Materials Letters 178 (2016) 316–319

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Remarkable photoconversion of carbon dioxide into methane using Bi-doped TiO_2 nanoparticles prepared by a conventional sol–gel method

Jae Hyung Lee, Homin Lee, Misook Kang*

Department of Chemistry, College of Science, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea

ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
18 April 2016
Accepted 24 April 2016
Available online 25 April 2016

Keywords:
Bi ion-incorporated TiO_2
Carbon dioxide
Photoreduction
Methane

ABSTRACT

Bi ions were inserted into a TiO_2 framework in order improve the CO_2 reduction. The x-mol% Bi ion-incorporated TiO_2s were prepared by a conventional sol–gel method, and characterized by XRD, TEM, UV–visible spectroscopy, photocurrent spectroscopy, and CO_2-TPD. The adsorption of CO_2 was significantly increased on Bi–TiO_2s, which demonstrated superior photocatalytic behavior compared to that of pure TiO_2. The 5.0 mol% Bi–TiO_2 produced 3400 μmol g_{cat}^{-1} L^{-1} CH_4 gases after an 8 h reaction. The photocatalytic activity was dramatically enhanced by the improved effective CO_2 gas adsorption and by the inhibited recombination of photogenerated electron–hole pairs due to the enhanced charge separation.

1. Introduction

Recently, there has been increasing interest in converting CO_2 to useful molecules, such as carbon monoxide, methane, formic acid, formaldehyde, or methanol, via chemical routes. The TiO_2 semiconductor has been assessed for CO_2 photoreduction because of its chemical stability and natural abundance. Although TiO_2 has several unique features, its use is limited by its large band gap. Therefore, the photocatalysts should have a lower bandgap and an increased lifetime of the photogenerated electrons and holes via effective charge carrier separation and the suppression of electron–hole recombination. Recently, Bi-based photocatalysts have been investigated widely [1–3]. The emerging Bi-based semiconductor has received increased attention because of its unique morphology and multifunctional application in photocatalysis, supercapacitors, sensing and antibacterial activity. Generally, Bi_2O_3 exhibits p-type electronic conductivity at room temperature which transforms to n-type conductivity at high temperature, depending on the oxygen partial pressure [4]. This behavior qualifies it as a photocatalyst. This study is based on the idea that the gas adsorption and charge separation are two important factors that could largely determine the photocatalysis efficiency from CO_2 reduction to CH_4 production. The Bi ion was selected as a dopant component in this study because of its suitable conductivity and excellent CO_2 absorption: Bi_2O_3 with CO_2 is easily transferred to $(BiO)_2CO_3$ [5]. Based on the expected synergistic effects between Bi and Ti in a photocatalytic system, this study therefore examined the effect of Bi ions as a dopant when inserted into a TiO_2 anatase framework.

2. Experimental

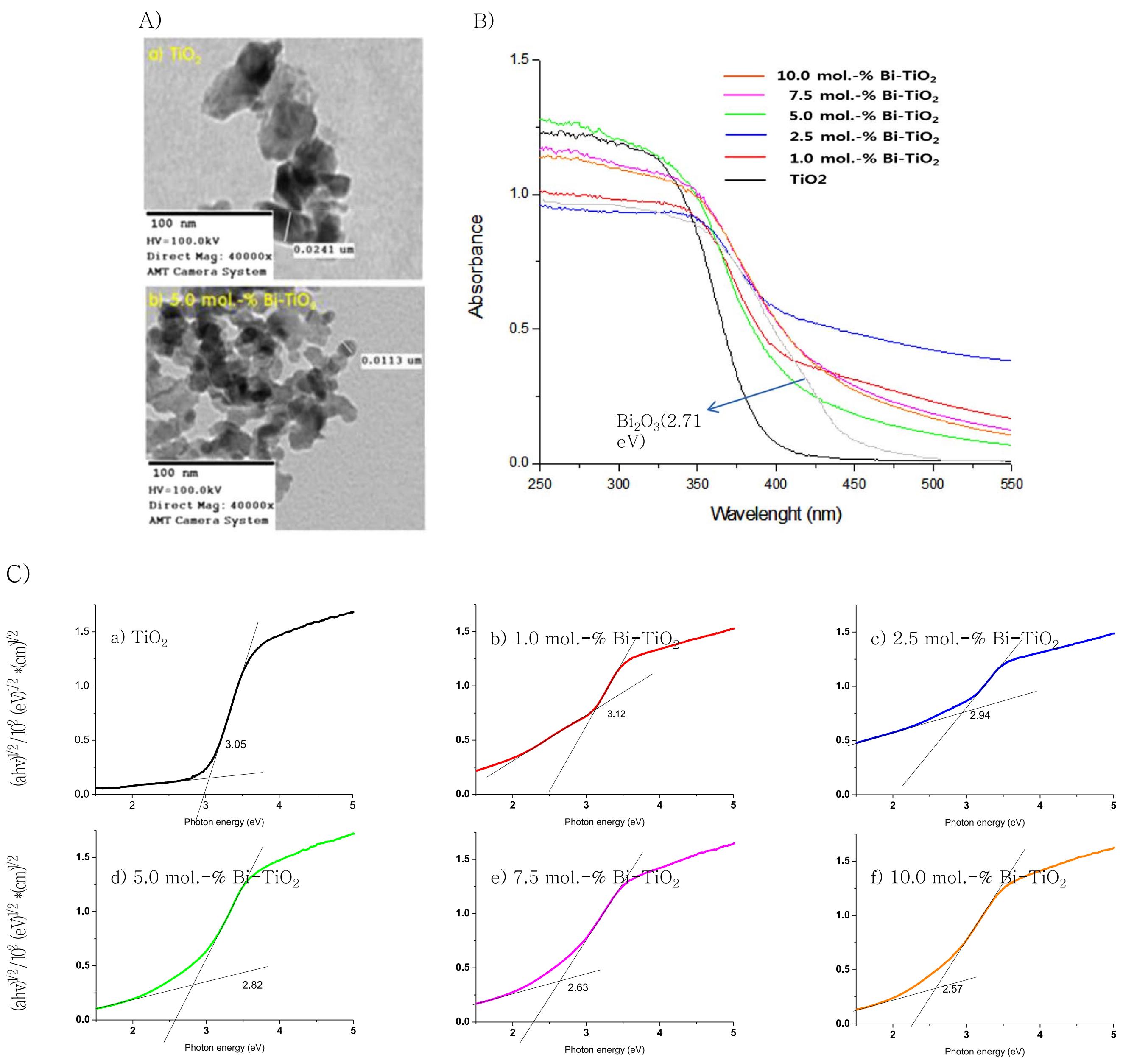
The x (0, 1.0, 2.5, 5.0, 7.5, and 10.0) mol% Bi–TiO_2 powders were prepared using a sol–gel treatment. To prepare a sol-mixture, titanium tetraisopropoxide (TTIP, 99.95%, Junsei Chemical, Tokyo, Japan) and bismuth chloride ($BiCl_3$, 99.97%, Junsei Chemical) were used as the Ti and Bi precursors, respectively, with DI water used as the solvent. Acetic acid was added to fix the pH=3.0 after 1.0 mol TTIP and 1.0, 2.5, 5.0, 7.5, and 10.0 mol% Bi precursor added stepwise, and then homogeneously stirred. The Ti and Bi precursors in the final colloidal solution were hydrolyzed via the OH group during evaporation at 80 °C, and then the colloidal was changed to a powdered gelatin. In the final step, the powders were calcined at 400 °C for 3 h to obtain the anatase structure. The synthesized Bi–TiO_2 powders were examined using an X-ray diffraction (XRD), a transmission electron microscope (TEM), an energy dispersive X-ray spectroscopy (EDS), a reflectance UV–visible spectra, and photocurrent densities. The adsorption of CO_2 on the Bi–TiO_2 powders was measured from CO_2-temperature programmed desorption (TPD) experiments. A batch-type photoreactor was designed in the laboratory [6]. Two 6.0 − W/cm^2 mercury lamps with a 365 nm wavelength were used and the CO_2:H_2O ratio was fixed to 1:2. During the photocatalysis process, the product mixtures were analyzed by gas chromatograph (GC) equipped with a thermal conductivity detector and a flame-ionized detector.

* Corresponding author.
E-mail address: mskang@ynu.ac.kr (M. Kang).

http://dx.doi.org/10.1016/j.matlet.2016.04.193
0167-577X/

3. Results and discussion

From XRD analysis, it was confirmed that all the peaks for the Bi–TiO_2s were assigned to the anatase TiO_2 tetragonal structure [7], and there are no peaks for the added Bi oxide forms, indicating that the Bi ions had been well-inserted into the TiO_2 framework. Fig. 1A, B, and C show the TEM images for pure TiO_2 and 5.0 mol% Bi–TiO_2 samples, the UV–visible absorption spectra, and their Tauc's plots of the Bi–TiO_2 powders. The TEM images showed that the Bi–TiO_2 particles were smaller than those of pure TiO_2, although the morphologies were a round shape in all of the samples. An absorption band for the anatase structured TiO_2 was observed in the UV-region around 380 nm when extrapolated, which is similar to the absorption wavelength reported elsewhere [8]. The band can be converted to the following adsorption terms using the Tanabe-Sugano's energy absorption: $T_{2g} \rightarrow E_g$ for the d^1 electron configuration TiO_2. As a reference, the absorption band for pure Bi_2O_3 was largely shifted to the visible range, compared to the other samples, and means that the Bi ingredient increases the photo-response in visible region. According to the addition of Bi species, there are different absorption band shifts, which were shifted to higher wavelengths compared to the absorption band of TiO_2. The Bi–TiO_2s showed broad curves for the metal oxides in the visible region: the maximum absorption was observed at 339, 343, 328, 344, and 344 nm for 1.0, 2.5, 5.0, 7.5, and 10.0 mol% Bi–TiO_2, respectively. Generally, the band gap in a semiconductor is closely



Catalysts	TiO_2	1.0 mol.-% Bi–TiO_2	2.5 mol.-% Bi–TiO_2	5.0 mol.-% Bi–TiO_2	7.5 mol.-% Bi–TiO_2	10.0 mol.-% Bi–TiO_2
Band gap (eV)	3.05	3.12	2.94	2.82	2.63	2.57

Fig. 1. TEM image (A), diffuse reflectance-UV–visible absorption spectra (B), and their Tauc's plots (C) of the prepared Bi–TiO_2 powders.