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Pd-doped β-Bi_2O_3/$Bi_2Sn_2O_7$ hybrid nanocomposites for photocatalytic fluorene oxidation: A green approach for the synthesis of fluorenone/fluorenol mixture

Mohamed Mokhtar Mohamed [a,*], Saleh A. Ahmed [b]

[a] Benha University, Faculty of Science, Chemistry Department, Benha, Egypt
[b] Umm Al Qura University, Faculty of Applied Science, Chemistry Department, Makkah, Saudi Arabia

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ABSTRACT

Bismuth oxide, tin oxide and Pd metal (Pd/$SnBi_{3SG}$) hybrids, synthesized via sol–gel technique while employing polyethylene glycol template at a ratio of 3 (Bi/Sn = 3) were tested toward the photocatalytic oxidation of fluorene under ultraviolet and visible light irradiations in comparison with Pd/Bi_{SG} and Pd free $SnBi_{3SG}$ photocatalysts. These catalysts were characterized using X-ray diffraction (XRD), UV–vis diffuse reflectance (DRUV–vis), N_2 sorptiometry, Raman spectroscopy, transmission electron microscopy (TEM) and GC–MS technique, which used for analyzing the photo-oxidation products. The actual photocatalyst exhibited the highest activity (100% conversion, TOF ≈ 9.4×10^{-6} s^{-1}, fluorenone/fluorenol = 3/1) following oxygen flushing for 30 min (35 ml/min) before UV irradiation. This was mainly due to the close proximity between β-Bi_2O_3 and $Bi_2Sn_2O_7$ heterojunction as well as increasing the mesoporosity margin comparatively. On the other hand, the Pd/Bi_{SG} catalyst that exhibited smaller crystallite size (20 nm vs. 44 nm) and higher surface area (21.0 vs. 12.0 m^2/g) than Pd/$SnBi_{3SG}$ indicated lower activity (Pd/Bi_{SG}, 72% conv.). This highlights the importance of the modified electronic structure of Pd/$SnBi_{3SG}$ in designing efficient charge separation as well as high quantum yield value ($\Phi \sim 0.1 \pm 0.05$) exceeding that of Pd/Bi_{SG} (3×10^{-2}) and $SnBi3_{SG}$ (10^{-2}) photocatalysts. The catalytic behavior and mechanism, reactivity–structure relationship and recyclable use of the hybrid photocatalysts have been thoroughly examined. An indirect chemical probe method using active species scavengers elucidated that the photo-oxidation mechanism was proceeded via holes and O_2^- moieties rather than singlet oxygen moieties.

1. Introduction

Fluorene, as a polycyclic aromatic hydrocarbon (PAH), is formed during the combustion of fossil fuels, such as in the oil processing plant, incomplete fuel combustion [1], asphalt transformation plants [2] and also emitted from automotive exhaust pipes [3–5]. They have a great impact on human health, most of these molecules provoking breathing diseases and cancers [6]. Fluorene is reported to possess extremely serious toxicity as well as potential mutagenic and carcinogenic properties [7]. These chemicals, which extended residence times in the environment usually enter into the atmosphere, rivers and soil through evaporation, spreading and penetration thereby causing environmental pollution. The influence of PAHs' transmission upon the nation's environmental quality and health has received extensive attention. Owing to the high toxicity of PAHs, numerous studies were performed to either degrade or remove them [8]. However, getting the maximum benefit of such high toxic compounds by performing reliable oxidation reactions to synthesize fluorenol/fluorenone was only carried out at small scale and via non-green paths [9]. Many applications in industry for fluorenone/fluorenol compounds can be attained since they are used as basic materials in antimalaria drugs, insecticides, algaecides, biopharmaceutical dyes and as optical brightening agents [10]. In addition, some of their characteristics such as light and temperature sensitivities, heat resistance, conductivity and corrosion resistance make them applicable for use in the areas of thermo and light sensitizers, luminescence chemistry, spectrophotometric analysis and molecular chemistry [11,12]. The study of oxidation reactions is at the maximum of scientific activity. As a result, numerous methods have been developed to facilitate oxidation reactions particularly photocatalysis [13], which has recently grown as a technology provider. Photocatalysis opened new

* Corresponding author.
E-mail address: mohmok2000@yahoo.com (M.M. Mohamed).

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approaches because it could be used under visible light irradiation and it also considered as a green method for synthesizing many organic compounds by substituting hazardous oxidizing compounds, of bad impact on the environment [14]. Correspondingly, investigations on alternative materials are uncommon. In this respect, bismuth oxide (Bi_2O_3) is an attractive material because of its good electrical conductivity and thermal properties. It is extensively used in various applications such as microelectronics, sensor technology and optical coatings [15,16]. As a photocatalyst, Bi_2O_3 is a p-type semiconductor with conduction and valence band edges +0.33 and +3.13 V relative to NHE, respectively. These values account for its capability to oxidize water and possibly generate highly reactive species, such as $O_2^{\cdot-}$ and $OH^{\cdot}$ radicals, which may act as initiators for oxidation reactions. On the other hand, SnO_2 is an important *n*-type wide-bandgap semiconductor with broad applications based on electrical and optical properties of the oxide, which also used as strong oxidation catalyst [17]. To the best of our knowledge, there are no reports on Pd doped SnO_2–Bi_2O_3. Such nanocomposites will have the potential to show the synergetic effect of Pd on the catalytic performance of the SnO_2–Bi_2O_3 catalyst towards partial oxidation of the fluorene pollutant. Many heterogeneous catalysts have been reported to be active for this transformation and recently supported Pd nanoparticles have been shown to be highly effective towards methyl orange degradation when supported on Bi_2O_3 [18]. With respect to palladium catalysis, it is known that this reactivity is due to small Pd nanoparticles and their interfaces with the supporting matrix are also important [8].

Accordingly, the aim of this study is to synthesize Bi_2O_3–SnO_2 composites with Bi/Sn atomic ratio of 3:1, loaded with Pd nanoparticles for fluorene partial oxidation; to fluorenol/fluorenone compounds, via using the photocatalysis approach. We employed UV–visible irradiations to create active species on the surface of the Bi_2O_3–SnO_2 catalysts to facilitate committing the oxidation processes at room temperature. This simple and low cost approach is a step forward towards tailoring photocatalysts for various purposes and it can valuably contribute to a photocatalyst design. The synthesized catalysts were thoroughly characterized using X-ray diffraction, Transmission electron microscope, UV–vis diffuse reflectance spectroscopy, N_2 sorptiometry and Raman-mapping spectrometry techniques.

2. Experimental section

2.1. Catalyst preparation

2.1.1. Synthesis of Pd/SnO_2–Bi_2O_3 nanostructures

All chemicals were analytical grade and used without further purification. In a typical procedure, appropriate amounts of $Bi(NO_3)_3{\cdot}5H_2O$ and $Sn(NO_3)_4$ were used so as to obtain a 3:1 atomic ratio in the final product. $Bi(NO_3)_3{\cdot}5H_2O$ was first dissolved in water containing polyethylene glycol-2000 [$(HO(CH_2CH_2O)_nH$)-PEG 2000-2 g/100 ml water)] (100 ml) and same for $Sn(NO_3)_4$. $Sn(NO_3)_4$ solution was poured onto the $Bi(NO_3)_3{\cdot}5H_2O$ solution under vigorous stirring. Ammonia solution (15%) was then added into the mixed solution in a drop wise manner until precipitation takes place and thus the reacting solutions were kept at 85 °C under vigorous stirring until a gel was formed. Then, the gel was transferred into a Teflon-lined stainless autoclave (300 mL capacity) at the temperature of 140 °C for 24 h via incubation in an electric oven. The system was then cooled to ambient temperature naturally. The as-prepared sample was collected and washed with distilled water and absolute ethanol several times, vacuum-dried and then calcined at 500 °C for 6 h to obtain SnO_2–Bi_2O_3 nanostructures. This sample was denoted as $SnBi3_{SG}$ where 3 accounts for the atomic ratio of 3/1(Bi/Sn) and SG is accounted for the sol–gel method of preparation. Palladium nitrate $Pd(NO_3)_2$ as to obtain a loading of 2% wt is taken as starting material to dope the $SnBi3_{SG}$ material, which has been dissolved in distilled water forming an emulsion using a ball mill. After mixing, PEG 6000 at a concentration of 3 g/100 ml was added step-wisely to the mixture for sake of Pd ions reduction. The mixture was left for one day under stirring, filtering and washing with distilled water for several times. Then, dried at 110 °C for 5 h and calcined at 500 °C for 6 h. This sample was denoted as Pd/$SnBi3_{SG}$.

2.1.2. Synthesis of Pd/Bi_2O_3 nanostructures

In a typical procedure, stoichiometric amounts of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 100 ml of distilled water containing polyethylene glycol-2000. The pH adjustment to a value of 8.8 via drop-wise addition of ammonia solution (15%, v/v) was performed until complete precipitation. After gelation for 24 h in a Teflon lined autoclave at 140 °C, the gel was then filtered, washed with distilled water for several times and dried at 110 °C over night. Finally, the sample was calcined at 500 °C for 6 h. To a portion of the calcined sample, an adequate amount of $Pd(NO_3)_2$ solution; so as to form a loading of 2% Pd, was added. Subsequently, vigorous stirring was achieved followed by drop-wise addition of PEG-6000 at a concentration of 3 g/100 ml. Calcinations at 500 °C for 6 h was accomplished following filtering, washing and drying at 110 °C. This sample was denoted as Pd/Bi_{SG}.

2.2. Catalyst characterization

2.2.1. X-ray diffraction

The X-ray powder diffraction patterns of various solids were carried out using a Philips 321/00 instrument. The patterns were run with Ni-filtered Cu Kα radiation ($\lambda = 1.541$ Å) at 36 kV and 16 mA with scanning speed of 2° in 2θ min^{-1}. The XRD phases present in the samples were identified with the help of ASTM powder data files.

2.2.2. N_2 adsorption

The surface properties namely BET surface area, total pore volume (V_p) and mean pore radius (r) were determined from N_2 adsorption isotherms measured at 77 K using conventional volumetric apparatus. The samples were out-gassed at 473 K for 3 h under a reduced pressure of 10^{-5} Torr before starting the measurement. The total pore volume was taken from the desorption branch of the isotherm at $p/p^0 = 0.98$, assuming complete pore saturation.

2.2.3. Ultraviolet–visible diffuse reflectance spectroscopy

Diffuse Reflectance Ultraviolet–visible spectroscopy (UV–vis DRS) of powder samples was carried out at room temperature using a PerkinElmer Lamda-900 spectrophotometer in the range of 200–800 nm. The UV–vis spectra were processed with Microsoft Excel software, consisting of calculation of the Kubelka–Monk function, $F(R_\infty)$, which was extracted from the UV–vis DRS absorbance. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of the plot of $[F(R_\infty)hV]^2$, for the direct allowed transition, vs. hV, where hV is the incident photon energy.

2.2.4. Transmission electron microscope (TEM)

TEM micrographs were measured using a Philips; model Tecani Feil2, at an accelerating voltage of 200 KV. The powder samples were put on carbon foil with a microgrid. TEM images were observed with minimum electron irradiation to prevent damage to the sample structure. The elemental compositions of the composite material were investigated by energy-dispersive X-ray attached to the TEM equipment. The average particle diameter (d) was calculated by the following formula: $d = \Sigma nidi/\Sigma ni$, where