Photocatalytic Degradation of Carbon Monoxide (CO) Using Bi$_2$O$_3$ Modified TiO$_2$ Photocatalyst

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Authors’ contributions

This work was carried out in collaboration between all authors. Authors NI and AR designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AR and SJP managed the analyses of the study. Authors AR and AKC managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

TiO$_2$ modified Bi$_2$O$_3$ nanoheterojunction was prepared using maleic acid as an organic linker. TiO$_2$ photocatalyst cannot perform photocatalytic reaction in the visible region. It only can work in the UV light region because of its band gap 3.2 eV. On the other hand Bi$_2$O$_3$ modified TiO$_2$ can perform photo activity in UV as well as visible region because Bi$_2$O$_3$ can absorb photon in the visible light. These Bi$_2$O$_3$/TiO$_2$ nanocomposite was characterized Transmission Electron Microscope (TEM), X-ray diffraction (XRD), UV-Vis spectroscopy and Gas Chromatography (GC). The as modified composite exhibited high photo oxidation activity under visible region of $\lambda$ up to 430 nm, whereof the modified photocatalyst can oxidize CO in UV as well as visible light. Because of the development of anti-air pollution technology, our modified nanoheterojunction could be a significant photocatalyst to oxidize pollutants in air to keep the environment clean.

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1. INTRODUCTION

In recent years photocatalytic oxidation (PCO) is widely studied in the field of water and air pollution control to clean-up the environmental hazardous pollutants [1-5]. The research on oxidation of carbon monoxide (CO) has become an important topic during the last few years. CO is a harmful air pollutant for the living environment and generally it produce in partial combustion of hydrocarbons. Photocatalytic oxidation process is one of the most promising resolutions to decompose CO. Especially TiO$_2$ photocatalyst can successfully degrade the volatile organic compounds present in air under normal temperature [6-9]. However, the limitation is TiO$_2$ only can work under UV light because of its large band gap of 3.2 eV [10]. Therefore, modification of TiO$_2$ is mandatory to absorb visible light in the photocatalytic process to enhance the reaction rate.

There are different ways to modify TiO$_2$ photocatalyst. Among them doping by metal and non-metal, photosensitizing with dye on TiO$_2$ surface, modification by semiconductors having narrow bandgap and noble metal depositions are widely used. Of the many processes modification of TiO$_2$ using noble metal deposition on its surface have recently been placed as one of the most feasible modification process for enhancing the photocatalytic oxidation reactions [11-13].

In this research, TiO$_2$ was modified by bismuth (III) oxide (Bi$_2$O$_3$) to enhance the photocatalytic activity of TiO$_2$. Maleic acid was used as an organic linker to develop the Bi$_2$O$_3$/TiO$_2$ nanoheterojunction. The presence of Bi$_2$O$_3$ on TiO$_2$ surface significantly enhances the photocatalytic oxidation rate of CO because the PCO reaction can possibly presence of UV as well as visible light [14]. On the other hand, research literatures have confirmed that Bi$_2$O$_3$ is comparatively cheap and less toxic than other metals like led, iron and antimony [10,14].

2. EXPERIMENTAL

Carbon Monoxide (CO), titanium dioxide (TiO$_2$) nanoparticle, bismuth oxide (Bi$_2$O$_3$), maleic acid (C$_4$H$_4$O$_4$) and absolute ethanol (CH$_3$CH$_2$OH) were purchased from Sigma Aldrich (Germany) and were used without further purification.

2.1 Modification of TiO$_2$ with Bi$_2$O$_3$

Different molar ratios of Bi$_2$O$_3$ modified TiO$_2$ were prepared using maleic as an organic linker. 5/95, Bi$_2$O$_3$/TiO$_2$ was synthesized using 5 mol% of Bi2O3 and 95 mole% of TiO$_2$. During synthesis process 0.24 g of Bi$_2$O$_3$ was dissolved in 50 mL of ethanol solution. Then 0.2 g of maleic acid was added in to the solution. Afterward, 0.76 g of TiO$_2$ was added in to the mixture and stirred for 5 h at room temperature until a homogenous solution. Then the suspension was stand in an oven for overnight at 60°C for drying. To increase the bonding between TiO$_2$ and Bi$_2$O$_3$ the prepared composite was annealed at 120°C in a muffle furnace. The same methodology was used to synthesize at ratios of 20/80, 35/65, 50/50, 65/35, Bi$_2$O$_3$/TiO$_2$ nanoheterojunction [14].

2.2 Photocatalytic Oxidation Test

Photocatalytic oxidation of CO was carried out in a gas reactor prepared in the laboratory. Gas chromatography (GC) was used to measure the remnant of CO after photocatalytic oxidation reaction. Our modified photocatalyst was placed inside the gas reactor and the light source was placed in front of the photocatalyst. The CO gas was inserted in to the gas reactor and after oxidation the remnant of CO was collected and was analyzed using GC.

2.3 Characterization Techniques

The surface structure of the pure and modified TiO$_2$ were observed using fei-TECNAI G2 Transmission Electron Microscopy (TEM). A D8 Bruker Advance X-ray diffractometer (Bruker, Germany) was used to analyze the X-ray diffraction measurements. A Shimazu UV-1601 spectrophotometer was used to record UV-Vis reflectance spectra. To observe the photocatalytic oxidation rate of CO a Gas Chromatograph was used with the gas reactor.

3. RESULTS AND DISCUSSION

3.1 Crystallite Shape and Compositional Analysis

In Fig. 1 the surface morphology of 65/35, TiO$_2$/Bi$_2$O$_3$ nanocomposite was analyzed using transmission electron microscope (TEM) and high resolution electron microscopy (HR-TEM).
The crystallite structure of TiO$_2$ nanoparticles can be clearly noticed from Fig. 1(a-b). In Fig. 1(c-d) the modification of TiO$_2$ using Bi$_2$O$_3$ was observed. Thus, the TEM analysis asserts that the Bi$_2$O$_3$ was finely distributed on the TiO$_2$ surface and no other unwanted particles observed.

The Energy-dispersive X-ray spectroscopy (EDX) elemental analysis was performed on Bi$_2$O$_3$ modified TiO$_2$ nanocomposite in a weight ratio of TiO$_2$:Bi$_2$O$_3$: 65:35 which shown in Table 1. From the analysis, it is clear that at the end of the modification process the rest of the maleic acid was evaporated from the nanocomposite. Only Ti, Bi and O elements were found from the analysis that represent the presence of TiO$_2$ and Bi$_2$O$_3$ in the nanocomposite.

Table 1. EDX data of Bi$_2$O$_3$ modified TiO$_2$ nanocomposite

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bi$_2$O$_3$ modified TiO$_2$ nanocomposite Wt.%</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>41.56</td>
</tr>
<tr>
<td>Bi</td>
<td>4.08</td>
</tr>
<tr>
<td>O</td>
<td>54.36</td>
</tr>
</tbody>
</table>

(Weight ratio of TiO$_2$ : Bi$_2$O$_3$: 65:35)

3.2 XRD Analysis

The XRD patterns of TiO$_2$, Bi$_2$O$_3$ and Bi$_2$O$_3$ modified TiO$_2$ nanocomposite is presented in Fig. 2. The TiO$_2$ nanoparticle curve showed peaks at 25.3°, 37.8°, 54°, and 62.10° which indicate the present of the anatase phase and at 43.9°, 56.9°, and 65.10° exhibited the rutile phase. The Bi$_2$O$_3$ curve also exhibited some diffraction peaks at 21.90°, 26.90°, 32.80°, 47.19° and 55.20°. The XRD patterns of Bi$_2$O$_3$ modified TiO$_2$ nanocomposite equalized the diffraction peaks of TiO$_2$ and Bi$_2$O$_3$ without added of any other compounds phases. This observation declares that in the composite formation process no other chemical reactions occur between Bi$_2$O$_3$ and TiO$_2$ nanoparticle.

3.3 UV-Vis Analysis

The UV-vis absorption spectra of TiO$_2$, Bi$_2$O$_3$ and the different ratios of Bi$_2$O$_3$/TiO$_2$ nanocomposite are illustrated in Fig. 3. The bandgap of TiO$_2$ is wide than Bi$_2$O$_3$ and were investigated to be 3.2 eV and 2.8 eV, respectively [15,16]. The optical absorptions of Bi$_2$O$_3$ is greater than of 400 nm and for that reason Bi$_2$O$_3$ can absorb the photon from the visible light of the solar spectrum. TiO$_2$ optical absorption is less than 385 nm therefore, TiO$_2$ is photo inactive in the visible light. On the other hand, the optical absorption of Bi$_2$O$_3$ modified TiO$_2$ nanocomposites are greater than 400 nm because of the presence of Bi$_2$O$_3$. The photon absorption rate in the visible light increase with the increasing of the molar percentage of Bi$_2$O$_3$ in the composite. This analysis demonstrate that Bi$_2$O$_3$/TiO$_2$ nanoheterojunction is effective for the photon absorption in the visible light.

Fig. 1. TEM images of (a, b) pure TiO$_2$ nanoparticle (c, d) Bi$_2$O$_3$ modified TiO$_2$ nanocomposite
3.4 Photocatalytic Oxidation of CO

Fig. 4 illustrate the photocatalytic oxidation of CO on pure TiO$_2$ and Bi$_2$O$_3$ modified TiO$_2$ under visible light. In case of pure TiO$_2$ no photo oxidation occurs because TiO$_2$ cannot absorb photon in the visible light. The different ratios of Bi$_2$O$_3$/TiO$_2$ composites perform different photocatalytic activity. With increasing the percentage of Bi$_2$O$_3$ in the composite the rate of oxidation also increase but 65/35, TiO$_2$/Bi$_2$O$_3$ exhibited highest photo oxidation of CO.
Fig. 4. Remnant CO after photocatalytic oxidation of CO on TiO$_2$, and different ratios of Bi$_2$O$_3$ modified TiO$_2$ nanocomposites

4. CONCLUSION

Bi$_2$O$_3$ modified TiO$_2$ photocatalyst was prepared using maleic acid as an organic linker. The Bi$_2$O$_3$ has finely distributed on the TiO$_2$ nanoheterojunction. The Bi$_2$O$_3$/TiO$_2$ composite successfully performed photocatalytic oxidation of CO in the visible light region. The role of Bi$_2$O$_3$ in the composite was to absorb the photon from the visible region and to be active of the Bi$_2$O$_3$/TiO$_2$ nanoheterojunction for the photooxidation of CO in the UV as well as visible light.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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