Electronic Supplementary Material

Clean production of lactic acid by selective carbon-carbon bond cleavage of biomass feedstock over a novel carbon-bismuth oxychloride photocatalyst

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1. Experimental

1.1 Preparation of photocatalyst

Novel photocatalysts, BiOCl-x and C/BiOCl-x, were prepared in different steps with different solutions. A solution of $Bi(NO_3)_3 \cdot 5H_2O$ was prepared by dissolving its 3 mmol in 20 mL of ethylene glycol in a 250 mL beaker and named solution A. Two types of solution B were prepared, in 1st type 1mmol of KCl was dissolved in 10 ml of DI water and named B1. The 2nd solution, 0.5 g xylose, was added to the solution prepared with the same protocol as the 1st type of solution and named as B2. In the next step, all solutions B were added to solution A dropwise under constant stirring for 30 min separately. The mixture of AB1 and AB2 was transferred to reaction kettles and kept in the furnace for 6 h at 180 ^{o}C. After the reaction was over, the reaction kettles were cooled to room temperature. The obtained solid samples were washed with a large quantity of deionized water and ethanol and filtered with the help of vacuum suction. The filtrates were dried at 80 ^{o}C for 4 h and dried products were named BiOCl-180 and C/BiOCl-180. The catalysts prepared at a higher temperature of 180 ^{o}C using the same protocols were named BiOCl-120 and C/BiOCl-120, the

scheme of preparations is graphically presented in Fig. S1.

1.2 Photocatalytic activity

The performance of the photocatalyst was tested with xylose in a 15 mL quartz flask under a 400 W Xe lamp as a light source. For this purpose, 10 mg of the catalyst and 100 mg of xylose were added to 10 mL 0.5 M KOH solution. For balanced adsorption and desorption, the reactor was magnetically stirred for 30 min under dark conditions. Then the reaction was continued at different temperatures for 60 min. After the reactions ended, the samples were syringed out, filtered with a 0.22 μm filter, and analyzed by high-performance liquid chromatography (HPLC). A series of tests were performed by changing the pH of the solvent, catalyst dosages, and reaction time to optimize the reaction conditions for higher yields.

1.3 Recyclability and universality of catalyst

The recyclability of our prepared photocatalyst was tested with some modifications in optimum conditions. 400 mg of photocatalyst and 4 g of xylose were added in 400 mL of KOH (2 M) and adsorption and desorption balance was achieved by stirring the mixture for 30 min in the dark, afterward followed by light irradiations for 80 min. The sample was syringed out diluted 5 times, filtered, and subjected to HPLC for product analysis. The catalyst was recovered by centrifugation of the reaction mixture. The recovered catalyst was washed, dried at 80 ^{o}C for 4 h, and reused for the next all cycles with the same protocol respectively.

To test the universality of our prepared catalyst we performed its activity with different biomass-derived basic sugars 100 mg of arabinose, mannose, glucose, fructose, and rhamnose with 10 mg of catalyst and were added to 10 mL 0.5 M KOH solution same protocol used for photocatalytic measurement.

1.4 Poisoning experiments

The effects of different radical scavengers as poisons were tested with a prepared catalyst at optimum conditions separately. In each typical experiment xylose 100 mg, catalyst 10 mg, with 0.5405 g benzo quinone (BQ), 0.6001 g isopropyl alcohol (IPA), 0.83 g potassium iodide (KI), and 1.02115 g of tryptophane (Trp) were added into a 10 mL of KOH solution in different quartz flask separately. Each reaction was carried

out under irradiation at 60 ^{o}C for 80 min. At the end of the reaction, samples were syringed out and analyzed with HPLC to study the role of reactive radicals on reaction efficiency.

1.5 1000-fold scale-up experiment

The scalability of photocatalytic reactions paves the way for their industrial applicability. Therefore, the scale-up reaction was performed with a few modifications. For the 1000-fold scaleup experiment, 10 g of catalyst and 100 g of xylose were added to 10 L of KOH (2 M), and the reaction was resumed at dark to achieve an adsorption/desorption balance before being irradiated under sunlight at room temperature for 80 min. Analyzing photocatalytic performance for green industrial applications, Sample was taken from the reaction mixture at the end of the reaction, diluted, filtered, and subjected to HPLC to analyze photocatalytic performance for green industrial applications.

1.6 Photoelectrochemical measurement

Electrochemical measurement was measured with the help of electrochemical center workstations (CHI 660E) stand with triple electrode systems. An electrode of Pt wire saturated in Ag/AgCl was used as a reference electrode. The working electrode is composed of F-dopped SnO_2. 5 mg of the photocatalyst was 20 μL of Nafion 5% was added to 980 μL ethanol to form a homogeneous slurry. The slurry was left on ultrasonic for 30 min and then coated on the FTO glass. The obtained was dried at a high temperature of about 150 ^{o}C. The supporting electrolyte was Na_2SO_4 (0.5 M) the solution with pH 6.8, the light source used Xe lamp (300 V). To analyze the photocurrent time working electrode was irradiated with Xe lamp 0.5 C bias vs Ag/AgCl. The impedance is a complex resistance of material, it was measured with alternating current (AC) 10 mV at 0.3 V vs Ag/AgCl frequencies range 10 K to 0.1 Hz. The Mott-Schottky recorded in 0.5 M Na_2SO_4 at 500, 800, and 1000 Hz at amplitude 5 mV.

1.7 Instrumentation specification used

XRD instrument Bruker D8 focus diffractometer (CuK/ Rad., λ = 0.15418 nm, 2θ mood) was used to record diffraction patterns. FTIR instrument Bruker Tensor 27

spectrophotometer range 400-4000 cm^{-1} with 4 cm^{-1} resolution was used to record FTIR interactions. HRTEM instrument JEM-20100 CXII for 2D images and SEM instrument Hitachis-4800 for 3D images while XPS and XPS-VB instrument Kratos Axis Ultra DLD spectrometer employed with monochromatic (1486.6 eV) a source of X-ray AlKR used for the surface elemental composition and valence band measurements. Micromeritics ASAP 2020 was used to calculate specific areas Brunauer-Emmett-Teller. UV-vis DRS instrument and specification were Cary 5000 spectrophotometer with the standard as $BaSO_4$. Edinburgh FLS-920 spectrometer was used to measure photoluminescence (PL) spectra.

2. Results and discussion

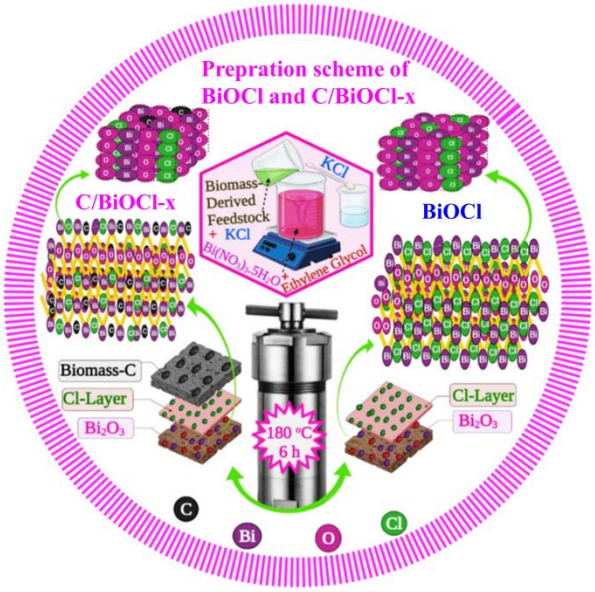

Fig. S1. Preparation scheme of BiOCl and C/BiOCl-x.

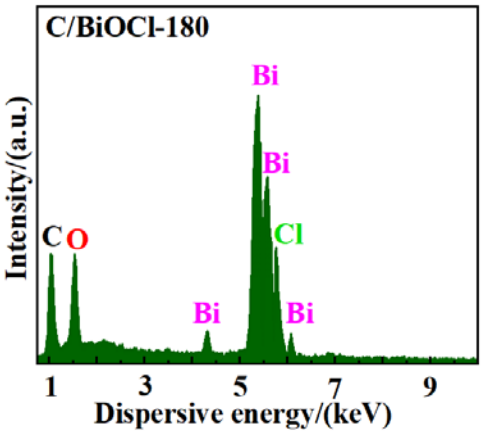

Fig. S2. EDS of C/BiOCl-180.

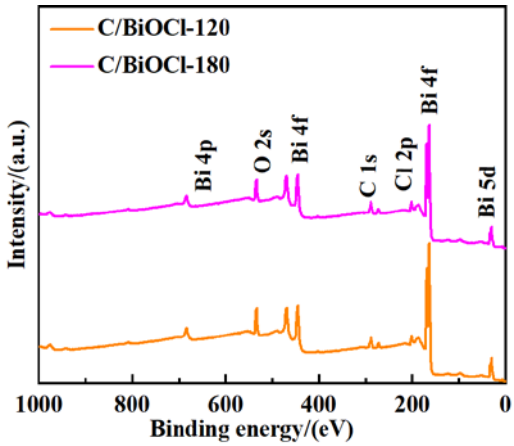

Fig. S3. XPS Survey of C/ BiOCl-120 and C/BiOCl-180.

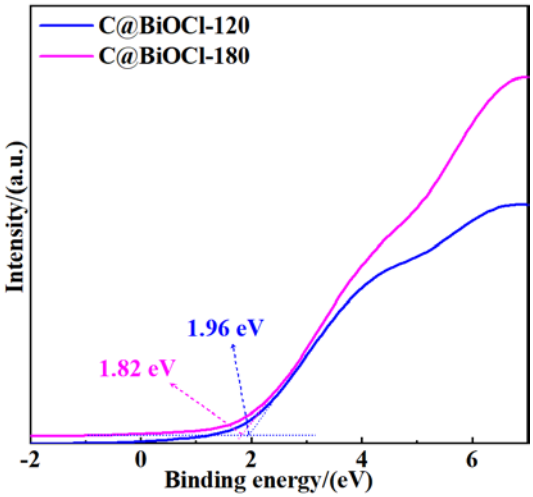

Fig. S4. XPS-VB of C/ BiOCl-120 and C/BiOCl-180.

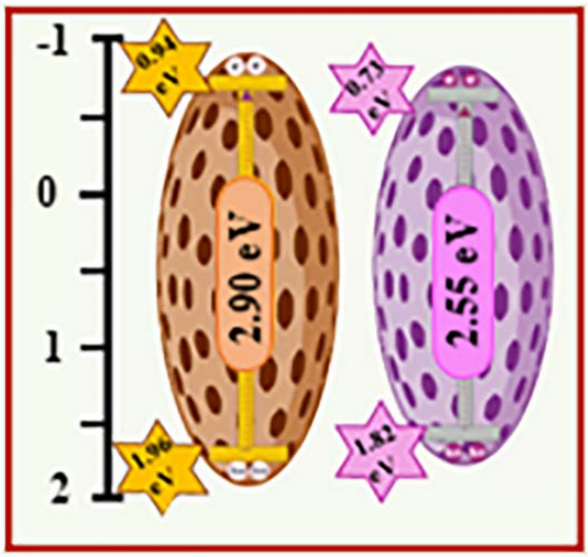

Fig. S5. Respective band energies (E) of C/BiOCl-120 and C/BiOCl-180.

Table S1. Comparison of lactic acid production of C/BiOCl-180 with other photo/thermo catalysts.

Entry	Photo/ thermocatalysts	Biomass feedstock	Reaction conditions (PH: Temperature: Catalyst dosage: Time)	Yield %	Ref.
1	C/BiOCl-180	Xylose	2M : 80 ^{o}C: 10 mg: 80 min, 400 W Xe lamp, $\lambda \geq 400$ nm	92.5	This work
2	p-n type BiOBr/Zn_x@SnO_2-n	Fructose	2.5M : 50 ^{o}C: 30 mg: 180 min, 300 W Xe lamp, $\lambda \geq 400$ nm	79.6	[1]
3	$Zn_{0.6}Cd_{0.4}S$	Glucose	25 ^{o}C, 5 h, 300 W Xe lamp, λ = 400-780 nm.	66.6	[2]
4	g-C_3N_4-B-Cu_2O	Xylose	60 ^{o}C, 120 min, Xe lamp, $\lambda \geq 400$ nm	91.2	[3]
5	Sn-Beta	Xylose	200 ^{o}C, 60 min, 4.0 MPa N_2	70	[4]
6	Cr/Al_2O_3	Xylose	170 ^{o}C, 240 min	74	[5]

References

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