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L-lysine monohydrate mediated facile and environment friendly synthesis of SnO_2 nanoparticles and their prospective applications as a catalyst for the reduction and photodegradation of aromatic compounds

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ABSTRACT

Herein, we present the preparation of SnO_2 nanoparticles successfully by simple chemical precipitation method employing amino acid, L-lysine monohydrate. The prepared nanoparticles were characterized in detail using different technique, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and Fourier transformed infrared spectroscopy (FT-IR) for morphological and structural analysis. The optical properties were studied using UV–vis spectroscopy. The characterization results revealed that the synthesized SnO_2 nanoparticles possess tetragonal rutile crystalline structure. The size of the SnO_2 nanoparticles was found to be increased (~4–17 nm) with increase in annealing temperature. The band gap energy was found to be increased from 3.8 eV to 4.1 eV with increase in size of the SnO_2 nanoparticles. The synthesised SnO_2 nanoparticles showed an invincible photocatalytic property in the degradation of malachite green oxalate dye and Victoria blue dye from aqueous phase under direct sunlight within 120 min. Both the dyes followed pseudo first order reaction and the rate of the constant (k) of photodegradation of malachite green oxalate dye and Victoria blue was found to be 1.6×10^{-2} min^{-1} and 1.06×10^{-2} min^{-1}, respectively. The SnO_2 nanoparticles was also found to have outstanding catalytic activity for the reduction of 4-nitrophenol into 4-aminophenol in aqueous medium. The complete reduction took place within 27 min. The kinetic of the reduction was found to be pseudo first order with a rate constant (k) 9.3×10^{-4} s^{-1}.

1. Introduction

Among the nanostructured semiconductor materials, nanoparticles are of great interest and spotlighted in the last decades with respect to their applications in various technology. The electrical, optical and magnetic properties of such nanoparticles are very much dependent on their particle size [1,2]. Various metal oxide nanostructures have been synthesized and reported recently [3–8]. Tin oxide (SnO_2) is an *n*-type semiconductor with wide band gap energy of 3.6 eV at room temperature [9]. Tin oxide (SnO_2) is the most exclusively studied metal oxide which has a rutile-type crystal structure. It is fully explored due to its potential applications in catalysis [10], gas sensors [11], dye-based solar cells [12], light emitting diodes [13], transistors [14] etc. SnO_2 nanocrystals were utilized as a catalyst for the photodegradation of various organic dyes.

Various methods including sol-gel [15], chemical precipitation [16], hydrothermal [17], ultrasonic spray pyrolysis [18], microwave methods [19], thermal evaporation [20] etc. have been adopted for the synthesis of SnO_2 nanoparticles. SnO_2 nanoparticles were found to have no significant carcinogenic properties. It also has a very low toxicity level. SnO_2 nanoparticles are poorly absorbed by the body when ingested or inhaled. In recent studies, it is found as an excellent antibacterial as well as antioxidant agent [21].

Synthesis of high-quality SnO_2 nanoparticles using cheap, non toxic regents and simple preparation routes are yet to be explored. Therefore, efforts were made to design simple, cost-effective safe routes for the preparation of SnO_2 nanoparticles using cheap and non-toxic reagents. The shape, size, stability and dimension of SnO_2 nanoparticles are vital parameters for their properties and should be taken into consideration.

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Hence, in this paper, we report the synthesis of SnO_2 nanoparticles by simple chemical precipitation method using an amino acid L-lysine monohydrate and stannous chloride dihydrate ($SnCl_2.2H_2O$). It is evident from the literature that amino acids are good complexing or capping agents in the synthesis of nanoparticles [22]. In the present study simple chemical precipitation method is adopted for synthesis of SnO_2 nanoparticles by using the amino acid, L-lysine monohydrate. Though lysine assisted synthesis employing hydothermal route have been reported to prepare SnO_2 nanocrystals [23]. In this study, for first time, simple chemical route is opted for the synthesis of SnO_2 nanoparticles using L-lysine monohydrate. In this route of synthesis, nanoparticles with diverse properties and small sizes can be obtained. It is evident from the literature that size and shape of the nanoparticle can be manipulated by increasing and decreasing the reaction temperature as well as annealing temperature. Herein, the synthesised SnO_2 nanoparticles were studied at three different annealing temperatures i.e. 200, 400 and 600 °C.

The immense uses of industrial dyes in the fields of paints, cosmetics, food and fabric industries leads to various risks on human health due to the stability and toxicity of these organic materials. The wastewater from paper, fertilizer and textile industries mostly contain organic dyes, heavy metals and harmful aromatic compounds [24–30]. Amongst the different industrial wastewaters with different types of color-causing substances, synthetic textile organic dye wastes inhabit a major position [31–39]. Treatment of water and examining it regularly is a strategic choice because of the ongoing water shortage [40–42].

Dyes are mostly organic and are very stable to light and oxidation and are very difficult to biodegrade due to its synthetic origin and complex aromatic structure. In the recent years, the effective removal of these dyes from effluent is considered as one of the greatest environmental challenges. Malachite green oxalate (MGO) dye is a green crystalline powder, highly soluble in water and ethanol with blue-green solution. Whereas, Victoria blue B (VBB) is a dark blue to brown powder soluble in water. It is a brilliant and the most fluorescent among all synthetic dyes but has poor light and wash fastness. Both Malachite green oxalate (MGO) and Victoria blue B (VBB) are triphenylmethane dyes. Triphenylmethane dyes are used in fish farming industries, paper and leather industries, food and cosmetic industries and in medicine [43]. The triphenylmethane dyes are naturally mutagenic and toxic towards living organisms [44]. They are also carcinogenic and highly toxic. Its toxicity leads to problems like altering the normal functions of kidneys, reproductive systems, liver, brain and central nervous systems [45]. On contamination with water, it causes long term adverse effects and is a real threat to aquatic and human life. Hence, wastewater that contains such dyes should be treated before disposal to the environment. It is clear from various literatures that nanostructured semiconductors (such as TiO_2, ZnO, SnO_2 and so on) are an excellent photocatalyst which can degrade many kinds of incessant organic pollutants [46–52]. It is now established that SnO_2 nanoparticles is considered as an excellent semiconductor that is widely involved in the removal of several toxic organic contaminants through photocatalytic process because of their stability in chemical structure, non-toxicity and low cost of the metal precursors [53–55]. In this study, we report the degradation of malachite green oxalate and Victoria blue B dye under direct sunlight employing SnO_2 nanoparticles as a photocatalyst.

p-nitrophenol is carcinogenic and genotoxic to human being as well as wildlife [56]. It damages the central nervous system, liver and kidney of both humans and animals. Since it is highly stable and less soluble in water unlike synthetic dyes this compound is difficult to degrade into harmless product. *p*-aminophenol is the reduced product of *p*-nitrophenol, which is a useful compound in industries for the synthesis of analgesic and antipyretic drugs and as corrosion inhibitor [57]. Developing an efficient, durable and eco-friendly method to produce *p*-nitrophenol is an important task for both industrially and environmentally. In current years, SnO_2 nanoparticles are widely exploited as a catalyst in the organic transformations [58]. Therefore, in this paper the catalytic activity of the synthesized SnO_2 nanoparticles for the reduction of *p*-nitrophenol into *p*-aminophenol has also been studied.

2. Experimental

2.1. Materials

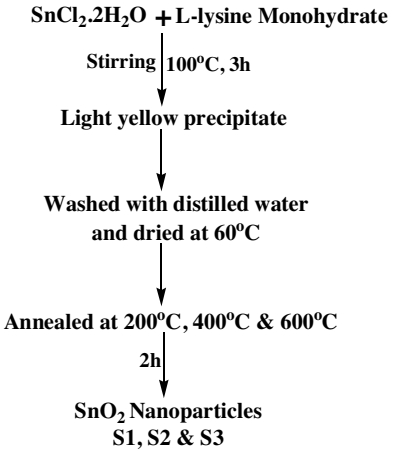
The reagents, stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$), L-lysine monohydrate sodium borohydride and *p*-nitrophenol were of analytical grade (AR). The reaction was carried out in a simple chemical method.

2.2. Synthesis of SnO_2 nanoparticles (NPs)

For the synthesis of SnO_2 nanoparticles, 0.01 M $SnCl_2{\cdot}2H_20$ was treated with 100 ml aqueous solution of 0.01 M L-lysine monohydrate. The reaction mixture was kept on a magnetic stirrer and stirred at 100 °C for 3 h. A light yellow precipitate was formed and it was kept at room temperature for 24 h. After 24 h, the precipitate was centrifuged and washed three times with double distilled water. The precipitate was then dried at 60 °C and finally annealed at three different temperature 200, 400 and 600 °C for 2 h and marked as S1, S2 and S3. The schematic representation of the SnO_2 nanoparticale synthesis is given below (Scheme 1).

2.3. Characterization of nanoparticles

Characterization of SnO_2 nanoparticles was carried out by powder X-raydiffraction(XRD) method using PhillipsX'Pert PRO diffractometer with Cu Kα radiation of wavelength 1.5418 Å. The determination of the size, morphology and diffracted ring pattern of SnO_2 particles was conducted by employing JEM-2100 Transmission Electron Microscope. Infrared spectrum was recorded in the wave number range from 400 to 4000 cm^{-1} by Bruker Hyperion 3000 FTIR spectrometer. UV–vis absorption spectra of synthesized SnO_2 nanoparticles were computed on Cary100 BIO UV–vis spectrophotometer equipped with 1 cm quartz cell.



Scheme 1. Schematic representation of the SnO_2 nanoparticale synthesis.