

**Construction of oxygen-functionalized $\text{Ti}_3\text{C}_2/\text{NH}_2\text{-MIL-68(In)}$
Schottky heterojunctions for Multiple Organic Pollutants
Degradation**

Shaohong Zang ^{*a}, Shuting Tang ^a, Zhiming Guo ^a, Lili Ji ^a, Zhe Leng ^a, Wei Ren ^{*b}, Shaozheng Zhang^c, Feng Lin ^{*c}

a Institute of Innovation & Application, National Engineering Research Center For Marine Aquaculture, Zhejiang Ocean University, Zhoushan 316022 (P. R. China).

b School of Food and Bioengineering, Fujian Polytechnic Normal University, Fuqing 350300 (P. R. China)

c State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116 (P. R. China).

* Corresponding author

Corresponding author: shzang@zjou.edu.cn; renwei@fpnu.edu.cn; linfeng@qzc.edu.cn

Materials and Characterization

Materials

All chemicals were used without further purification.

Titanium aluminum carbide, hydrofluoric acid, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 2-aminoterephthalic acid were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). N,N-Dimethylformamide (DMF) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Characterization

The Fourier transform infrared spectroscopy (FT-IR) was performed on a Shimadzu FT-IR spectrometer from Japan, with KBr pellet preparation for sample measurement in the $500\text{-}4000\text{ cm}^{-1}$. Morphology and elemental distribution of samples were observed and analyzed by scanning electron microscopy (SEM Zeiss Group, Germany) and transmission electron microscopy (TEM, FEI Co., USA). Surface chemical element composition and valence states were examined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific). Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was conducted on a PerkinElmer spectrometer with BaSO_4 as the reference background, and the measurement range was set at 200-800 nm. Specific surface area and pore size distribution were determined by a BET analyzer (Micromeritics Co., USA) after vacuum degassing overnight. Photoluminescence (PL) spectra was employed to investigate the optoelectronic properties of the semiconductors. Photoelectrochemical measurements, including photocurrent response, electrochemical impedance spectroscopy (EIS), and Mott-Schottky plots, were performed on an electrochemical workstation (Shanghai Chenhua, China) using a three-electrode system in 0.1 M Na_2SO_4 aqueous (working electrode: FTO with sample; counter electrode: Pt sheet; reference electrode: Ag/AgCl). Electron paramagnetic resonance (EPR) signals were collected on an A300 spectrometer (Jinghong, China).

DFT calculations

Spin-polarized density functional theory (DFT) calculations were conducted using the Vienna ab initio simulation package (VASP), employing the projector augmented-

wave (PAW) method.^{17, 24} The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation was adopted for the exchange–correlation functional, with van der Waals interactions accounted for via the DFT-D3 scheme. A plane-wavecut-off energy was 450 eV and a 12 Å vacuum layer was introduced along the direction normal to the slab to avoid interlayer interactions. Structural relaxations were conducted using convergence thresholds of 0.03 eV·Å⁻¹ for atomic forces and 10⁻⁵ eV for the total energy per self-consistent iteration. The Brillouin zone integration was carried out by a gamma k-mesh to ensure computational accuracy. Work function (Φ) was evaluated by incorporating dipole corrections.

Table S1 The results of BET and pore size of pure MIL(In), TC and 1 wt% TC/MIL(In).

Sample	BET surface area/ m ² g ⁻¹	pore volume / cm ³ g ⁻¹	Pore size/ nm
TC	2.07	0.0047	9.0999
MIL(In)	307.41	0.2046	2.2099
1 wt% TC/MIL(In)	175.43	0.2253	5.1374

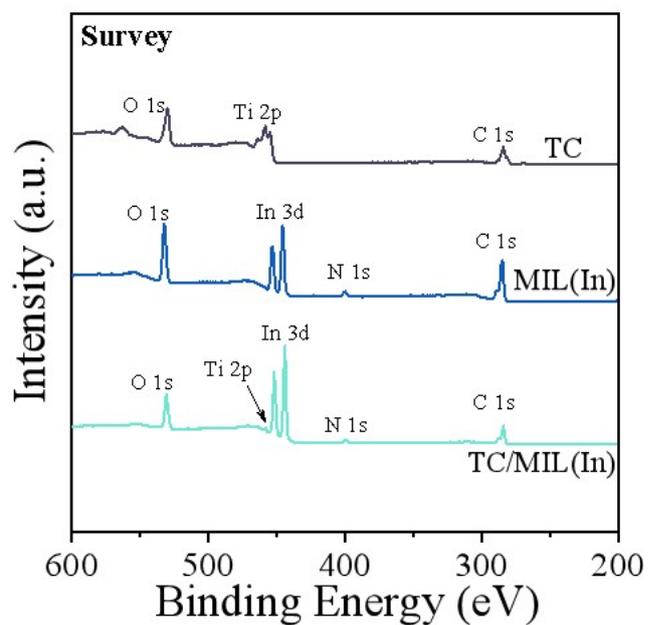


Figure S1. Survey spectra of of TC, MIL(In) and TC/MIL(In).

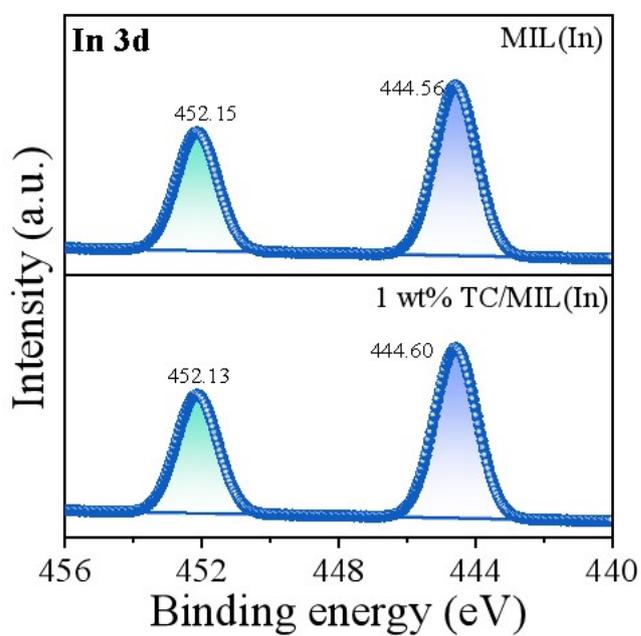


Figure S2. In 3d XPS spectra of of MIL(In) and TC/MIL(In).

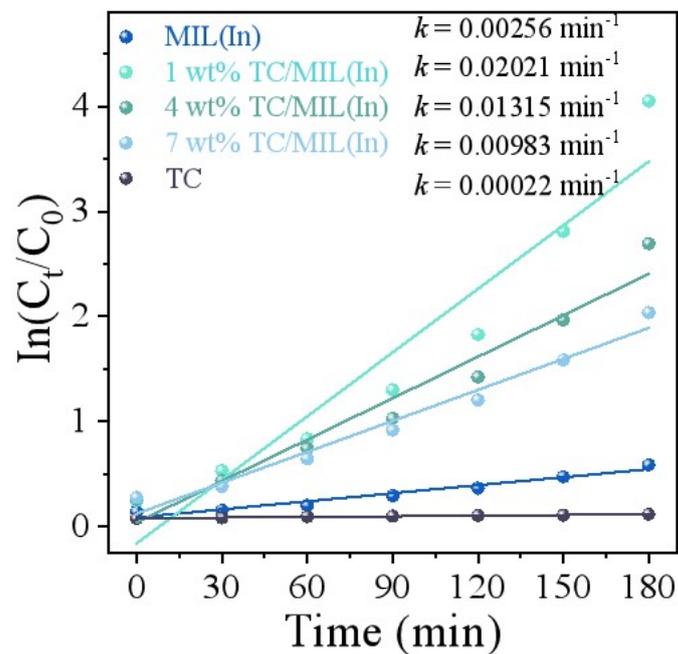


Figure S3. Photodegradation of Rh B ($\lambda = 420 \text{ nm}$) kinetic fitting curve of TC, MIL(In), and X wt% TC/MIL(In).

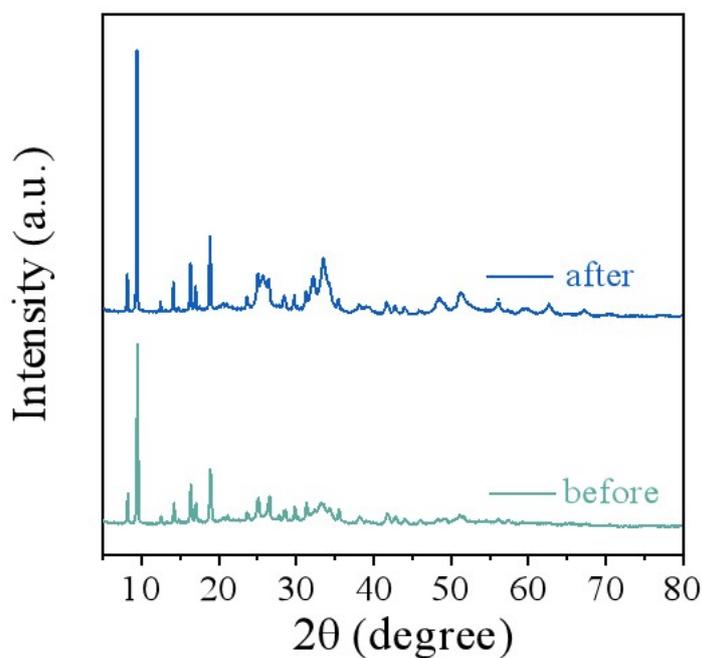


Figure S4. XRD spectra of 1 wt% TC/MIL(In) before and after photodegradation of Rh B.