Supplementary Information (SI) for Nanoscale.

Supporting Information

MXene-Derived Ti_3C_2–TiO_2/BiOCl Heterojunctions with Enhanced Visible-Light Photocatalysis and Electrochemical Activity

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2.1. Preparation methods

2.1.1. Preparation of BiOCl

BiOCl was prepared by the sol-gel method. 1.0 g $BiCl_3$ was dropwise included to 40 mL of ethanol and stirred for an hour as far as $BiCl_3$ dissolved completely to form homogeneous solution. Simultaneously, a second solution was obtained through dissolution of 0.1 g sodium dodecyl sulfate (SDS) in distilled water (20 mL) by stirring for 20 min. The third solution was prepared by a dissolution of 0.1 g urea in 20 mL distilled water under stirring over 20 min. These solutions were mixed simultaneously, the SDS solution and urea solution was added into $BiCl_3$ solution. The newly formed transparent mixture was blended for 1 h at 40°C until became homogeneous, the temperature was then raised to 80°C and stirred for 1 h. The product was rinsed with distilled water (5-6 repetitions) to remove possible contaminants. Subsequently, after filtration the precipitates were dried and calcined at 500°C for 5 hours to attain the final BiOCl product.

2.1.2. Preparation of TiO_2 and Ti_3C_2-TiO_2 hybrid structures

Sol-gel technique was employed to synthesize TiO_2 nanoparticles by using a precursor titanium tetra butyl titanate (TBT). A mixture of deionized water and ethanol in a 2:3 proportion was prepared and 4–5 drops of HCl were incorporated into the solution. Then, 10.0 mL of TBT solution was gradually introduced into the final solution under constant stirring for duration of 30 min followed by sonication of the mixture. The resulting sol was placed in a vacuum oven at 160 °C for a time of 2–3 h. After centrifugation, the product was dried on hotplate and finely grounded to get the TiO_2 nanoparticles. For the preparation of Ti_3C_2-TiO_2 hybrid composite, 0.1 g graphite was introduced into the TiO_2 solution and sonicated. The product was further dried in a vacuum oven at 180–195°C for 2 hours and Ti_3C_2-TiO_2 hybrid powder was obtained.

2.1.3. Synthesis of Ti_3C_2-TiO_2/BiOCl composites.

The 1.0 wt. % Ti_3C_2-TiO_2/BiOCl composite structures were prepared using a two-stage synthesis approach: the specific amount of BiOCl nanoplates were first dispersed into distilled water, and sonication was performed for 30 min to obtain a uniformly dispersed suspension. Afterward, the as-prepared Ti_3C_2-TiO_2 MXene based hybrid dispersion was gradually introduced into the BiOCl solution while stirring. The above mixture was stirred for 2 hours to assure the Ti_3C_2-TiO_2 uniformly coating on BiOCl nanoparticle. The composite obtained was centrifuged, repeatedly washed and then dried at 60 °C for 12 h. A calcination step was performed on the dried product at 400°C for 2 h to increase stability and crystallinity of the composite. Ti_3C_2-TiO_2 are exhibited compositional variations with weight ratios from 1.0-4.0 wt. %. The schematic representation of the synthetic route for Ti_3C_2-TiO_2/BiOCl composite catalysts is given in manuscript Scheme 1.

2.1.4. Photocatalytic degradation

The photocatalytic performance of Ti_3C_2-TiO_2/BiOCl composite catalysts for phenol degradation was determined. In dark experiment, absorption value of phenol was determined without exposure to light. For light experiment, 0.1 g of Ti_3C_2-TiO_2/BiOCl composite catalyst was added to 100 mL phenol solution (25 ppm). Illumination was provided by a 300W tungsten lamp with UV cutoff filter ($\lambda > 420$ nm) was used to ensure visible light irradiation which had a wavelength range of 400−600 nm. The solution was stirred continuously to guarantee homogeneous blending of the catalyst and phenol. 5 mL aliquots were withdrawn from the solution at 60 min intervals and analyzed on a UV−vis spectrometer to check the degradation process. The charge transfer process of Ti_3C_2-TiO_2/BiOCl heterojunction can be further confirmed by comparing the band edge positions using Mullikan electronegativity theory, the following equations apply:

$$E_{VB} = \chi - E_c + 0.5\, E_g$$

$$E_{CB} = E_{VB} + E_g$$

Where E_{VB} and E_{CB} are the edge potentials of the valance and conduction band, E_c represents the energy of free electrons on the hydrogen scale (4.50 eV), and χ is absolute electronegativity.

Chemicals and Experimental Conditions

All chemicals were of analytical grade and used without further purification. Bismuth chloride ($BiCl_3$), Urea, Sodium dodecyl sulfate (SDS), Tetrabutyl titanate (TBT), Graphite powder, Ethanol, and Hydrochloric acid (HCl) were purchased from Sigma-Aldrich (USA), and deionized water was used throughout the experiments. Photocatalytic activity was evaluated under visible-light irradiation using phenol as a model organic pollutant. Electrochemical studies were carried out in a conventional three-electrode system using KOH alkaline electrolyte to investigate the charge-storage behavior of the prepared electrodes.

Characterization

The crystalline composition of the synthesized specimens is examined by X-ray diffractometer (Rigaku D/MAX 2550) using Cu Kα radiation, the scan was performed from 20-90° with a current of 30 mA with 40 kV. Optical studies in the 200-600 nm are probed using a UV-visible diffuse reflectance spectrometer (UV-2600, Shimadzu, Japan) with Barium Sulphate ($BaSO_4$) as a reflectance calibration standard. The FTIR spectral data of the samples were acquired using a (FT-IR, Bruker ALPHA) Fourier transform infrared spectrometer. In order to investigate the vibrational frequencies of the synthesized material, Raman spectroscopy is used by employing a Horiba Labram-HR 800 (Horiba Jobin-Yvon) with an argon laser having 514.0 nm wavelength and stimulating power of 20.0 mW with 100x resolution lens. Scanning electron microscopy (SEM, Zeiss ULTRA 55) was adopted to examine the morphology. Photoluminescence (PL) spectra were recorded via Horiba Fluoromax-4 Spectrofluorimeter utilizing a wavelength of 500 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried out via Thermo Scientific spectrometer (ESCALAB 250Xi) with Al Kα radiation to analyze surface chemical states. Electrochemical analysis was performed using a combination of cyclic voltammetry (CV), Galvanostatic charge/discharge (GCD), Linear Sweep Voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) by electrochemical workstation (Auto lab PGSTAT302N), where Hg/HgO served as reference electrode, platinum (Pt.) as a counter electrode and nickel foam impregnated slurry as a working electrode.

Table.S1. Elemental quantitative data of Ti_3C_2-TiO_2 hybrid structure, BiOCl and 4.0% Ti_3C_2-TiO_2/BiOCl heterojunction.

Ti_3C_2-TiO_2			**BiOCl**			**4.0% Ti_3C_2-TiO_2/BiOCl**		
Element	**Weight %**	**Atomic %**	**Element**	**Weight %**	**Atomic %**	**Element**	**Weight %**	**Atomic %**
O K	43.64	69.64	**O K**	1.62	4.13	**O K**	12.43	29.88
C K	1.73	1.21	**Bi M**	74.15	32.69	**Ti K**	21.63	36.20
Ti K	54.63	29.15	**Cl K**	24.23	63.18	**C K**	11.39	13.63
-	-	-	-	-	-	**Bi M**	42.99	7.89
-	-	-	-	-	-	**Cl K**	11.56	12.40
	100	100		100	100		100	100

Table S2. Comparative investigation of photocatalytic degradation of different pollutants reported in literature.

Catalysts	**Compounds**	**Light Sources**	**Reaction Time (min)**	**Degradation %**	**References**
C doped TiO_2-Ti_3C_2	Rhodamine B	UV-Vis light	300	94	[16]
TiO_2@Ti_3C_2/g-C_3N_4	RhB	300W Xe lamp	60	99	[44]
TiO_2@Ti_3C_2/g-C_3N_4	Aniline	300 W Xe lamp	480	66.4	[44]
AgNPs/TiO_2/$Ti_3C_2T_x$	Rhodamine B	Stimulated Solar light	120	88	[45]
AgNPs/TiO_2/$Ti_3C_2T_x$	Methyl Blue	Stimulated Solar light	120	96	[45]
BiOBr/Ti_3C_2	RhB	UV-Vis light	180	99	[46]
Ti_3C_2-TiO_2/BiOCl	Phenol	Tungsten Lamp	300	96	Present work

Table S3. Optical characteristics and absolute electronegativity of the photo catalyst (eV vs. vacuum)

Photo catalysts	**χ (eV)**	**E_g (eV)**	**E_{CB} (eV)**	**E_{VB} (eV)**
BiOCl	3.0	2.9	2.29	0.59
TiO_2	5.81	3.01	2.68	-0.16
1.0 wt. % Ti_3C_2-TiO_2/BiOCl	-	2.96	2.69	-0.16
2.0 wt.% Ti_3C_2-TiO_2/BiOCl	-	2.93	2.68	-0.15
3.0 wt.% Ti_3C_2-TiO_2/BiOCl	-	2.89	2.66	-0.13
4.0 wt. % Ti_3C_2-TiO_2/BiOCl	-	2.82	2.62	-0.1

Table S4: Comparison of the electrochemical performance of optimized 4 wt% Ti_3C_2–TiO_2/BiOCl electrode with representative MXene and MXene-based composites reported in recent literature

Electrode material	**Electrolyte**	**Specific capacitance/capacity**	**Scan rate**	**References**
Ti_3C_2-TiO_2/BiOCl	1M KOH	609 Cg^{-1}	5 mVs^{-1}	Present work
TiO_2-$Ti_3C_2T_x$ MXene	1M KOH	117 Fg^{-1}	10 mVs^{-1}	[57]
TiO_2-$Ti_3C_2T_x$	6M KOH	143 Fg^{-1}	5 mVs^{-1}	[58]
MXene coated CNFs	1M Na_2SO_4	514 Fg^{-1}	0.5 Ag^{-1}	[59]
Ti_3C_2 MXene	1M KOH	370 Fg^{-1}	1 Ag^{-1}	[60]