catalysts

MDPI

Supplementary Materials

Photocatalytic Conversion of Fructose to Lactic Acid by BiOBr/Zn@SnO_2 Material

Hong-Juan Qin, Yu-Hang Zhang, Zhen Wang * and Gui-Hua Yang

State Key Laboratory of Biobased Material and Green Papermaking, School of Environmental Science and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China; 15662590920@163.com (H.-J.Q.); zyh1002638702@163.com (Y.-H.Z.); ygh2626@126.com (G.-H.Y.)
* Correspondence: wz@qlu.edu.cn

Abstract: Photocatalysis provides a prospective approach for achieving high-value products under mild conditions. To realize this, constructing a selective, low-cost and environmentally friendly photocatalyst is the most critical factor. In this study, BiOBr/Zn@SnO_2 is fabricated by a one-pot hydrothermal synthesis method and BiOBr: SnO_2 ratio is 3:1; this material is applied as photocatalyst in fructose selective conversion to lactic acid. The bandgap structure can be regulated via two-step modification, which includes Zn doping SnO_2 and Zn@SnO_2 coupling BiOBr. The photocatalyst shows excellent conversion efficiency in fructose and high selectivity in lactic acid generation under alkaline conditions. The conversion rate is almost 100%, and the lactic acid yield is 79.6% under optimal reaction conditions. The catalyst is highly sustainable in reusability; the lactic acid yield can reach 67.4% after five runs. The possible reaction mechanism is also proposed to disclose the photocatalysis processes.

Keywords: fructose; photocatalysis; biomass; doping; lactic acid; coupling

1. Specific operations related to characterization tests

FT-IR: An appropriate amount of BiOBr, BiOBr/SnO_2 and BiOBr/Zn@SnO_2 samples were collected and scanned for analysis by Fourier transform infrared spectrometer (IRAffinity-1S, SHIMADZU, Japan). After the blank test is completed, weigh 1-2 mg of samples to be tested and 200 mg of anhydrous spectral pure KBr, grind them with a mortar and disperse them evenly, take out the mixed samples after grinding and pour them into the tablet press. After the tablets were pressed under a certain pressure for three minutes, the samples were taken out as translucent slices, and the infrared spectra of the samples were scanned in the wave number range of 4000 cm^{-1} ~ 400 cm^{-1}.

XRD: An appropriate amount of BiOBr, BiOBr/SnO_2 and BiOBr/Zn@SnO_2 powders were placed in the fluted sample preparation area on the slide, and after being flattened, X-ray diffrotometry (D8-Advance, Bruker AXS Co. Lxd, German) was used for analysis and characterization tests. The parameters were set as follows: the excitation ray was copper target Ka ray, the tube current was 40 mA, the tube current voltage was 40 KV, the incident wavelength was 1.54 nm, the scanning step was 0.03°, the scanning speed was 20°(2θ)·min^{-1}, and the scanning range was 5 ~ 80°.

SEM: The surface morphology of samples was characterized by scanning electron microscopy (Hitachi Regulus 8220, Japan). Grinding fine and dry sample first, sample preparation when using double-sided conductive adhesive as binder, stick to the sample of the sample stage, add a small amount of dry grinding fine powder samples makes it evenly distributed on the conductive adhesive with blowing tube light blow after confirmed that it will not drop, then spray gold processing samples, and then spray the gold samples under SEM observation room, Adjust the parameters of the SCANNING electron microscope to observe the clear sample structure, and find out the desired morphology

and structure for shooting by constant adjustment. At the same time, take EDS scanning to determine the distribution of elements.

TEM: The samples were characterized by transmission electron microscopy (JeOL-2100, Japan), and their particle size and lattice morphology were observed. During sample preparation, the sample was added into about 1 mL of anhydrous ethanol, and dispersed evenly by ultrasonic shock. Then, a small amount of sample was dropped into the copper net for sample preparation. The copper net was dried in a vacuum drying oven and placed in a transmission electron microscope observation room. By observing the particle size structure and lattice fringe of the sample.

BET: The specific surface area and pore size distribution of samples were characterized and analyzed by auto SORB-IQ (USA). Firstly, a certain amount of samples to be tested were weighed and put into the special sample feeding tube for BET test, which was dried at 150 ℃ for 2h. Then, the sample feeding tube was put into the instrument and the sample was degassed at 150 °C for 6 h. During instrumental analysis and determination, helium is used to exhaust air, and nitrogen is used as adsorption gas to fill the sample tube. After testing by the equipment, the aperture and specific surface area of the sample can be obtained by using BET theory and formula.

XPS: The final sample was analyzed using ESCALAB Xi+ (Thermo Fisher Scientific). Now the sample is ground evenly, take a small amount of samples with double-sided adhesive fixed on the known tablet, tiled evenly with the tablet press to make the tablet into a uniform plane, after cutting the size of the stick to the test table for elemental analysis test.

UV-VIS: Diffuse UV-vis (UV-VIS DRS) is one of the mandatory spectroscopic techniques used to study the electronic structure of materials. It uses relatively high energy electromagnetic radiation to measure the correlated pops in a wavelength range of 200 to 800 nm (UV-vis range).

2. Supplementary SEM images of BiOBr and SnO_2

The SEM image of BiOBr (Fig. S1 a) exhibited layered stacking structure, while the SEM image of SnO_2 (Fig. S1 b) showed ordinary agglomeration state. Compared with the SEM image of the synthesized material in the paper, the morphology and structure of sample have undergone great changes.

(**a**) (**b**)

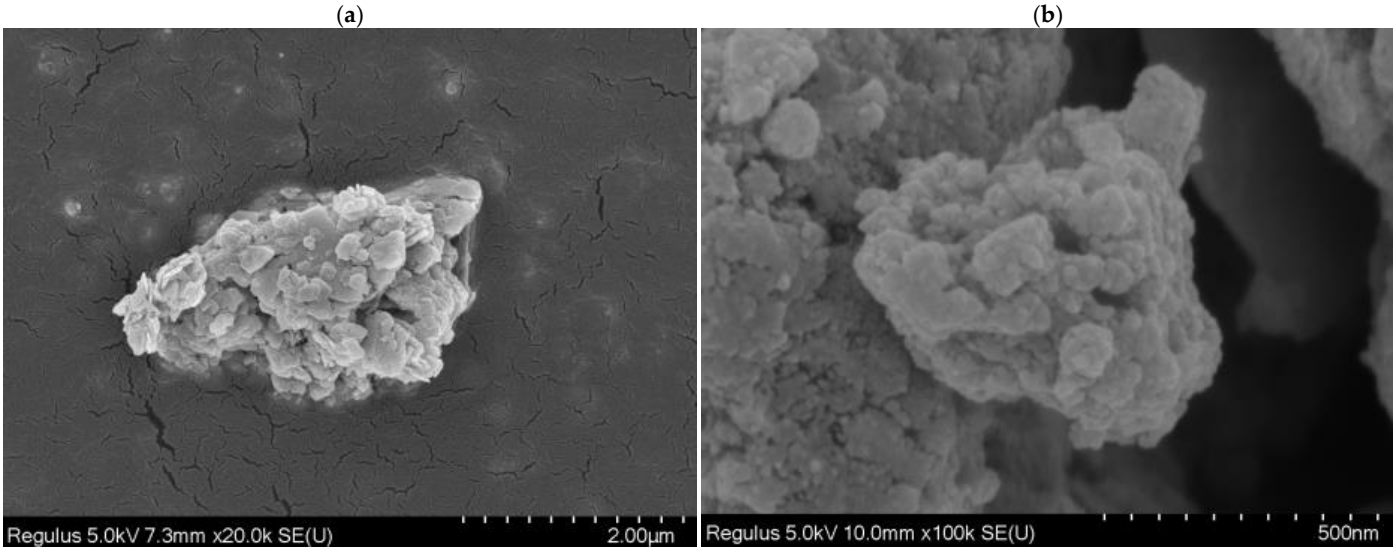

Figure S1. SEM figure for BiOBr and SnO_2.

3. XRD patterns of SnO_2, ZnO and Zn@SnO_2

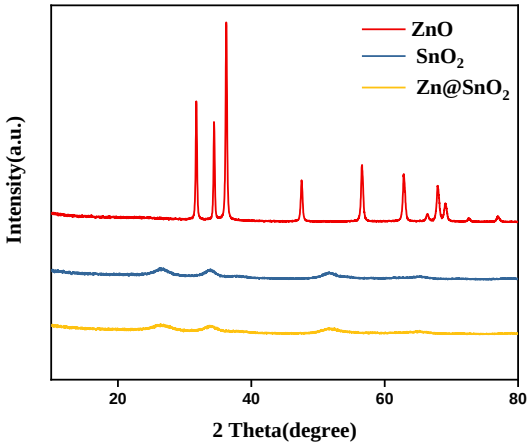

Figure S2. XRD patterns of SnO_2, ZnO and Zn@SnO_2.

It can be seen that the peak position of SnO_2 is basically the same as that of BiOBr (manuscript), and the response value is not highly covered.

4. Actic acid transformation formula

$$Lactic\ acid\ Conversion = \frac{Lactic\ acid\ \text{yield}}{Raw\ material\ content} \times 100\% \quad (1)$$

$$Fructose\ conversion = \left(1 - \frac{Residual\ fructose\ content}{Raw\ material\ content}\right) \times 100\% \quad (2)$$

$$Lactic\ acid\ selectivity = \frac{Lactic\ acid\ Conversion}{Fructose\ conversion} \times 100\% \quad (3)$$