Design and synthesis of graphene-SnO$_2$ particles architecture with polyaniline and their better photodegradation performance

M. Karpuraranjith, S. Thambidurai*

Bio-nanomaterials Research Lab, Department of Industrial Chemistry, School of Chemical Sciences, Alagappa University, Karaikudi 630003, Tamil Nadu, India

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ABSTRACT

The photodegradation in two different types of dyes like a cationic and anionic dye, namely, methylene blue and reactive yellow 15 under the direct sunlight irradiation respectively, have been carried out using graphene-SnO$_2$/PANI matrix as photo catalyst. The graphene-SnO$_2$ particle architecture PANI matrix was successfully synthesized via two step methods Firstly, graphene-SnO$_2$ colloidal suspension was prepared by hydrothermal precipitation method and secondly, the resulting graphene-SnO$_2$ colloidal suspension was effectively attached on the PANI matrix by in situ chemical oxidative polymerization method. The resulting respective nanocomposite materials of graphene, SnO$_2$ and PANI were characterized and confirmed by FTIR, X-ray diffraction, UV–vis DRS, HR-SEM with EDAX, TEM, BET and TG-DTA analysis. Thus results demonstrate that graphene-SnO$_2$ nanoparticle-architecture PANI matrix was synergistic effect among the three component of graphene, SnO$_2$ and PANI. Therefore, graphene-SnO$_2$ particles architecture PANI acts as an efficient photo catalyst for the degradation of methylene blue and reactive yellow 15 dyes under the direct sunlight irradiation.

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1. Introduction

Various kinds of dye molecules are appear in the effluent of industries such as textiles, leather, paper, plastic etc. The textile dying industry consumes large quantities of water at its different steps of dyeing and finishing process. Textile dyeing effluent has a serious environmental impact because disposal of this effluent into the received water body causes damage to aquatic biota, humans by mutagenic and carcinogenic effects. The various treatment techniques have been largely used to remove the dye molecules from contaminated water. Recently many researchers have studied the feasibility of using cheaper adsorbent for the removal of various dye molecules, such as the activated carbon, peat, silica, cellulose, chitin and chitosan [1–5].

Graphene is a single layer with perfect two dimensional honeycomb structures of carbon atoms. It has extensively interesting research topic for the reason that distinctive property such as the mechanical, thermal, optical and excellent electrical conductivity. It’s promising candidate in wide range of the numerous applications for storage devices, catalysts, optoelectronic, chemical sensors, ash memory storage devices, transparent conductors and super capacitors [6–10]. Polyaniline (PANI) has received in the three redox forms; First form pernigraniline is fully oxidized state second form, leucoemeraldine is fully reduced state. Two states are poor conductors even when doped with an acid. Third emeraldine form of PANI usually referred to as emeraldine base is either neutral or attached with imine nitrogen protonated by an acid. The doped and undoped with acid and base can be interchange forms of PANI (emeraldine base and salt form). The useful form emeraldine base is regarded as the PANI due to higher stability at room temperature, less expensive, easily synthesis, good electrical conductivity and main functional group of nitrogen present in the structure and applied in various applications such as batteries, corrosion protecting paint and photo catalyst [11–16].

Among the semiconducting nanoparticles of SnO$_2$ have a large wide direct band gap (E$_g$ = 3.6 eV). It’s thoroughly investigated for their applied aspect such as in the thin films resisters, gas sensing, photo catalysts and antireflecting coating in solar cells [17–19]. In current year’s researchers have been interesting synthesized photo catalyst materials in the field of PANI-SnO$_2$ [20], PANI-ZnO [21], Graphene-PANI [22], Graphene-TiO$_2$ [23], Graphene-ZnO [24] and Graphene-SnO$_2$ [25] was reported. However, to the best our knowledge, there is no report about synthesis of graphene based
SnO₂ particles architecture with PANI matrix for their better photo degradation performance.

The present work report, to synthesize graphene-SnO₂ particles architecture PANI matrix were successfully prepared via in situ polymerization of aniline, HCl and APS in the presence of graphene-SnO₂ composite prepared by hydrothermal precipitation method. The synthesized nanocomposites are characterized and confirmed the functional groups identification by FTIR analysis. The crystalline behavior was analysed by XRD analysis. The optical properties were measured by UV–vis DRS and surface morphological structures were evidenced by HR-SEM with EDAX and FEG-TEM analysis. The specific surface area and thermal stabilities of nanocomposite was analyzed by BET and TG-DTA analysis. The photocatalytic activity was analyzed by UV–vis spectroscopy and following the the under sunlight irradiation of MB and RH-15 dyes.

2. Experimental details

2.1. Materials

Tin (IV) chloride and graphite powder was purchased LOBA Chemie (P) Ltd, Sulphuric acid, Hydrochloric acid, Sodium nitrate, Hydrogen peroxide, Hydrazine monohydrate, Sodium hydroxide, Ammonium persulphate (APS) and Potassium permanganate were purchased from Fischer chemical Ltd., Aniline were obtained from Qualigens fine chemicals. Commercially available Methylene blue (C₁₅H₁₈ClN₅S₂; 3H₂O; MW 319.85 g mol⁻¹) and Reactive yellow 15 dye (C₉₀H₇₀Na₂₅O₁₁S₁; MW 634.57 g mol⁻¹) was purchased from Merck and yongjia fine chemical factory were of an analytical reagent grade and used without any further purification. Millipore water was used in all experimental purposes.

2.2. Preparation of graphene from graphene oxide

Graphene oxide (GO) was prepared from graphite powder through a modified hummers method [7]. To take 4 g of GO dispersion in 250 ml water ultrasonic treatment for 3 h to form a homogeneous aqueous dispersion solution and continuously stirring for 2 h using magnetic stirred. Then 2 ml of hydrazine monohydrate added in drop wise, the mixture solution was heated at 100 °C for 6 h with continuous stirring and finally obtained the block precipitate. The precipitate was settled for 24 h at room temperature and supernatant solution was discarded, washed several times with Millipore water and filtered using suction pump and dried in an hot air oven at 120 °C for 12 h, which is designed as graphene.

2.3. Synthesis of graphene-SnO₂ particles architecture PANI matrix (GSP)

The graphene-SnO₂-PANI nanocomposites were fabricated in two steps. The first step is to prepare graphene-SnO₂ by hydrothermal precipitation method; 0.25 g of graphene was dispersed in 5 ml water and ultrasonic treatment for 1 h to form a homogeneous aqueous dispersion solution. Then added into the 10 ml of 0.5 M SnCl₄ solution was sonicated for 2 h uniform dispersion and then 10 ml of freshly prepared; NaOH (2 M) solution was added drop by drops, The mixture solution was transferred into a 30 ml Teflon stainless steel autoclave and put in the hot air oven at 180 °C for 8 h. The ash-brown precipitate was continuously stirrer for 4 h using magnetic stir, then allowed settling for 24 h at room temperature and supernatant solution was discarded. The residue was washed several times with Millipore water and ethanol, collects the suspension and the beaker was labeled as graphene-SnO₂.

In second step is to synthesis graphene-SnO₂-PANI nanocomposites; Subsequently, 1.25 ml of aniline was doped with 25 ml of 1.0 M HCl and the reaction vessel was kept at ice bath condition (0–5 °C) for 30 min stirring with using magnetic stir and followed by 0.25 M APS was dissolved in 25 ml of 1.0 M HCl was immediately added into the above solution. During the addition, solution slowly turns to the emerald green confirmed the polymerization of aniline. The reaction vessel was continued stirring for 4 h by maintaining below 5 °C to ascertain the completion of reaction.

Then allowed to settle for 24 h at room temperature and supernatant solution was discarded. The residue was washed several times with Millipore water and collected the suspension labeled beaker as PANI. Finally the colloidal suspension of graphene-SnO₂ slowly poured into PANI matrix with stirred 2 h, and settled for 24 h at room temperature and filtered in suction.

![Scheme 1. Schematic preparation of graphene-SnO₂ particles architecture with PANI matrix.](image-url)
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