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Holmium-TiO_2 thin film for methanol preparation from photocatalytic reduction of carbon dioxide

E.S. Aazam

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203 Jeddah 21589, Saudi Arabia, Tel. +966-6400000, Fax +966-2-6952292, email: elhamaazam@gmail.com

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ABSTRACT

Holmium-TiO_2 thin films were fabricated by a sol-gel technique. Holmium-TiO_2 thin films were identified by many characterization techniques, such as UV-Vis, TEM, XPS, BET and XRD. The performance of the holmium-TiO_2 thin film photocatalyst was studied by studying methanol preparation from the photocatalytic reduction of carbon dioxide under visible light. The results showed that holmium-TiO_2 thin film photocatalytic properties can be adjusted by adjusting the holmium weight percent. XPS results revealed that holmium species were present as Ho^{3+} ions due to the presence of a peak for $Ho3d_{5/2}$ at 163.1 eV. BET results reveal that the addition of holmium to TiO_2 led to an increase in the BET surface area of the TiO_2 thin film. Additionally, the addition of holmium species decreased the band gap and increased the e-h recombination rate of titanium dioxide thin films. The highest photocatalytic activity and lowest band gap of the holmium-TiO_2 thin film were achieved at 0.4 wt % holmium. The yield of methanol obtained using a 0.4 wt % Ho/TiO_2 thin film is approximately 32 times that of the TiO_2 thin film. The Holmium-TiO_2 thin film has stable photocatalytic activity until five times for methanol preparation from the photocatalytic reduction of carbon dioxide under visible light.

Keywords: Holmium; Titanium dioxide; Thin film; Methanol; Carbon dioxide reduction

1. Introduction

For the last century, human industrial activities have increased substantially, and as a result, CO_2 emissions have reached unprecedented amounts. Accordingly, the balance between the CO_2 produced and consumed on earth has gradually been disrupted, leading to the global warming phenomenon, which has caused many environmental problems. Therefore, researchers and scientific communities have focused on different routes to reduce the emission of CO_2 or decrease its concentration in the atmosphere for environmental protection. One of the main routes for reducing CO_2 production is its conversion into useful materials [4–6] through different process, such as the electrochemical reduction or artificial photosynthesis, has attracted the interest of scientists worldwide because of the economic and environmental benefits. During this process, electrical energy is supplied between two electrodes to establish a potential and reduced CO_2 to other forms [4,7–10]. Usually, a variety of products produced from the electrochemical reduction of CO_2 depend on the used catalytic materials and the reaction medium. There are different pathways for electrochemical reduction of CO_2, such as through eight-, six-, four- and two-electron pathways in non-aqueous, gaseous and aqueous phases at different electrode and cell configurations. Electrochemical products for reduction of CO_2 greatly depend on the medium; carbon monoxide, methanol, formaldehyde, formic acid, or formate, oxalic acid or oxalate produced in basic solution, whereas in acidic medium methane, ethanol, or ethylene may produce [11]. One of the great challenges is the conversion of CO_2 into methanol due to their potential applications in various industries. Although methanol is one of the most important precursors for different chemical industries, which is vital to our daily life, such as silicone, paint, and plastics, it is also considered a green fuel due to its low density com-

*Corresponding author.

pared with other fuels [12]. TiO_2 is a widely used photocatalyst because it possesses properties that include chemical stability, nontoxicity, possible reuse, possible incorporation in other materials, and favorable physical properties. Recently, the focus on the application of TiO_2 for the photocatalytic reduction of CO_2 to fuels such as C_2H_5OH, CH_3OH and CH_4, which suffer from the low efficiency due to its wide band gap [23–28]. However, TiO_2 has a wide band gab (E_g = 3.2 eV), making it active when used in reactions that involve UV light, which constitute approximately 3%–5% of the solar spectrum; for this, researchers always try to manipulate its structure to narrow the band gab which in turn makes the derived material active in the natural or artificial sunlight. Accordingly, many research works have been devoted to the design of novel photocatalysts for CO_2 reduction with higher selectively, conversion efficiency, and harvesting visible light [29–37]. Many studies have shown that doping semiconductor oxides greatly enhances their photocatalytic activities for CO_2 reduction. According to my knowledge, there are no reports available to date for the preparation of holmium-TiO_2 thin films or methanol preparation by holmium-TiO_2 thin films. In this research, we report the synthesis of a new holmium-TiO_2 thin film through the sol-gel method, and we will apply this material in a methanol production reaction.

2. Experimental

2.1. Preparation of photocatalysts

Ti precursor, which was used for the preparation of titanium dioxide thin film, is tetrabutyl titanite and holmium precursor, which was used for the preparation of holmium/titanium dioxide thin film is holmium(III) nitrate pentahydrate. The titanium dioxide thin film was prepared by dissolving tetrabutyl titanite in a mixture of propanol and distilled water and the pH of resulting mixture was adjusted by nitric acid to become 2.0 to form stable titania sol. Then, the titania film was formed by dipping the glass plate into titania sol, and the glass plate was calcined at 550°C for 2 h and dried for 2 h at 60°C. The holmium/titanium dioxide thin film samples were prepared by the same method described above in addition to holmium(III) nitrate pentahydrate as a source of holmium, and we used different weight percentages of holmium(III) nitrate pentahydrate to prepare different weight percentages of Ho, such as 0.1, 0.2, 0.3, 0.4 and 0.5 wt %.

2.2. Characterization

X-ray diffractograms of nanocomposites were measured using XRD analysis via Cu-Kα radiation (λ =1.540Å). A Nova-2000 instrument was adopted for specific surface area determination of nanocomposites through N_2 adsorption at 77 K. Before each measurement, specimens were heated at approximately 250°C for 4 h to remove gases from these specimens. Band gap energies corresponding to the synthesized nanocomposites were measured by applying a spectro-photometer (V-570, JASCO, Japan) via determination of UV-Visible diffuse reflectance spectra (UV-Vis-DRS) in air at ambient temperature within the wavelengths range of 200–800 nm. The morphology and microstructure of the prepared nanocomposites were investigated using scanning electron microscopy (JEOL-JEM-5410). The elemental analysis of the synthesized specimens was attained using X-ray photoelectron spectroscopy (XPS) of Thermo Scientific K-ALPHA type, England.

2.3. Photocatalytic experiment

The photocatalytic performance of thin film samples was studied for the photocatalytic reduction of CO_2 under visible light. First, the required dose of the photocatalyst was dispersed in 50 ml of 0.08 M sodium bicarbonate solution. The dimension of the reactor used is 30 cm × 15 cm × 5 cm. To remove oxygen from the reaction mixture, nitrogen gas was passed through the reaction mixture for 1 h. To obtain adsorption-desorption equilibrium, the reaction mixture was kept in the dark for 30 min. A 500-W high-pressure Xe lamp was used as the source of irradiation, and we used 2 M $NaNO_2$ solution to cut off the UV region below 400 nm. The obtained methanol was analyzed using GC-FID. The yield of evolved methanol can be calculated by dividing the total amount of methanol evolved by reaction time. No methanol was detected in any of the tested samples when the reaction was carried out in the dark only. Additionally, no methanol was detected in any of the tested samples when the reaction was carried out using the source of irradiation only.

3. Results and discussion

3.1. Characterizations of thin film samples

XRD patterns of TiO_2 and Ho/TiO_2 thin film samples are shown in Fig. 1. The results demonstrate that the phase of the thin film samples is the anatase titanium dioxide phase and that there are no peaks for holmium or holmium oxide due to the high dispersion of holmium above titanium dioxide or holmium below the detection border of XRD.

Fig. 2. TEM image of the 0.4 wt % Ho/TiO_2 thin film sample. The results reveal that the surface of the thin film is homogenous and smooth.

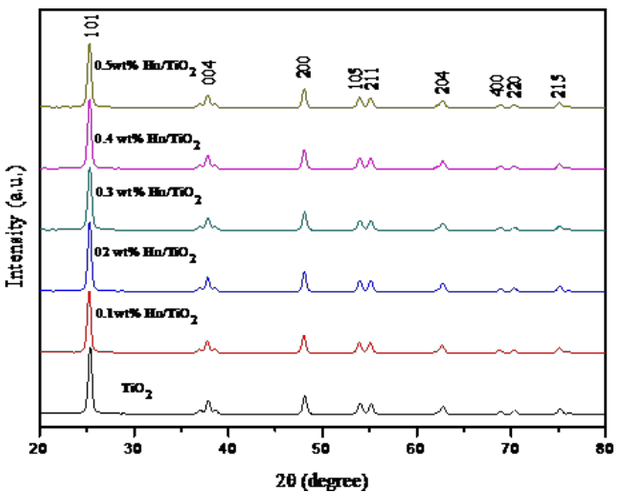

Fig. 1. XRD patterns of TiO_2 and Ho/TiO_2 thin film samples.

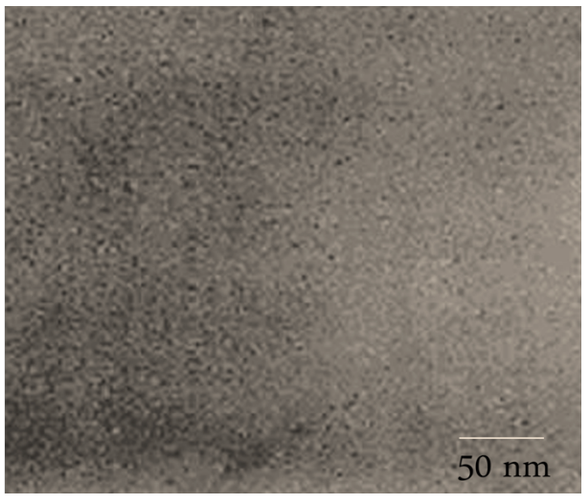

Fig. 2. TEM image of a 0.4 wt % Ho/TiO_2 film sample.

XPS spectra for Ti2P, O1s, and Ho3d for the 0.4 wt % Ho/TiO_2 film sample are shown in Figs. 3A, B and C, respectively. The results reveal that titanium species were present as Ti^{4+} ions due to the presence of two peaks for Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 459.1 and 464.4 eV, respectively, as shown in Fig. 3A. Additionally, oxygen species were present as O^{-2} ions due to the presence of a peak for O1s at 529.9 eV, as shown in Fig. 3B. Therefore, TiO_2 is the formed phase due to the presence of Ti^{4+} and O^{-2} ions. Holmium species were present as Ho^{3+} ions due to the presence of a peak for Ho$3d_{5/2}$ at 163.1 eV, as shown in Fig. 3C.

3.2. Characterizations of surface area

Table 1 shows the BET surface area of the TiO_2 and Ho/TiO_2 thin film samples. The S_{BET} values for TiO_2, 0.1 wt % Ho/TiO_2, 0.2 wt % Ho/TiO_2, 0.3 wt % Ho/TiO_2, 0.4 wt % Ho/TiO_2 and 0.5 wt % Ho/TiO_2 are 60, 65, 75, 88, 91 and 93 m^2/g, respectively. Therefore, the Ho/TiO_2 thin film samples have a surface area higher than that of the TiO_2 sample.

3.3. Characterizations of optical properties

UV-Vis spectra of UV-Vis spectra of TiO_2 and Ho/TiO_2 thin film samples (Fig. 4) reveal a redshift of absorption edges of TiO_2 toward higher wavelengths going from Ho addition. The band gap energies of TiO_2, 0.1 wt % Ho/TiO_2, 0.2 wt % Ho/TiO_2, 0.3 wt % Ho/TiO_2, 0.4 wt % Ho/TiO_2 and 0.5 wt % Ho/TiO_2 samples, which calculated from their respective UV-Vis spectra were 3.2, 2.72, 2.65, 2.57, 2.49 and 2.47 eV, respectively, Therefore, increase wt % of Ho from 0 to 0.4 wt % decrease band gap energy of TiO_2 from 3.2 to 2.49 eV, respectively. Additionally, we noticed that a high wt % of Ho (above 0.4 wt %) has no significant effect on the band gap energy of TiO_2. Therefore, the optimum wt % of Ho is 0.4 wt %.

Pl spectra of TiO_2 and Ho/TiO_2 thin film samples (Fig. 5) show a peak intensity decrease in the following order: TiO_2 > 0.1 wt % Ho/TiO_2> 0.2 wt % Ho/TiO_2> 0.3 wt % Ho/TiO_2> 0.4 wt % Ho/TiO_2> 0.5 wt % Ho/TiO_2.

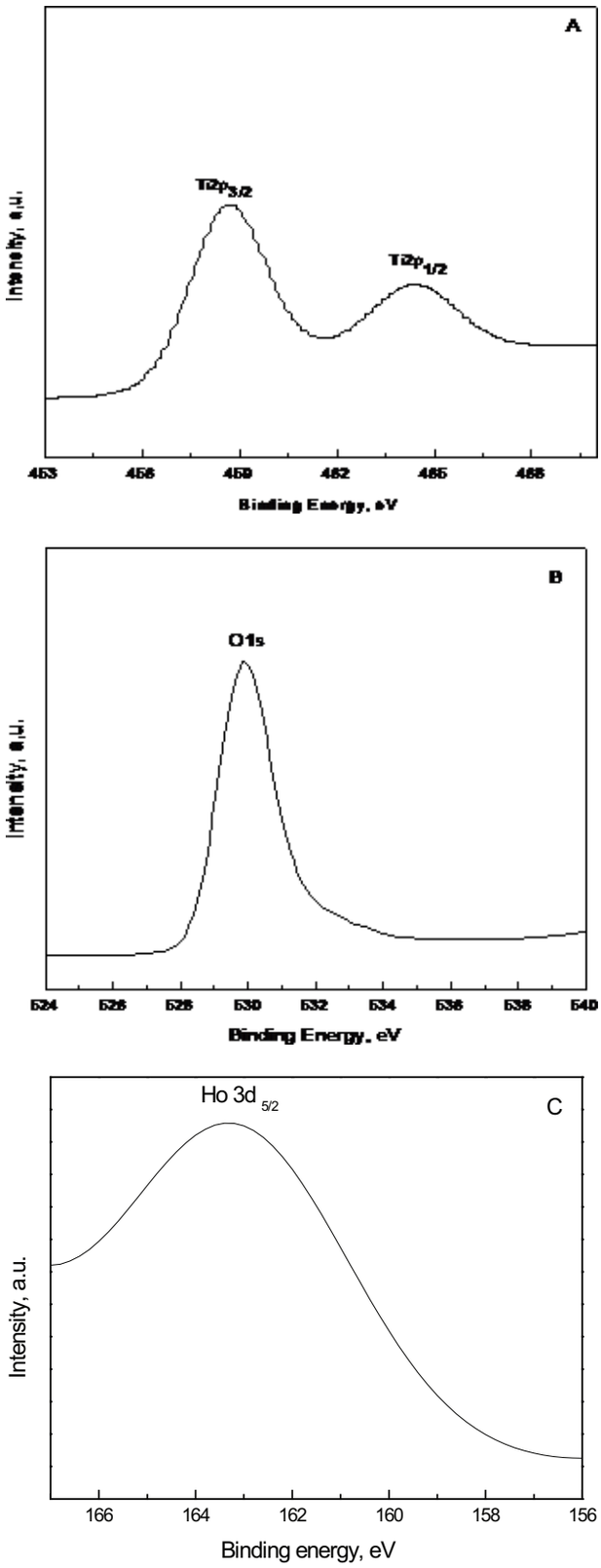

Fig. 3. XPS spectra for Ti2P(A); O1S(B) and Ho3d (C) for the 0.4 wt % Ho/TiO_2 film sample.

Table 1
BET surface area of TiO_2 and Ho/TiO_2 thin film samples

Samples	S_{BET} (m^2/g)
TiO_2	60
0.1 wt Ho/TiO_2	65
0.2 wt Ho /TiO_2	75
0.3 wt Ho /TiO_2	88
0.4 wt Ho /TiO_2	91
0.5 wt Ho /TiO_2	93

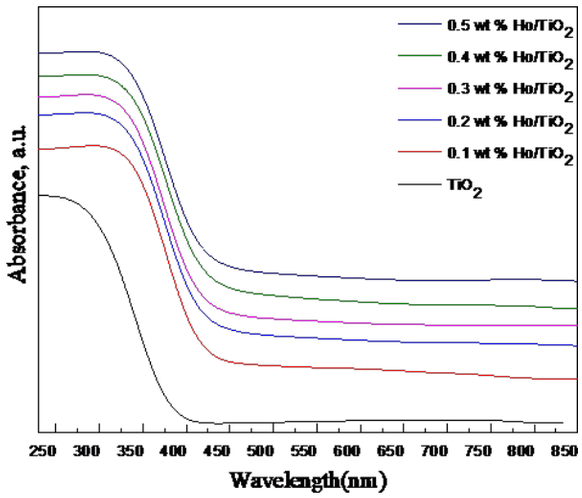

Fig. 4. UV-Vis absorption spectra of TiO_2 and Ho/TiO_2 thin film samples.

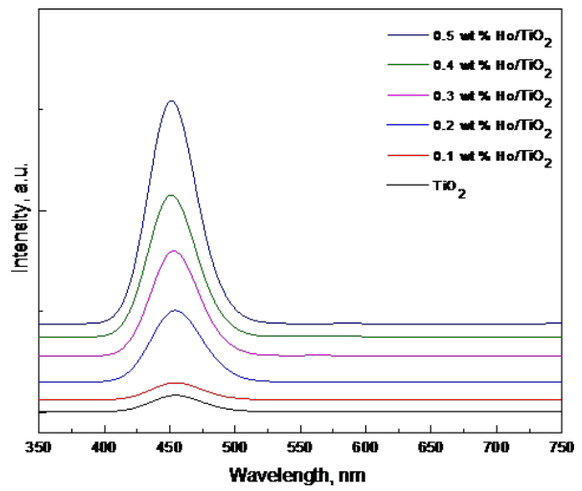

Fig. 5. Pl spectra of TiO_2 and Ho/TiO_2 thin film samples.

3.4. Evolution of photocatalytic performance

The type of photocatalyst and recycling and reuse of 0.4 wt % Ho/TiO_2 photocatalyst were studied to measure the photocatalytic performance for methanol production under visible light conditions.

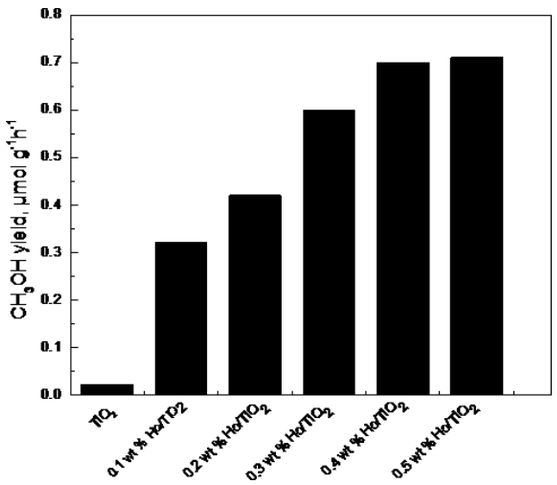

Fig. 6. Effect of the Ho wt % on the photocatalytic activity of TiO_2 and Ho/TiO_2 thin film samples for carbon dioxide photocatalytic reduction.

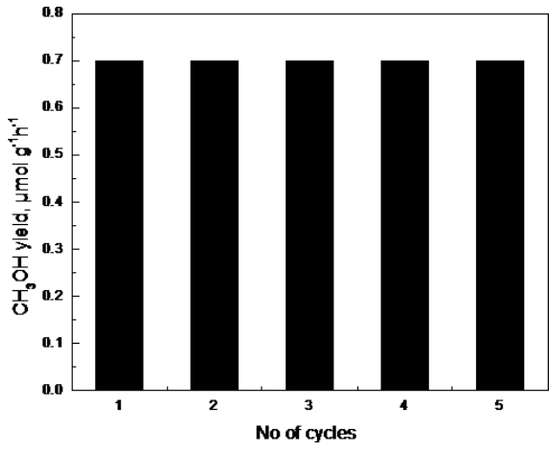

Fig. 7. Recycling and reuse of 0.4 wt % Ho/TiO_2 photocatalysts for carbon dioxide photocatalytic reduction.

The effect of the type of photocatalyst on methanol production was studied. Fig. 6 shows the effect of the type of photocatalyst on methanol production. The TiO_2 sample has almost no photocatalytic activity, as TiO_2 absorbs in the UV region, and the reaction was carried out under visible light. The yield of the Ho/TiO_2 samples for methanol preparation was increased from 0.022 to 0.7 µmol g^{-1} h^{-1}, respectively, due to the decrease in the band gap of TiO_2 from 3.20 to 2.49 eV by the addition of different wt % of Ho from 0 to 0.4 wt%. Additionally, we noticed that a high wt % of Ho (above 0.4 wt %) has no significant effect on the photocatalytic activity of TiO_2. Therefore, the optimum wt % of Ho is 0.4 wt %, which agrees with previous work [38,39].

Recycling and reuse of 0.4 wt % Ho/TiO_2 photocatalyst on methanol preparation was studied. Fig. 7 shows the recycling and reuse of 0.4 wt % Ho/TiO_2 photocatalyst on methanol preparation. It is clear that the 0.4 wt % Ho/TiO_2 photocatalyst has photocatalytic stability and can be used and recycled many times.

4. Conclusions

In summary, a Holmium-TiO_2 thin film was fabricated by a sol-gel technique. The performance of the holmium-TiO_2 thin film photocatalyst was studied by studying methanol preparation from the photocatalytic reduction of carbon dioxide under visible light. The results showed that holmium-TiO_2 thin film photocatalytic properties can be adjusted by adjusting the holmium weight percent. The highest photocatalytic activity and lowest band gap of the holmium-TiO_2 thin film were achieved at 0.4 wt % holmium. The yield of methanol obtained using a 0.4 wt % Ho/TiO_2 thin film is approximately 32 times that of the TiO_2 thin film. The Holmium-TiO_2 thin film has stable photocatalytic activity until five times for methanol preparation from the photocatalytic reduction of carbon dioxide under visible light.

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