling the requirement for a measured delivery rate of the mobile phase. The injector was a Rheodyne (Cotati) 8125 valve fitted with a 20 μ L loop. The analysis was carried out using a C18 column (5 μ m silica) maintained at room temperature. After elution from the

column, the eluent passed through a Variable Wavelength Detectors (VWD-3400RS) set at 245 nm for phenol and its intermediates detection. The mobile phase for the HPLC separation was prepared by mixing methanol with water in the ratio 45:55 and then adjusting the pH at 3.0 by adding sulfuric acid (H_2SO_4). The mobile phase was degassed in an ultrasonic bath, and then passed through a Millipore filtration apparatus (0.2 µm). Photodegraded phenol and control samples were then eluted at a flow rate of 1 mL/min.

The change in phenol concentration in each photodegraded solution was also monitored by an ultraviolet-visible (UV-Vis) spectrometer (Perkin Elmer Lambda 45), and the maximum absorbance of phenol was measured at $\lambda_{max} = 269$ nm.

Results and discussion

Crystallinity of SnO₂ nanoparticles doped with lanthanum

The XRD pattern (Fig. 1) showed that the diffraction angles at $2\theta = 26.3^{\circ}$, 33.6° , 51.5° , and 65° that can be assigned to (110), (101), (211), and (112) planes of the of SnO₂, respectively, matching with the standard XRD file of the rutile phase of SnO₂ (JCPDS-#41-1445) [40–43]. SnO₂ crystallite sizes obtained from the Debye Scherrer equation considering the most intense peak (110) follows the well-known trend of crystallite size reduction upon doping. An increase in surface area was also observed, which was attributed to the decrease in grain size as it can be seen from Table 1.



Fig. 1 X-ray diffraction (XRD) patterns of SnO₂:La and pure undoped particles synthesized by the solgel process

Table 1 Comparison of surfaceareas and estimated crystallite	Dopant	Size nm	Surface area
sizes for undoped and lanthanum doped SnO ₂ nanoparticles	Undoped	7.5	28
	SnO ₂ :La	3.4	40



Fig. 2 Typical scanning Electron Micrograph of SnO_2:La nanoparticles synthesized by the sol-gel process

The 3.4 nm crystallites agglomerate to form 50 nm particles as observed by SEM (Fig. 2). In order to get a better insight into the morphology, we carried out high resolution HRTEM as shown in Fig. 3.The crystallite sizes are comparable to what was estimated from the XRD. The surface area of the synthesized nanoparticles was found to be between around $28-40 \text{ m}^2/\text{g}$.

Photocatalytic degradation

Photodegradation occurs due to the formation of active radicals during redox reaction. When a photocatalyst absorbs a photon of light (hv), it is enough to excite the electrons to the higher states creating an electron (e^-) and a positive-hole (h^+) pair

$$\text{SnO}_2 + hv \rightarrow \text{SnO}_2(e_{CB}^-h_{VB}^+).$$

The holes (h^{+}) dissociates water molecules to generate hydroxyl radicals and hydrogen gas

$$\text{SnO}_2(h_{VB}^+) + \text{H}_2\text{O}_{ads} \rightarrow \text{SnO}_2\text{OH}_{ads}^{\cdot} + \text{H}^+$$

The holes (h^+) mostly react with water (i.e., hydroxide ions, $OH^-)$ to produce OH^- , which is very a powerful oxidant.

Fig. 3 Typical high resolution transmission Electron micrograph of SnO₂:La nanoparticles synthesized by the sol-gel process



$$\text{SnO}_2(h_{VB}^+) + OH_{ads}^- \rightarrow \text{SnO}_2 + OH_{ads}^-$$

The electron reacts with an oxygen molecule to form superoxide radicals $(O_2^{-\cdot})$. The hydroxyl radical is an extremely powerful oxidation agent, and the cycle continues until light is available.

$$\text{SnO}_2(e_{\text{CB}}^-) + \text{O}_{2ads} \rightarrow \text{SnO}_2 + \text{O}_2^{-1}$$

The hydroxyl radical will oxidize the pollutant and any intermediates, and the final product is carbon dioxide and water.

 $SnO_2(h_{VB}^+) + phenol \rightarrow SnO_2 + oxidized products$

UV-Vis spectroscopy

UV scans (200–400) were used to investigate possible intermediates formed in solution during photodegradation of phenol by using SnO₂:La. Previous research on phenol degradation has shown that phenol first degrades to benzoquinone and then the ring is opened to form other smaller byproducts like the carboxylic acids [44, 45]. The adsorption ability of the samples were tested, and it was found that after 30 min in dark conditions, very minimal changes of phenol adsorption were observed on the SnO₂:La nanoparticles. The UV–Vis spectra at different time intervals during phenol photodegradation with SnO₂:La are shown in Fig. 4. At the outset only one broad peak was present at 269 nm that was observed due to



Fig. 4 Spectra of phenol photodegradation and reduction in the intensity of phenol peak observed by UV–Vis spectrophotometry in the presence of 0.6 wt% lanthanum doped SnO_2 nanoparticles. The appearance of different phenol byproducts appear in the Figure

absorption in the aromatic ring. This absorption band was used as a reference for the photodegradation analysis. A clear decrease of the 269 nm absorbance band intensity was observed with increasing photo irradiation time (Fig. 4). A slight decrease of the 269 nm absorbance band, but a simultaneous increase at the 290 nm band and a higher increase of the 246 nm absorbance band can be associated with the formation of phenol, hydroquinone (HQ), and benzoquinone (BQ), respectively, within 15 min of photo irradiation. After 30 min of light irradiation, the phenol absorbance band was reduced, but a concurrent increase and broadening of the 290 nm band and a rising increment with broadening of a 246 nm band was observed. After 60 min of irradiation, the characteristic peak at 290 nm reduces, and the 246 nm peak intensity decreases with the disappearance of the phenol peak. After 90 min of irradiation, it is clear that all phenol was degraded and also the formed intermediates are being further degraded.

Intermediates of phenol degradation

HPLC separation technique

In order to conclusively characterize the byproducts formed during the photocatalytic reaction, chromatographic techniques were used to study the degraded phenol



Fig. 5 Separation of phenol and its by-products form benzoic acid and paraben mixture observed by (HPLC)

mixture. Degradation of phenol in water, followed by the formation of many intermediates, some of which could be more toxic than phenol itself, which causes symptoms such as muscle weakness, convulsions, and coma upon contact to human skin. Phenol, upon oxidation, produces several aromatic intermediates, such as benzoquinone, catechol, resorcinol, and some acyclic compounds, including oxalic acid, formic acid maleic acid, and fumaric acid. We have been able to separate phenol by-products in solutions during photocatalysis, by different techniques such as GC/MS and also using techniques to quantify these intermediates by HPLC and CE. Here, we used a simple reverse phase HPLC technique to separate the parabens, benzoic acid, phenol, benzoquinone, catechol, resorcinol, hydroquinone, acetic acid, and isopropanol in less than 5 min as shown in Fig. 5. Maximum concentration of intermediates obtained is in the order catechol > resorcinol > hydroquinone > benzoquinone as shown in Fig. 6.

In fact OH generated from photocatalytic degradation of phenol reacts with OH^- , either to produce catechol or hydroquinone. Catechol or hydroquinone reacts with OH^- to form benzoquinone. Upon continuous oxidation, the benzene ring will be opened leading to the formation of aliphatic compounds, which would finally mineralize to CO_2 and water. The degradation as observed by optical spectroscopy is different from what was registered using chromatography as the extinction coefficients play a part in the final optical absorption of the by-products. For example, benzoquinone absorbs nearly ten times more than phenol around 269 nm, which is the peak absorption of phenol. Thus, the formation of the by-products would mask the degradation level of phenol if only optical spectroscopy is used. In effect UV–Vis spectroscopy would not render a correct picture of the phenol degradation process, thus all subsequent discussion are based on chromatographic studies (Fig. 7).



Fig. 6 Evolution of phenol by-products during phenol photodegradation in the presence of SnO₂:La nanoparticles in a 10 ppm aqueous phenol solution



Fig. 7 Degradation of phenol and its by-products after 2 h treatment with SnO₂:La

Degradation mechanism of phenol involving the O-H bond

Formation mechanism In order to better understand the degradation mechanism, the major degradation by-products were studied independently upon photo irradiation.

The reaction of phenol starts by breaking the O–H bonds resulting in giving up a proton thus forming an anion stabilized by the aromatic ring as shown in Fig. 8.



Fig. 8 Possible degradation mechanism of phenol and resonance stability of phenoxide, and the formation of the benzoquinone intermediate

Activation of the phenol by hydroxyl radicals will produce phenoxy radicals, which are in resonance with radical structures in ortho and para positions [46]. The three mesomeric forms of the radical are the initial formation of the different intermediates. These radicals can react with the hydroxyl radicals to form compounds such as hydroquinone, benzoquinone, and catechol as explained above.

Benzoquinone

Benzoquinone was traced in the degradation process for the first 30 min of photodegradation. The formation rate of benzoquinone was found to be 0.0107 ppm/min, and the degradation rates were calculated from the reduction of benzoquinone peak to be 0.00357 ppm/min.

Catechol

Degradation of phenol produces higher concentrations of catechol compared to any other by-products, which might be related to the ortho directed properties group of phenol. Catechol was formed within 15 min of phenol degradation and its concentration increased to a maximum of 0.7 ppm, and kept increasing until it reached 3 ppm after 45 min increasing at a rate of 0.1249 ppm/min. After 75 min, concentration of catechol decreased at a rate of 0.0292 ppm/min. We can observe from the graph that catechol keeps being produced until all the phenol is degraded.

Resorcinol

Resorcinol appeared from the beginning, and its concentration increased from 0.3 ppm until it reached to 1.5 ppm and became stable at that point after 75 min of photocatalytic degradation at a rate of 0.0075 ppm/min. The almost stable concentration of resorcinol production in our mixture means that it will be produced by the same rate until all phenol can be removed from the solution. We also noticed that resorcinol concentrations were higher than hydroquinone. In this

case it seems that the substitution rules of OH⁻ radicals attacking the phenol molecule with higher probability in 1 and 4 positions (ortho and para directing effect) are weaker than the nonselective nature of attack of the OH⁻ group of the aromatic ring.

Hydroquinone

During phenol degradation, hydroquinone appeared after 30 min, and it was at a maximum after 45 min of photo-irradiation at a rate of 0.0025 ppm/min. After 60 min of phenol photodegradation, benzoquinone concentrations decrease sharply and further slow reduction was observed until all phenol was removed from the solution.

Acetic acid

Ring opening of the by-products lead to the formation of acetic acid; pH also increases (results not shown) [47]. Acetic acid appeared in the reaction medium after 45 min at a rate of 0.0015 ppm/min.

Iso-propanol

The 2-Propanol is also known as isopropanol, and has a neutral pH level of approximately 7 (as we obtained from our previous analysis, result not shown) [47], almost similar to pure water. It seems that propionic acid competes with acetic acid, a reason why we are getting traces of this compound sometimes before acetic acid, and at other occasions, after acetic acid. Iso-propanol appeared in the solution after 75 min of photocatalytic degradation at a rate of 0.0813 ppm/min.

Photocatalytic degradation of different aromatic compounds

To compare the photocatalytic activity of phenol and its intermediates, the photocatalytic activity of phenol and its by-products in lanthanum doped tin dioxide was investigated in a series of experiments with a control and 0.6 wt% La^{3+} -SnO₂. The influence of lanthanum doped tin dioxide nanoparticles on the degradation of phenol and removal of its by-products in aqueous solution is presented in Fig. 7. The overall degradation rate of phenol and its by-products was higher upon using SnO₂:La than those with pure (control) tin dioxide nanoparticles (Fig. 9).

A maximum rate of removal of the by-products, such as phenol was achieved using La: SnO_2 (Fig. 9). An observed rate of phenol degradation was fitted with first-order rate constants (Table 2). The rate of degradation of propanol was quite similar to phenol. The rate of degradation of phenol was slightly higher than that of acetic acid. Slower degradation rates were also observed with catechol and resorcinol.



Fig. 9 Kinetic study of photodegradation of phenol and its intermediates in the presence of 0.6 wt% lanthanum doped SnO_2 nanoparticles

Table 2Kinetic parameters ofphenol and its byproductsdegradation in a photocatalysisprocess by La:SnO2nanoparticles	Organic molecule	Rate constant $K (\min^{-1})$	R^2
	Phenol	0.02228	0.9977
	Propanol	0.02228	0.9961
	Benzoquinone	0.0209	0.9952
	Hydroquinone	0.017066	0.9834
	Catechol	0.013839	0.9544
	Resorcinol	0.013753	0.9158
	Acetic acid	0.013412	0.9135

Conclusions

In summary, undoped and La doped SnO_2 nanoparticles were successfully synthesized by the sol-gel method, and the phenol intermediates formed during photodegradation were studied. Photocatalytic experiments showed that La doped SnO_2 degraded all the by-products albeit with different rate constants. La doped SnO_2 nanoparticles are expected to be a promising candidate for effective photocatalysis processes using sunlight irradiation that can find applications in the real world.

Acknowledgments The authors would like to thank partial financial support from the Chair in the Nanotechnology programme of the Research Council of Oman and the college of science (Chemistry Department) for giving us this opportunity to carry out the research at Sultan Qaboos University.

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