Research Article

Structural and Morphological Studies of V_2O_5 /MWCNTs and ZrO_2 /MWCNTs Composites as Photocatalysts

Sajid Iqbal ¹, Tanveer Hussain Bokhari,¹ Shoomaila Latif,² Muhammad Imran,³ Ayesha Javaid,³ and Liviu Mitu ⁴

¹Department of Chemistry, Government College University, Faisalabad 38000, Pakistan

²School of Physical Sciences, University of the Punjab, Lahore, Pakistan

³Institute of Chemistry, University of the Punjab, Lahore, Pakistan

⁴Department of Nature Sciences, University of Pitesti, Pitesti 110040, Romania

Correspondence should be addressed to Sajid Iqbal; h.sajid588@gmail.com and Liviu Mitu; ktm7ro@yahoo.com

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The present study outlines the synthesis of transition metal oxide- (TMO-) multiwall carbon nanotubes- (MWCNTs-) based composites for photocatalytic application. MWCNTs were functionalized/purified by treating with H_2SO_4 and HNO_3 to improve their dispersion in water. The TMOs (ZrO_2 , V_2O_5) were decorated on MWCNTs by the hydrothermal method to yield V_2O_5 /MWCNTs and ZrO_2 /MWCNTs composites. Subsequently, these composites were characterized for their structural/morphological studies by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Photocatalytic activities of TMO/MWCNTs composites were investigated by degradation phenomenon of methylene blue (MB) dye in aqueous solution. It was observed that the prepared composites best performed in the presence of H_2O_2 under ultraviolet irradiation. The maximum observed degradation efficiencies for ZrO_2 /MWCNTs and V_2O_5 /MWCNTs were 49% and 96%, respectively.

1. Introduction

Carbon nanotubes (CNTs) have attracted many researchers since their discovery by Iijima in 1991. Their remarkable properties include mechanical strength, large surface area, enhanced electrical conduction, and high chemical and thermal stability [1]. Due to these properties, the CNTs-based materials have become promising candidates as nanocomposites [2], photovoltaics [3], photocatalysts [4], optical biosensors [5], chemical sensors [6], and optoelectronic and energy storage devices [7]. Several strategies have been reported to enhance their fruitful applications in various fields. Some notable strategies include their use in combination with metals, polymers, and metal sulfides/oxides/phosphides/nitrides [1]. Recently, nano-structured transition metal oxides (TMOs) have become promising nanomaterials for versatile applications mainly in semiconducting devices and catalysis. TMOs are usually wide

band gap semiconductor materials and their electronic conductivities could be improved by tailoring them with the materials having better electrical conductivity such as graphene oxide and functionalized CNTs [8]. Among TMOs, ZrO_2 is an attractive photocatalyst due to high specific surface area, thermal stability, chemical resistance, ionic conduction, mechanical stability, and optical and electrical properties [9, 10]. Similarly, excellent chemical and physical characteristics of V_2O_5 have also been reported for potential applications as photochromic, electrochromic devices [11], optoelectronic devices [12], sensors [13], and especially as photocatalyst [14].

In recent years, enormous research has been conducted on carbon nanotubes-based composites materials in combination with transition metal oxides. Though extensive progress has been made on TMOs-CNTs composites, however, a facile method to functionalize CNTs and to obtain controlled morphology of TMO-CNTs composite is

an emerging area which needs further exploration. Therefore, in this work, ZrO₂/MWCNTs- and V₂O₅/MWCNTs-based composite materials have been synthesized by simple one pot hydrothermal reaction. The morphological and photocatalytic studies of these composites are part of this study.

2. Experimental

2.1. Materials. MWCNTs, zirconium oxide (ZrO₂) (99%), vanadium pentoxide (V₂O₅) (99.5%), sulfuric acid (H₂SO₄) (98%), nitric acid (HNO₃) (70%), acetic acid (CH₃COOH) (99%), ethanol (C₂H₅OH) (99.9%), methanol (CH₃OH) (99.9%), hydrogen peroxide (H₂O₂) (30%), and methylene blue (MB) (100%) were used as raw materials. The morphological/structural aspects of prepared composites were studied by scanning electron microscopy (Hitachi, S-2380N), Fourier transform infrared spectroscopy (Cary 630-Agilent technologies), and X-ray diffractometer (Bruker D8 ADVANCE diffractometer).

2.2. Purification/Oxidation of Multiwalled Carbon Nanotubes. Purification of MWCNTs was carried out according to previously reported protocol with minor modifications [15]. Briefly, for purification of raw MWCNTs, concentrated H₂SO₄ and HNO₃ (3:1 v/v%, 40 mL) were added into raw MWCNTs (250 mg) and sonicated for 3 h at 40°C. The reaction mixture was allowed to cool down and then was diluted with cold distilled water (5 times). Then, it was centrifuged at 5000 rpm for 15 min. The resulting precipitate were washed with distilled water, followed by ethanol and dried at 60°C for 4 h in oven. Finally, the blackish purified/oxidized powdered MWCNTs were obtained which were used for further preparations. To obtain the stable suspension of MWCNTs, purified/oxidized MWCNTs (30/60 mg) were added in 30 mL deionized water, and the mixture was sonicated for 1 h.

2.3. Synthesis of TMOs/MWCNTs Composite Materials. Synthesis of TMOs/MWCNTs composites were prepared by following reported method with some modifications [16]. It was performed by adding respective TMOs solutions (10 mL) drop wise into the prepared stable suspension of MWCNTs with continuous magnetic stirring at room temperature for 5 minutes. Subsequently, 2 mL acetic acid was added in the above mixture and magnetically restirred for more 5 minutes. The reaction mixture was then refluxed at 120°C for 6 h. The resulting mixture was then allowed to cool down to room temperature and centrifuged at 5000 rpm for 20 minutes. The precipitates were washed with distilled water and ethanol to remove the impurities. The black precipitates were heated at 60°C for 12 hours. The dried precipitates were calcined at 350°C (heating rate 10°C per min.) for 3 hours.

2.4. Photocatalytic Studies. Photocatalytic properties of prepared composites were investigated for the degradation of MB dye in aqueous media in the presence of ultraviolet

(UV) light source. This study was conducted in three ways: first, MB (100 ppm, 50 mL) was placed in UV lamp setup; second, H₂O₂ (2 mL) was added in 50 mL dye solution and then placed under UV radiation for catalytic reaction; third, catalytic activities were checked in the presence of TMOs/MWCNTs catalysts. Typically, in 50 mL MB solution (100 ppm), catalytic dose was added up to 10 mg. The adsorption-desorption balance was obtained by magnetic stirring in the dark for 30 min. Then, the mixture was exposed to UV light as it (without adding H₂O₂) and after subsequent addition of H₂O₂ (2 mL). The samples were taken out after regular intervals of 30 min, and the concentrations of MB were analyzed in the supernatant by the UV-visible double beam spectrophotometer (Lambda 25, Perkin Elmer) at 660 nm. All photocatalytic experiments were carried out at room temperature, and pH values were maintained to neutral.

3. Results and Discussion

Raw MWCNTs were purified/oxidized by acid treatment. TMO/MWCNTs composites were synthesized by the hydrothermal process. The calcinated final products were further characterized by FT-IR, XRD, and SEM analyses. FT-IR spectrum of raw MWCNTs exhibits several peaks especially in fingerprint region <1500 cm⁻¹, which indicates the presence of metal catalysts and carbonaceous impurities (Figure 1(a)). The absorption peaks around 2849 cm⁻¹ and ~2920 cm⁻¹ can be attributed to symmetric and asymmetric stretching vibrations of the CH group, respectively [17]. The peak at ~3275 cm⁻¹ is attributed to O-H stretching vibration. Similarly, the peaks at the wave numbers of ~1726 cm⁻¹, ~1676 cm⁻¹, and ~3638 cm⁻¹ are assigned to C=O, C=C, and O-H, respectively. Another strong peak at ~2114 cm⁻¹ is due to the stretching vibrations of isothiocyanate [18]. Figure 1(b) depicts the FT-IR spectrum of the acid-treated MWCNTs. The broad peak that appeared at wave number ~3426 cm⁻¹ together with a peak at ~1750 cm⁻¹ corresponds to the OH and C=O groups of carboxylic acid [19, 20]. Figure 1(c) represents the FT-IR spectrum of ZrO₂, and the peaks appeared at around 1052 cm⁻¹ and 793 cm⁻¹ are assigned to the absorption of monoclinic Zr-O bond. Moreover, a peak below 650 cm⁻¹ is ascribed to the vibration modes of the ZrO₃⁻² group [21]. Figure 1(d) represents the FT-IR spectrum of V₂O₅, and the peaks that appeared below 1200 cm⁻¹ are attributed to the characteristic vibration bands of V-O [22]. Sharp peaks at ~1052 cm⁻¹ and ~1014 cm⁻¹ are the characteristics of the V=O vibrations mode. Two peaks centered at ~730 cm⁻¹ and below 650 cm⁻¹ are attributed to asymmetric and symmetric stretch of V-O-V [23].

FT-IR spectra of V₂O₅/acid treated-MWCNTs (ratio 1 : 3, 1 : 6 wt.%) are shown in Figures 2(a) and 2(b). The peaks that appeared at around 1200 cm⁻¹ and ~830 cm⁻¹ are assigned to symmetric and asymmetric stretching modes of the V-O-V bond. When compared with symmetric and asymmetric stretching modes of the V-O-V bond of simple V₂O₅ (Figure 1(d)), these peaks shifted towards higher wave numbers 1200 cm⁻¹ and 830 cm⁻¹, respectively, might be

FIGURE 1: FTIR spectra of (a) raw MWCNTs, (b) acid-treated MWCNTs, (c) ZrO_2 , and (d) V_2O_5 .

due to the interactions between V_2O_5 and acid treated-MWCNTs [24, 25]. Figures 2(c) and 2(d) represent the FT-IR spectra of ZrO_2 /acid treated-MWCNTs (ratio 1:3, 1:6 wt. %), and the peaks observed at around 757 cm^{-1} are due to symmetric stretching vibrations of Zr-O-Zr and support the successful modification of acid treated-MWCNTs with ZrO_2 . These results are in agreement with similar studies [21].

Powder XRD (PXRD) is an effective analytical technique widely used to analyze the bulk crystal structures of materials. The PXRD patterns for ZrO_2 /acid treated-MWCNTs and V_2O_5 /acid-treated MWCNTs (ratio 1:3 wt. %) have been determined and presented in Figures 3(a) and 3(b), respectively. In Figure 3(b), the diffraction peaks observed at 2θ 15.2° , 20° , 21.6° , 26.2° , 30.8° , 32.2° , 34° , 41° , and 47.2° correspond to (200), (001), (101), (110), (301), (011), (310), (002), and (600) reflection planes in accordance with JCPDS

card no: 03-065-0131 [26, 27]. The diffraction peak at $2\theta = 20.1^\circ$ with Miller index (001) suggests the characteristic orthorhombic shape of V_2O_5 . The peak at angle $2\theta = 26.2^\circ$ matching with (110) confirms the presence of both orthorhombic V_2O_5 and graphite structure of MWCNTs and is in accordance with reported literature about it [26, 28]. Figure 3(a) shows the PXRD pattern of ZrO_2 /acid-treated MWCNTs (ratio 1:3 wt.%) with peak at $2\theta = 26.2^\circ$ assigned to (002) reflection plane of graphite structure of MWCNTs [29]. Moreover, the peaks appeared at 2θ angle 28.1° (-111), 31.4° (111), 34° (002), 35.2° (200), 38.5° (021), 40.5° (-112), 44.6° (112), 45.3° (-202), 49° (220), 50° (022), 53.8° (300), and 55.3° (310) show the presence of monoclinic ZrO_2 and are in accordance with JCPDS card no: 37-1484 [30]. The crystallinity of V_2O_5 /acid treated-MWCNTs and ZrO_2 /acid treated-MWCNTs as calculated by crystallinity equation were 62.5% and 61.93%, respectively.

FIGURE 2: FTIR spectra of (a) V_2O_5 /acid-treated MWCNTs (ratio 1 : 3 wt. %), (b) V_2O_5 /acid-treated MWCNTs (ratio 1 : 6 wt. %), (c) ZrO_2 /acid-treated MWCNTs (ratio 1 : 3 wt. %), and (d) ZrO_2 /acid-treated MWCNTs (ratio 1 : 6 wt. %).

SEM images of MWCNTs, V_2O_5 /acid-treated MWCNTs, and ZrO_2 /acid-treated MWCNTs were taken using a scanning electron microscope. MWCNTs are randomly orientated showing nanoscale morphology with the average diameter of 23.5 nm calculated by using histograms (Figure 4(a)).

Figures 4(b)–4(f) show the SEM images of V_2O_5 /acid-treated MWCNTs (ratio 1 : 6 wt. %) composites at different resolutions. The clusters of V_2O_5 are anchored on the nanonetwork of MWCNTs.

A close-up view of microstructured V_2O_5 cluster in Figure 4(e) confirms the porous morphology of composite making it a favorable candidate for adsorption/catalytic studies.

The morphology of ZrO_2 /acid-treated MWCNTs (ratio 1 : 6 wt. %) nanocomposite is shown in Figure 5. The flakes

like microstructures are formed that can be seen in low magnification image (Figure 5(a)). Highly magnified image (Figure 5(c)) confirms the homogenous coating of ZrO_2 on the surface of MWCNTs.

3.1. Photocatalytic Activity. The prepared V_2O_5 /MWCNTs and ZrO_2 /MWCNTs were investigated to check out their photocatalytic activities against MB ($\lambda_{\max} = 660$ nm) using an UV-visible spectrophotometer.

First of all, the effect of UV radiations on the dye degradation was checked without using any catalyst. Figure 6(b) shows the degradation efficiency (removal of MB) of UV radiation alone, made after regular intervals (30, 60, 90, and 120 min). The data obtained in case of UV radiations as catalyst indicate that the removal of MB dye from

FIGURE 3: PXRD patterns of (a) ZrO_2 /acid-treated MWCNTs (ratio 1 : 3 wt. %) and (b) V_2O_5 /acid-treated MWCNTs (ratio 1 : 3 wt. %).

100 ppm aqueous solution is negligible with degradation efficiency 0.3%, 0.4%, 0.4%, and 0.4% at 30, 60, 90, and 120 min, respectively. Thus, the UV radiations are not enough for the degradation of MB dye. It is well established that radicals are highly reactive species and can decompose organic effluents from wastewater. Among these, H_2O_2 is low-cost oxidant which can be used to degrade such pollutants. When H_2O_2 is irradiated with UV radiation, it is converted into hydroxyl radicals (OH) which can enhance the degradation efficiency [31, 32]. Keeping in view the role of H_2O_2 , degradation of MB was studied by using H_2O_2 in the presence of UV radiations. After first interval (30 min), the degradation efficiency was 14%; furthermore, a continuous increase in efficiency (%) was observed with respect to time. For instance, after 60, 90, and 120 min, the degradation efficiencies were 21.2%, 29.3%, and 31.6%, respectively (Figure 6(c)).

Generally, the efficiency was better compared to UV light alone but too much long-time was required.

In the second step, the efficiency of UV radiations along with ZrO_2 /MWCNTs and V_2O_5 /MWCNTs was studied. The ZrO_2 /MWCNTs composites appeared as poor catalyst because their maximum efficiency of 1 : 3 wt. % and 1 : 6 wt. % is only 16.2% and 9.3%, respectively (Figure 7(a)). However, the V_2O_5 /MWCNTs (1 : 3 wt. % and 1 : 6 wt. %) composites relatively performed better than ZrO_2 /MWCNTs (Figure 7(b)). It may be due to the small energy band gap of V_2O_5 (2.1–2.4 eV) compared to ZrO_2 (5.0–5.5 eV).

In the third step, combination of ZrO_2 /MWCNTs, V_2O_5 /MWCNTs, and H_2O_2 as an effective electron scavenger was studied for the said purpose. The treatment of MB with

ZrO_2 /MWCNTs in the presence of H_2O_2 is under continuous UV light. This time, the efficiency of ZrO_2 /MWCNTs composite was significantly increased up to 44.7% in 120 min (Figure 7(c)).

The best results for MB removal were obtained for the combination of H_2O_2 and V_2O_5 /MWCNTs catalysts. When V_2O_5 /MWCNTs (1 : 3, 1 : 6 wt. %) were added in aqueous solution of MB in presence of H_2O_2 , the degradation of MB approached up to 91% within 60 min. In next 60 min, 3% and 5% degradation occurred for V_2O_5 /MWCNTs (1 : 3 wt. %) and V_2O_5 /MWCNTs (1 : 6 wt. %), respectively.

The dramatic increase in degradation efficiencies of V_2O_5 /MWCNTs and ZrO_2 /MWCNTs in the presence of H_2O_2 is due to the formation of heterojunction between the TMO and MWCNTs. The basic principal of the photocatalytic process in the present study is that the MWCNTs trapped the photoexcited electrons from the conduction band of TMO; hence, the recombination process is prevented. Furthermore, the scavenging of photoexcited electrons by H_2O_2 promotes the production of (OH) radicals. Basically, hydroxyl radicals introduced from three ways into the system, i.e., (i) when H_2O molecules are oxidized by excess holes in valence band of photocatalysts, (ii) when H_2O_2 scavenged the trapped/photoexcited electrons from MWCNTs/conduction band, and (iii) to some extent, when H_2O_2 is irradiated by UV light [33]. The produced hydroxyl radical is very reactive specie and plays a major role in the degradation of MB dye into nonharmful products. Furthermore, the better degradation efficiency of V_2O_5 /MWCNTs can be justified by the role (OH) radical and small energy band gap of V_2O_5 (Figures 7(d), 8(a), and 8(b)).

FIGURE 4: SEM images of (a) MWCNTs and (b–f) V_2O_5 /acid-treated MWCNTs (ratio 1 : 6 wt. %) at different resolutions and magnifications.

FIGURE 5: SEM images of (a-c) ZrO₂/acid-treated MWCNTs (ratio 1 : 6 wt. %) at different resolutions and (d) diameter distribution of MWCNTs (histograms).

FIGURE 6: Continued.

(c)

FIGURE 6: (a) UV-visible absorption spectra of MB solution (100 ppm) and degradation efficiencies of (b) UV radiation alone and (c) UV radiation and H₂O₂.

(a)

(b)

(c)

(d)

FIGURE 7: Degradation efficiency of (a) UV radiation and ZrO₂/MWCNTs composites, (b) UV radiation and V₂O₅/MWCNTs composites, (c) UV radiation, H₂O₂, and ZrO₂/MWCNTs composites, (d) UV radiation, H₂O₂, and V₂O₅/MWCNTs composites.

FIGURE 8: Schematic diagrams illustrating the photocatalytic mechanism of (a) V_2O_5 /MWCNTs and (b) ZrO_2 /MWCNTs composites.

4. Conclusions

In this study, the composites of V_2O_5 , ZrO_2 , and MWCNTs were successfully synthesized in different ratios (TMO: MWCNTs, 1:3 wt. % and 1:6 wt. %) through one-pot hydrothermal reaction followed by the calcination. The V_2O_5 /MWCNTs composite exhibited the superior photocatalytic activity in comparison with ZrO_2 /MWCNTs composite. Hence, the prepared composites can be used as a highly efficient catalyst for degrading dyes and other organic pollutants from industrial effluents, a continuous threat to environment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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