



Silica–tin nanotubes prepared from rice husk ash by sol–gel method: Characterization and its photocatalytic activity

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ABSTRACT

Silica–tin material has been synthesized by simple sol–gel method using rice husk ash as the source of silica and cetyltrimethylammonium bromide as the surfactant at room temperature. Calcination of the material at 500 °C for 5 h gave nanotubes with external diameter of 2–4 nm and an internal diameter of 1–2 nm. The BET specific surface area was found to be 607 m² g⁻¹. Nitrogen sorption analysis exhibits a type IV isotherm with H3 hysteresis loop. The powder X-ray diffraction pattern showed that the material is amorphous. The photocatalytic activity of the prepared material was studied towards degradation of methylene blue under UV-irradiation. According to the experimental results the silica–tin nanotubes exhibit high photocatalytic activity compared to pure rice husk silica.

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1. Introduction

Nanotechnology is the ability to synthesize and use materials that have basic particle dimension of the order of ca. 1–100 nm [1]. Nanomaterials such as nanowires, nanotubes, nanorods, nanoribbons and nanobelts provide interesting physical and chemical properties compared to conventional materials. It has attracted many scientists to explore its potential scientific significance and technological applications. It is well known that most nanomaterials exist in more than one conformation, size and shape such as hollow spheres [2], tubular, cone-like [3] or irregularly shaped particles and can exist in fused, aggregated or agglomerated forms. These nanomaterials are expected to play a vital role in many different areas such as nanoelectronic technology, i.e. as visible display devices, gas sensors, dye-sensitized solar cells and optoelectronics [4,5]. Due to its high surface area (naturally due to its small size), nanomaterials can also be used as heterogeneous catalyst for chemical transformation [6] and as photocatalyst [7] for decomposing organic pollutants.

At present, various metal nanoparticles like tin [2], nickel [4], palladium [6], and titanium [7] have been developed by scientists for special technological applications. It had been reported that, silicon nanotubes were synthesized using silane as the silicon source [3,8] and amorphous silica was used

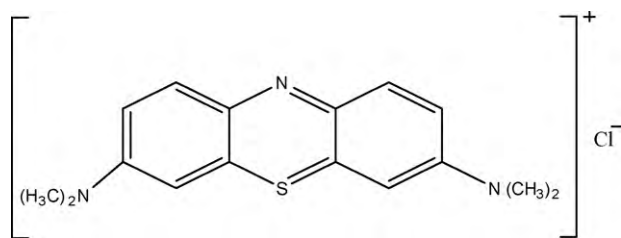
to produce nanowires to be used in silicon based electronic devices [4]. More recently an inorganic nanomaterial, i.e. tin dioxide (SnO₂) had attracted much attention as a semiconductor because of its typical wide band gap ($E_g = 3.6$ eV), and has been explored for its photocatalytic activity [9]. Tin nanotubes electrodeposited with platinum were found to promote the oxidation of methanol [10]. Up to now, various methods had been used to produce SnO₂ nanomaterial. These include solvothermal [7], hydrothermal [2], and hydrogen radical-assisted deposition methods [11] to produce high quality nanomaterials. However, due to the complexity and expensive nature of the current methods, researchers are still looking for a simple and inexpensive preparation route to synthesize these nanomaterials.

Rice husk (RH) is an agricultural waste and the ash contains about 92–95% silica (SiO₂). It is highly porous and lightweight, with high surface area. Most published reports using rice husk ash describe its use as catalyst support for metals. Several methods are used to incorporate the metals, i.e. by physical incipient-wet method [12], and heat treatment methods [13]. Some researchers had also used direct hydrothermal synthesis [14] and gasification process [15] to obtain rice husk ash as MCM-41 for catalytic reaction. In our previous work, heterogeneous ruthenium catalyst supported on rice husk ash (RHA) [16,17] had been prepared and shown to form well-defined flat elongated nanosized rods and nanofibers.

This paper describes a very simple process to obtain silica–tin nanotubes from rice husk silica to be utilized as a photocatalyst in the degradation of methylene blue.

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Scheme 1. The molecular structure of MB.

2. Experimental

2.1. Materials

Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SYSTERM) was used as the source of tin. Other chemicals used were nitric acid (Q Rec, 65%), sodium hydroxide pellets (R&M Chemicals, 99%), acetone (Q Rec, 99.5%), cetyltrimethylammonium bromide (CTAB, Riedel-de Haen, 98%) and methylene blue (Sigma–Aldrich) (MB: C.I. 52015, M.W.: 373.9 g mol^{-1} , λ_{max} 661 nm). The molecular structure of MB is illustrated in Scheme 1.

Rice husk was obtained from a local rice milling company in Penang. All chemicals were of AR grade and used directly without purification.

2.2. Catalyst preparation

About 30.0 g of clean rice husk (RH) was stirred in 750 mL of 1.0 M HNO_3 at room temperature for 24 h. The cleaned RH was washed with copious amount of distilled water to constant pH. Washed RH was dried in an oven at 100°C for 24 h and burned in a muffle furnace at 600°C for 6 h so as to obtain white rice husk ash (RHA). About 3.0 g of RHA was added to 350 mL of 1.0 mol L^{-1} NaOH in a plastic container and stirred for 24 h at room temperature to get sodium silicate solution. Cetyltrimethylammonium bromide (CTAB, 3.6 g) (1 Si:1.2 CTAB molar ratio) was added into the sodium silicate solution and stirred to dissolve completely. This solution was titrated with 3.0 mol L^{-1} HNO_3 with drop wise addition at a rate of ca. 1.0 mL min^{-1} with constant stirring until pH 3.0 [18]. The resulting gel was aged for 5 days and then centrifuged (4000 rpm), filtered and washed thoroughly with distilled water. A final washing was done with acetone. It was dried at 110°C for 24 h, ground to fine powder and calcined at 500°C in a muffle furnace for 5 h. The obtained powder was labeled as RHA-silica.

To prepare the silica–tin material, the titration was conducted using a solution of 10.0 wt. % Sn^{2+} (0.57 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) dissolved in 50 mL of 3 mol L^{-1} HNO_3 . The resulting gel was aged for 5 days, and processed as described above. The resulting powder was labeled as RHA-10Sn (yield was ca. 4.00 g).

2.3. Characterization

The specific surface area, pore volume and pore distribution of the prepared material was carried out using N_2 adsorption–desorption on porosimetry instrument model NOVA 2000e from Quantachrome. Powder X-ray diffraction pattern was obtained by Siemens Diffractometer (D5000, Kristalloflex) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). FT-IR spectra were recorded on Perkin Elmer System 2000 using potassium bromide (KBr) discs. The thermogravimetric analysis (TGA) was carried out on 851e Mettler Toledo equipment. The measurement was carried out from 50 to 850°C with a heating rate of $10^\circ\text{C min}^{-1}$ with nitrogen flow rate of 40 mL min^{-1} .

Table 1

The nitrogen adsorption–desorption analysis parameters of materials.

Catalyst	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Pore volume (cc g^{-1})	Average pore diameter (nm)
RHA-silica	315	0.367	7.33
RHA-10Sn	607	1.18	7.39

Transmission electron (TE) micrographs were obtained on a Phillips CM12 microscope. Scanning electron (SE) micrographs were collected on a Leica Cambridge S360, equipped with EDX Falcon System which was operated at 10 keV. Atomic absorption spectroscopy (AAS) (Perkin Elmer AAnalyst-200) was used to verify the material composition. The surface topography of the sample was observed by atomic force microscope (AFM), model ULTRAOjective in non-contact acquisition mode.

2.4. Photocatalytic activity

20.0 mL aqueous solution of MB (50 mg L^{-1}) and 20 mg of the prepared catalyst were introduced into a sample cell. The experiments were carried out at room temperature for 60, 120, 180, 300, 420 and 960 min. To reach an equilibrium adsorption as deduced from the steady-state concentration, the suspension was first stirred in the dark for 60 min before irradiation. The mixture was then irradiated with UV light (model: USHIO Optical Modulex) at $\lambda \sim 380 \text{ nm}$. The photocatalytic set up was placed in a closed dark compartment to avoid interference from ambient light. The distance from UV light source to the sample cell was kept constant at 30 cm.

After irradiation, the aqueous solution of MB was filtered with $0.20 \mu\text{m}$ Nylon Millipore filter to remove the suspended catalyst. The absorbance of the solution was determined with a UV–vis spectrophotometer (model: HACH DR/2000, direct reading spectrophotometer) at 661 nm (λ_{max}) corresponding to the maximum absorption of MB. Ion chromatography (IC, model: Metrohm 792 Basic IC) analyses were carried out to confirm the degradation of MB. Analysis was conducted on IC equipment, with anions column, METROSEP ASUPP 5-150 (size: $150 \text{ mm} \times 4.0 \text{ mm}$, particle size: $5.0 \mu\text{m}$), conductivity detector and ICNet 2.3 computer software for data handling to determine the presence of anions. The mobile phases were 1.0 mmol L^{-1} sodium carbonate with 3.2 mmol L^{-1} sodium bicarbonate as first eluent and 100 mmol L^{-1} of sulphuric acid as the second eluent. The flow rate was 0.70 mL min^{-1} , and the injection volume was 1 mL.

Photolysis studies were also conducted as a control experiment to determine the percentage removal of MB. About 20 mL of 12 mg L^{-1} MB solution was irradiated with UV light in the absence of catalyst and absorbance was taken within 60 min using UV–vis spectrophotometer at 661 nm.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. N_2 adsorption–desorption analysis

The N_2 adsorption–desorption isotherm of RHA-silica and RHA-10Sn are shown in Fig. 1. The isotherm was determined as type IV with H3 hysteresis for both materials, which is associated with capillary condensation taking place in mesopores [17]. This is also a characteristic of solids consisting of aggregates or agglomerate particles forming slit shaped pores with non-uniform size and shape [19]. The surface area, pore diameter and pore volume were calculated using Barret–Joiner–Halenda (BJH) model and the results are tabulated in Table 1. The BET surface area of RHA-10Sn was found

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