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Synthesis, characterization and photocatalytic applications of N-, S-, and C-doped SnO_2 nanoparticles under ultraviolet (UV) light illumination

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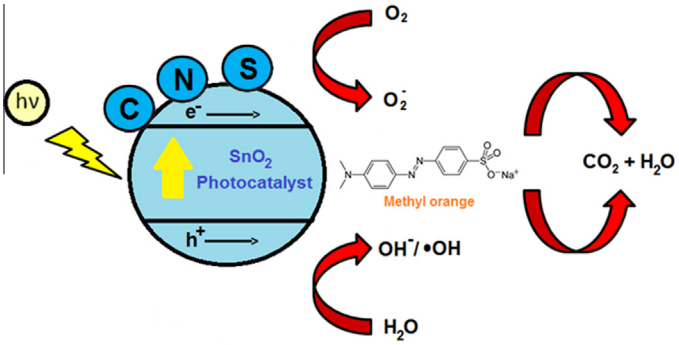
HIGHLIGHTS

- Successful synthesis of N-, S-, and C-doped SnO_2 photocatalyst by precipitation method.
- Doping N-, S-, and C- into SnO_2 nanoparticles increases the absorbance of SnO_2 nanoparticles in UV region.
- Photocatalytic properties of N-, S-, and C-doped SnO_2 powder are studied.

GRAPHICAL ABSTRACT



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ABSTRACT

N-, S-, and C-doped SnO_2 nanoparticles were synthesized via a precipitation method and were characterized by X-ray diffractometer (XRD), X-ray photoelectron spectra (XPS), scanning electron microscopy (SEM), Transmission Electron Microscope (TEM), UV–vis diffuse reflectance spectral (UV–vis DRS) and Brunauer–Emmett–Teller (BET) techniques. The photocatalytic activities of these SnO_2 samples were investigated with methyl orange as the organic pollutant under UV light illumination. UV–vis spectroscopy demonstrated that dopants N,S,C-species can shift the absorption edge to the near UV and visible light region. N,S,C-SnO_2 nanoparticles achieved the best photocatalytic efficiency and the most optimal doping ratio was 3 (T/S). The degradation of methyl orange by N,S,C-SnO_2 nanoparticles fitted well with the Langmuir–Hinshelwood kinetics model. The results of subsequent experiments indicate that enhanced adsorption ability of light and high separation rate of photo induced charge carriers all play an major role in promotion of photocatalytic activity of N,S,C-SnO_2 nanoparticles.

Introduction

Environmental pollution has enhanced the general concern nowadays. Especially, treatment of polluted water and air by photocatalysis has been attracting a lot of attention. The discharge of dye effluents from food industries, cosmetic and textile into the aquatic environment is a major environmental concern. Most of the dyes are difficult to degrade owing to its highly toxic and chemically stable nature. Photocatalysis is a technology for the degradation of any pollutants to CO_2 and inorganic constituents using semiconductors as catalysts [1]. Amongst the various metal oxide semiconductors, TiO_2 [2], ZnO [3], WO_3 [4], Fe_2O_3 [5] and Bi_2O_3 [6] are extensively investigated photocatalysts owing to their band gap, chemical stability, and non-toxicity. Tin dioxide (SnO_2) is a wide

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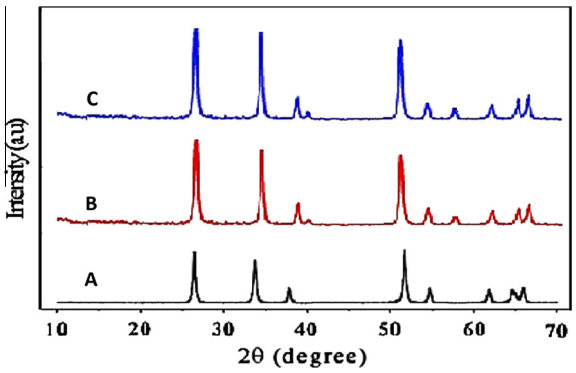

Fig. 1. The XRD patterns of the TS11 samples at different calcination temperatures; (A) 400 °C, (B) 600 °C and (C) 800 °C.

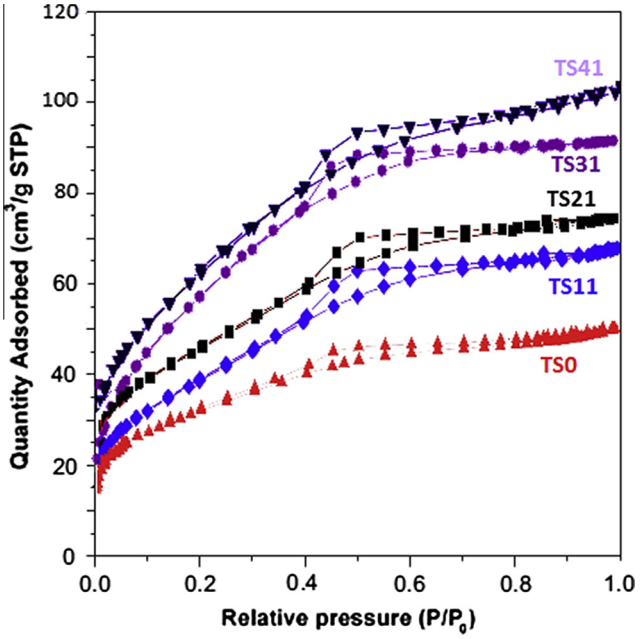

Fig. 2. Adsorption–desorption isotherm plots of TS0, TS11, TS21, TS31, and TS41 samples.

band gap (3.6 eV) n-type semiconductor which receives major attention in the fields of solar cells, gas sensors, lithium-ion batteries and light emission [7–12]. However, the broad band gap of SnO_2 prevents its photocatalytic activity under visible light. The photocatalytic activity is also surrounded by the fast recombination of hole-pairs and photogenerated electron. Whereupon massive efforts have been taken to modify the photocatalytic activity of SnO_2 and make it suitable for receiving source light such as doping with non-metals, metals and coupling with other metal oxides [13–18]. Therefore, the present work attempts to modify SnO_2 photocatalysts with non-metal dopants to enhance their photocatalytic activity under ultraviolet (UV) light illumination. Methyl orange is used as the model pollutant to evaluate the photocatalytic activity of the modified SnO_2 nanoparticles under UV light illumination due to their non-biodegradable and toxic properties.

Material and methods

Preparation of nanosized photocatalysts

In this study, raw materials were procured from Sigma-Aldrich Ltd. N,S,C-SnO_2 nanoparticle were synthesized using a precipitation method. Stannic chloride pentahydrate was mixed with Thiourea in 500 ml distillated water to form a 0.25-M aqueous solution. Then, the solution was stirred for 3 h. Following complete dissolution, the solution was treated with an ammonia solution (25%) until the solution pH obtained 7. The resulting solution was stirred for another 2 h. Precipitated products were separated from the solution by centrifugation, and dried at 100 °C for 24 h. The obtained products were ground and calcined at an elevated temperature for 3 h with a heating rate of 5 °C/min. The T/S ratio demonstrates the molar ratio of thiourea to Stannic (IV) chloride. Samples were denoted as TS0, TS11, TS21, TS31, and TS41 to indicate the T/S ratios of 0, 1, 2, 3, and 4, respectively.

Table 1
Brunauer–Emmett–Teller (BET) measurements.

Samples	Total pore volume ($cm^3\ g^{-1}$)	Specific surface area ($m^2\ g^{-1}$)
TS0	0.052	20.21
TS11	0.062	41.22
TS21	0.085	63.54
TS31	0.101	81.87
TS41	0.127	103.55

Characterization

The X-ray diffraction (XRD) patterns obtained on a X-ray diffractometer (type HZG41B-PC) using Cu Kα irradiation. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD XPS system. UV–vis diffuse reflectance spectral measurements were carried out in a JASCO V-550 double beam spectrophotometer. The surface morphology was examined using scanning electron microscopy (SEM) (JSM 6701F—6701). The particle size of the N,S,C-SnO_2 photocatalyst powders was measured using Transmission Electron Microscope (TEM) (Zeiss EM-900). The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in an ASAP2020 surface area and porosity analyzer (Micromeritics, USA).

Photocatalytic experiments

Photocatalytic activity was carried out in a thermostatic cylindrical Pyrex reactor with a 500 ml capacity and appraised by monitoring the degradation of methyl orange under UV light irradiation. A 125-W mercury lamp (Philips; Emission at 365 nm), was used as the UV light source. The solution pH was adjusted by diluted NaOH and HCl solutions. The resulting solution was then stirred continuously in the dark for 20 min to ensure that the suspension is uniform. Then, the photocatalytic run was started under UV light illumination. Samples were periodically taken from the reactor, centrifuged at 6000 rpm for 5 min, and then filtered before being measured on a UV–vis spectrophotometer (Hitachi, U-3010). Photocatalytic activity was evaluated according to the photoabsorbance of methyl orange at the maximum absorption wavelength of 486 nm.

Results and discussion

Characterization of doped SnO_2 nanoparticles

Fig. 1 indicates the XRD patterns of the N,S,C-SnO_2 nanoparticles calcined at various temperatures. The diffraction pattern for TS11 demonstrates several peaks at $2\theta = 27.2$, 34.4, 52.2 that referred to N,S,C-SnO_2 with cassiterite tetragonal structure (ICDD card No. 41-1445) and the absence of other peaks indicating the high purity of N,S,C-SnO_2. When the calcination temperature