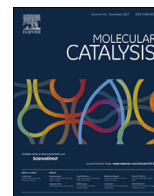




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Editor's choice paper

Simultaneous photocatalytic degradation of *p*-cresol and Cr (VI) by metal oxides supported reduced graphene oxide

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ABSTRACT

The visible light active photocatalysts WO₃ (C1), Fe₂O₃ (C2), WO₃/rGO (C3), Fe₂O₃/rGO (C4) were synthesized under *in-situ* hydrothermal method. The physico-chemical characteristics were studied and characterized by XRD, Raman, UV-vis-DRS, TEM, SEM, BET, EDX and XPS. The formation of WO₃ and Fe₂O₃ was confirmed by XRD and the average crystallite size of the prepared samples was less than 50 nm. The Raman spectroscopy confirms the decreasing I_D/I_G ratio of WO₃/rGO composite than the pure rGO. The band gap calculated by UV-vis diffuse reflectance spectroscopy was found to be lower for the composites C3 and C4 than C1 and C2. The TEM results confirmed that the WO₃ nanoplates are uniformly distributed on rGO sheets and no significant lattice distortion was observed on growing WO₃ nanoplates on rGO. The chemical composition and oxidation states of synthesized nanocomposites (C3 and C4) can be characterized by X-ray Photoelectron Spectroscopy. The surface area of photocatalyst C3 was found to be 16 m²/g. The visible light activity of prepared photocatalysts was tested for the degradation of *p*-cresol and the reduction of Cr (VI). Typical results highlighted that WO₃/r-GO (C3) is the best active catalyst and the simultaneous degradation of the pollutants is beneficial over the removal of individual pollutants. The mineralization of the organic pollutant was confirmed by the TOC analyzer and the percentage of mineralization for the best active photocatalyst was ~80%.

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1. Introduction

Phenolic compounds are one of the important classes of aqueous pollutants discharged from the various industries. These are extensively used in the production of antioxidants. *p*-cresol is one of the toxic phenolic compound that causes irritation and burning of skin, eyes and it can damage liver and kidneys [1–4]. In a similar way, heavy metals like Pd (II), Pt (II), Cd (II) and Cr (VI) are toxic to human/environment. Especially Cr (VI) is extremely harmful, even in trace quantities. The usual practice of handling Cr(VI) is to convert it into Cr (III) which is a less toxic form [5–7]. Conventional methods like electro-dialysis, cementation, ion-exchange, precipitation, coagulation, reverse osmosis, etc. are used to remove the aqueous pollutants. However, the main drawbacks of these methods are either incomplete removal of pollutant and/or generation of toxic by-products [8]. The best solution is to degrade and mineralize the organic pollutants and convert the toxic heavy metal ions into non-toxic forms. Photocatalysis has often been tested for this

purpose and the literature highlights the potential of some of the semiconductor metal oxides (TiO₂, ZnO, WO₃, Fe₂O₃, Bi₂O₃) [9–12]. However, the active photocatalysts like TiO₂ and ZnO are mainly active under UV- irradiation. To shift the adsorption edge into the visible region by incorporating the metal nanoparticles into the TiO₂/ZnO matrix improves the visible light response [13–20]. On a closer look, pure WO₃ and Fe₂O₃ are less efficient photocatalysts because of their high recombination rate of photo-exactions (e⁻ and h⁺) [21–25]. Many carbon materials like CNTs, CNFs, graphene oxide, g-C₃N₄ are used as supporting materials for various semiconductors to improve the photocatalytic activity. Among them, graphene has the excellent chemical and thermal stability, high surface area and the adequate mobility of charge carriers. Generally, the reduction of GO gives graphene, which acts as an excellent support. For example, Xiang et al., reported graphene and graphitic carbon nitride composites prepared by combined impregnation and chemical reduction method and its visible light photocatalytic activity for hydrogen with 451 μmol h⁻¹ g⁻¹ rate [26]. Qin et al., reported Cds-graphene nanosheets by solvothermal method and photocatalytic activity was tested for production of H₂ with 1.12 mmol h⁻¹ rate [27]. Recently Putri et al., reported nitrogen and

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boron doped graphene and its visible light activity was tested by production of H₂ with highest rate [28].

The present study deals with the synthesis of WO₃/graphene, Fe₂O₃/graphene nanocomposites for the simultaneous photocatalytic oxidation of *p*-cresol and the reduction of Cr (VI). Chai et al., and Fu et al., reported the WO₃/graphene composite synthesized by hydrothermal method and photocatalytic activity was tested for the degradation of methylene blue [29,30]. Zhang et al., has synthesized the hematite Fe₂O₃/rGO nanocomposite by hydrothermal method and photocatalytic activity was assessed during the degradation of various organic dyes [31]. G. K. Pradhan et al., reported the hematite Fe₂O₃ nanorods/graphene synthesized by hydrothermal method and photocatalytic activity was tested for phenol degradation [32]. Even though various attempts were made, for the removal of individual pollutant *via* either oxidation or reduction. However, the recent studies highlight the simultaneous removal of redox species are beneficial over the removal of individual pollutants [33–35]. With this background, the present study deals with the synthesis of WO₃ (C1), Fe₂O₃ (C2), WO₃/rGO (C3) and Fe₂O₃/rGO (C4) photocatalysts by *in-situ* hydrothermal method. The photocatalytic activity was tested for the simultaneous oxidation of *p*-cresol and the reduction of Cr (VI).

2. Experimental section

2.1. Materials

Sodium tungstate dihydrate (Na₂WO₄·2H₂O) (Sigma Aldrich), hydrochloric acid (HCl), oxalic acid (C₂H₂O₄) (Sigma Aldrich), graphite powder (Sigma Aldrich), concentrated sulphuric acid (H₂SO₄), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄) (Sigma Aldrich), hydrogen peroxide (H₂O₂), ethanol, ferrous chloride hexa-hydrate (FeCl₃·6H₂O) (Sigma Aldrich) are analytical grade chemicals.

2.2. Synthesis of WO₃/rGO and Fe₂O₃/rGO nanocomposites

The graphene oxide (GO) was synthesized from graphite powder by modified Hummer's method [36]. The WO₃/rGO and Fe₂O₃/rGO nanocomposites were synthesized by *in-situ* hydrothermal method [37]. The WO₃/rGO nanocomposite was synthesized by dispersing 10 mg of GO in 30 ml of water and ultrasonicated for 60 min. To this GO dispersed solution, 0.3 g of Na₂WO₄·2H₂O and 0.03 g of NaCl were added and stirred continuously for 1 h. The pH of the solution was adjusted to 2.0 by using 10% HCl solution and stirred continuously for 30 min. The resulting solution was taken in a Teflon sealed autoclave and heated at 180 °C for 24 h. The final product was centrifuged, washed with water and followed by ethanol to remove impurities present in the solution and finally dried at 70 °C for overnight. In similar way, 10 mg of GO was dispersed in 30 ml of DI water by sonication, and 1 g of FeCl₃·6H₂O was added to the above GO dispersion and stirred continuously. The mixture was transferred into 50 ml Teflon sealed autoclave heated at 180 °C for 12 h. The final solution was centrifuged, washed with water and ethanol and dried at 70 °C. Pure WO₃ (C1) and Fe₂O₃ (C2) were synthesized by similar procedure only in the absence of GO.

2.3. Characterization

The crystallite size and phase identification of WO₃ (C1), Fe₂O₃ (C2), WO₃/rGO (C3), Fe₂O₃/rGO (C4) were done by using a PANalytical X'Pert Pro Powder X-ray diffractometer with Cu-K α radiation and Ni filter. The morphology of active photocatalyst C3 was collected by a Scanning Electron Microscopy (FESEM-FEI, QUANTA 400) with an applying voltage of 20 kV and elemental composition

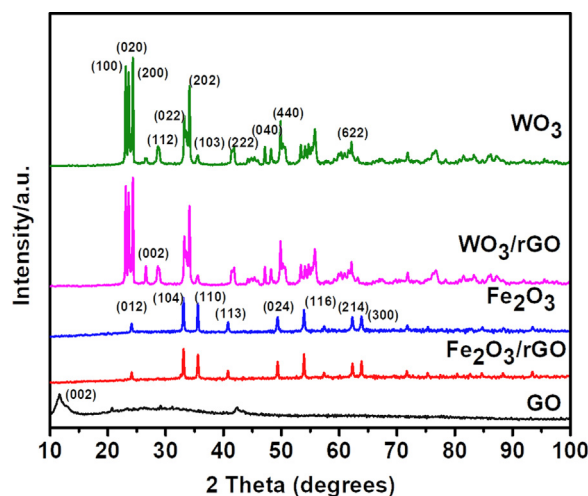


Fig. 1. The powder XRD spectrum of WO₃, Fe₂O₃, WO₃/rGO, Fe₂O₃/rGO and GO.

of synthesized samples can be measured by Energy-dispersive X-ray Spectrometry (EDX). The optical properties of prepared samples were measured by UV-vis-DRS spectrophotometer (SHIMADZU-3600) with BaSO₄ as the standard reference. The Raman spectra of prepared samples can be measured by using BRUKER SENTERA dispersive Raman microscopy with an excitation wavelength of 532 nm. The Transmission Electron microscopy images of the photocatalyst C3 was recorded on a TECNAI G-2 instrument. The X-ray Photoelectron Spectroscopy (XPS) of prepared samples were analyzed with Krato axis Ultra Spectrometer with Al-K α source at 1489.5 eV, emission current and voltage at 10 mA and 15 kV. The Surface areas of WO₃ (C1), Fe₂O₃ (C2), WO₃/rGO (C3) and Fe₂O₃/rGO (C4) are 11 m²/g, 8 m²/g, 16 m²/g and 12 m²/g respectively [38,43,45].

2.4. Photocatalytic experiments

The photocatalytic experiments were carried out in a photoreactor which are powered by three 250 W lamps. The visible light photocatalytic activity of C1–C4 was tested for the individual and simultaneous reduction of Cr(VI) and oxidation of *p*-cresol. Before exposure to light source, the samples along with catalysts are kept under dark conditions for an hour to allow it to reach the adsorption-desorption equilibrium. The concentration after equilibrium was considered as initial concentration (20 mg/L). During the light exposure for every 30 min small aliquots were collected and centrifuged at 2000 rpm. The degradation of *p*-cresol was estimated at 277 nm using UV-vis spectrophotometer. The photoreduction of Cr(VI) was estimated by using 1,5-diphenyl hydrazide solution and monitoring the absorbance of purple colored complex at 540 nm. The degradation efficiency was calculated by using the following formula.

$$\eta = C_0 - C / C_0 \times 100\%$$

Where, C₀ is the initial concentration and C is the concentration at time 't' and 'η' is the conversion efficiency of photocatalytic degradation.

3. Results and discussion

3.1. X-ray diffraction

The phase composition and crystal structure of synthesized samples were measured by powder X-ray technique. The diffraction peaks related to C1–C4 are represented in Fig. 1. The peaks

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