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Semimetal bismuth mediated UV–vis-IR driven photo-thermocatalysis of $Bi_4O_5I_2$ for carbon dioxide to chemical energy

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ABSTRACT

Semimetal bismuth has attracted extensive interests, which were ascribed to the photo-thermal effect and co-catalyst properties. In this paper, $Bi/Bi_4O_5I_2$ composites were synthesized through a molecular precursor hydrolytic process, and the sunlight induced semimetal Bi mediated photo-thermocatalysis of $Bi_4O_5I_2$ for carbon dioxide to chemical energy was studied. When the optimal mole ratio of Bi: I was selected at 1.95:1, $Bi/Bi_4O_5I_2$ displayed outstanding photo-thermocatalytic carbon dioxide to chemical energy (CO and CH_4). Under simulate sunlight (UV–vis-IR) irradiation, the CO and CH_4 generation over $Bi/Bi_4O_5I_2$ enhanced to 40.02 μmol h^{-1} g^{-1}, and 7.19 μmol h^{-1} g^{-1}, respectively. The light to chemical energy (LTCE) conversion efficiency (80.2×10^{-6}) was about 6.47 times than $Bi_4O_5I_2$ (12.4×10^{-6}), and 68.55 times than $Bi_4O_5I_2$ without IR irradiation (1.17×10^{-6}). The dramatically enhanced photo-thermocatalysis activity of $Bi/Bi_4O_5I_2$ can be attributed to the co-catalyst and photo-thermal effect of Bi nanoparticles, which prohibiting the electron–hole recombination and accelerating light to thermal energy conversion, respectively. Furthermore, the enhanced photo-induced carrier separation rate and reaction system temperature of $Bi/Bi_4O_5I_2$ was testified.

1. Introduction

Energy and environment issues are the topical words in the 21st century, and numerous of technologies have been applied to eliminating those problems. Photocatalysis allures abundant interesting of workers to research it, which is a green technology for environmental protection and hydrocarbon fuel generation. With the purpose of conquering the obstacles of traditional TiO_2 semiconductor material [1–4], all kinds of news photocatalysts are exploited in recent years, such as sulfide-based [5–7], silver-based [8–10], bismuth-based [11–13], and polymer semiconductors [14]. Among the above new styles of photocatalysts, bismuth-rich $Bi_xO_yX_z$ (X = Cl, Br, I) photocalalysts displayed ascendant photocatalytic property for energy and environment applications. For examples, Bi_3O_4Cl, $Bi_{12}O_{17}Cl_2$, and $Bi_4O_5X_2$(X = Br and I) exhibited efficient photocatalytic reduction activities for H_2 generation [15–17]. Bi_5O_7X (X = Br and I), Bi_3O_4Br, and $Bi_{24}O_{31}Cl_{10}$ can availably activate molecular oxygen [18–20]. $Bi_4O_5X_2$ (X = Br and I) also displayed the prominent photocatalytic of carbon dioxide (CO_2) reduction [21–23]. $Bi_{12}O_{15}Cl_6$ and $Bi_7O_9I_3$ degraded the Bisphenol A under Visible-Light Irradiation [24,25]. $Bi_{24}O_{31}Br_{10}$ can photoreduced Cr(VI) [26], Bi_3O_4Cl showed superior photocatalytic activity for SA degradation [27], Bi_5O_7I was firstly used for photocatalytic N_2 fixation [28]. Among above $Bi_xO_yX_z$ photocalalysts, $Bi_4O_5I_2$ showed most commonly photocatalytic performance, such as dye degradation, H_2 generation and CO_2 reduction.

Recently, diffusely modification methods were used to boost the photoactivity of $Bi_xO_yX_z$, such as doping [29–31], and combination [32,33]. For examples, flower-like $Bi_4O_5I_2/Bi_5O_7I$ nanocomposite [34], $BiOI/Bi_4O_5I_2/Bi_2O_2CO_3$ p-n-p heterojunctions [35], g-$C_3N_4/Bi_4O_5I_2$ heterojunction were synthesized [23]. On the other hand, noble metal loading also was a viable strategy for enhancing activity, which play the role of co-catalysts to control carrier recombination, or act as the sensitizer [36]. With the lower fermi level of noble metal Pt, Ag and Au, which acted as the co-catalysts to enhance activity [37–40]. In consideration of the distinctive merits of inexpensive and ample reserves, semimetal bismuth (Bi) could potentially serve for an perfect substitute for noble metals. Lately, Bi element deposited on the photocatlyst was reported, which present incremental photocatalytic performance under

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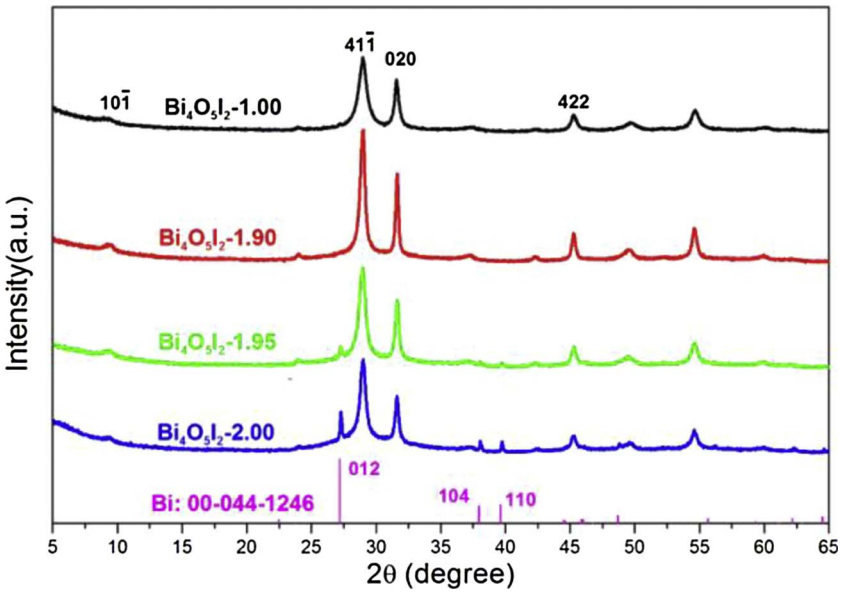

Fig. 1. XRD patterns of $Bi_4O_5I_2$-1.00, $Bi_4O_5I_2$-1.90, $Bi_4O_5I_2$-1.95 and $Bi_4O_5I_2$-2.00.

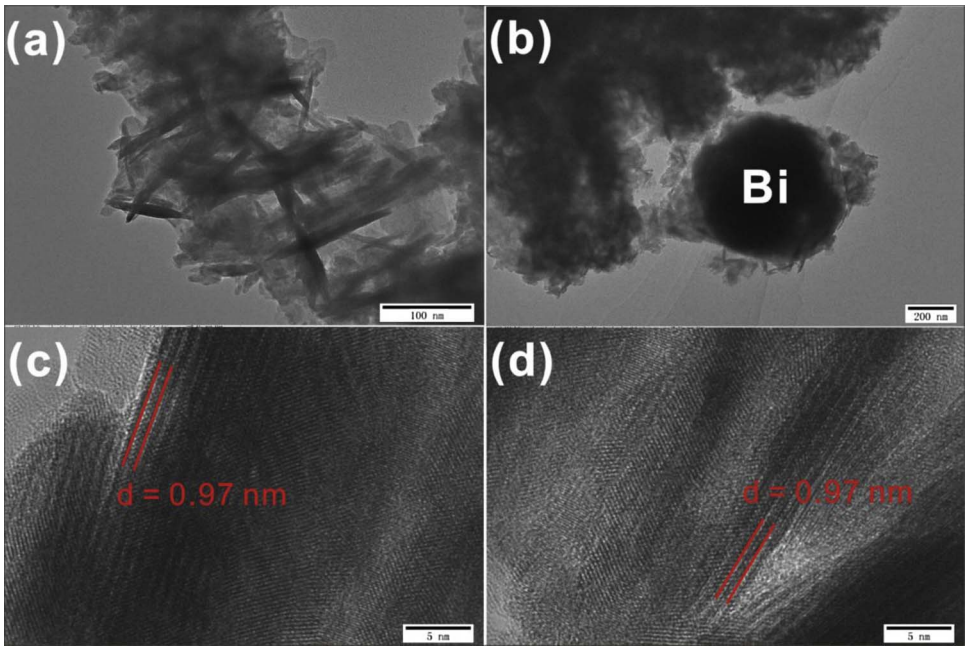

Fig. 2. TEM and HRTEM images of $Bi_4O_5I_2$-1.00 and $Bi_4O_5I_2$-1.95.

UV–vis light irradiation, such as Bi/Bi_2O_3 [41], Bi/BiOI [42], $Bi/(BiO)_2CO_3$ [43], Bi/BiOCl [44,45], $Bi/BiOBr_xI_{1-x}$ [46]. These cases have demonstrated that Bi nanoparticles can be worked as co-catalyst and sensitizer. However, to our best knowledge, there is no report with utilizing Bi nanoparticles to increase photocatalytic activity of bismuth-rich $Bi_xO_yX_z$ photocatlysts. And the photo-thermal effect of Bi nanoparticles was not report to improve that catalytic activity for photo-thermocatalysis.

As we known that there are two ways to utilize infrared (IR) light in sunlight induced reactions: photo-excitation and photo-thermal effect. It have reported that $Cu_2(OH)PO_4$, WS_2, $Co_{2.67}S_4$ and olive-green few-layered BiOI can display photoactivity with IR light exciting [47–50]. However, most semiconductor pholocatalysts still cannot be excited by IR light, and the light conversion efficiency was very low. For IR light induced photo-thermal effect in catalytic system has been proved. For examples, pollutants was degraded under the full solar spectrum via photo-thermocatalytic [51–53]. photothermal effect of infrared light can improve the solar catalytic hydrogen production [54]. However, to the best of our knowledge, there few report about photo-thermal effect of IR light to improve photocatalysis or photo-thermocatalysis for CO_2 to chemical energy.

In this study, the hydrolytic method was used to prepared the Bi nanoparticles, which firstly as a co-catalyst for $Bi_4O_5X_2$ (X = Br, I) nanosheets. By changing the mole ratio of $Bi(NO_3)_3{\cdot}5H_2O$ and KX (X = Br, I) in the solvothermal reaction, the content of Bi nanoparticles can be command. At an ideal proportion of Bi:I = 1.95:1, the $Bi/Bi_4O_5I_2$ exhibited the best activity for photo-thermocatalytic carbon dioxide to chemical energy (CO and CH_4). Under simulate sunlight (UV–vis-IR) irradiation, the light to chemical energy (LTCE) conversion efficiency (80.2×10^{-6}) was about 6.47 times than $Bi_4O_5I_2$ (12.4×10^{-6}), and 68.55 times than $Bi_4O_5I_2$ without IR irradiation (1.17×10^{-6}). The present work demonstrated the feasibility for the utilization of low-cost Bi nanoparticles as the co-catalyst and light to thermal energy conversion assistant to promote the sunlight Induced photo-thermocatalytic performance of bismuth-rich photocatalytic materials.