Supplementary Material

Construction of Z-scheme heterojunction with Camellia-like $MnCo_2O_4/TiO_2$ for photogenerated cathodic protection

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Reagents and materials

Ti foil (99.96% purity), 304SS, Ammonium fluoride (NH_4F), sodium sulfide ($Na_2S\cdot 9H_2O$), sodium chloride (NaCl), sodium hydroxide (NaOH), glycol, manganese acetate tetrahydrate ($(CH_3COO)_2Mn\cdot 4H_2O$), Cobalt acetate tetrahydrate ($(CH_3COO)_2Co\cdot 4H_2O$), polyvinyl pyrrolidone (PVP), nitric acid and 30% hydrogen peroxide (H_2O_2) were obtained from Sinopharm Chemical Reagent Co., Ltd. All existing reagents are AR. Ultrapure water is taken from the Flom ultrapure water system (Qingdao, China). Saturated calomel electrode and platinum foil electrode were purchased from Tianjin Aida Hengsheng Technology Co., Ltd. (Tianjin, China).

Characterization methods

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Hitachi, S-4800, Japan) and transmission electron microscopy (TEM, JEM-2100P, Japan). X-ray diffraction (XRD, Bruker D8ADVANCE, Germany) was used to study the crystal structure of samples. X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, USA) was used to detect the surface element composition and valence states of samples, and in situ XPS technology was used to study the electron transfer process on the surface of composite materials before and after irradiation. The light absorption characteristics of the sample were characterized by UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Hitachi U-3900H, Japan). Ultraviolet photoelectron spectroscopy (UPS) can obtain information on the work function, energy level structure, and other aspects of solids. A 300 W high-pressure xenon lamp (PLS-SXE 300C, Beijing Perfectlight, China) equipped with a 420 nm filter simulated visible light, and the light intensity was 320 $mW\cdot cm^{-2}$.

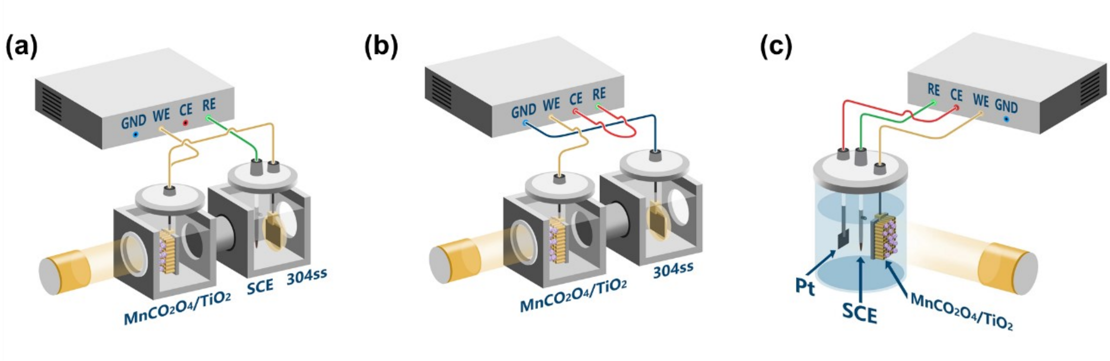

Fig. S1 Photochemical test device diagram, (a) for OCP; (b) for i-t; (c) for i-V and EIS.

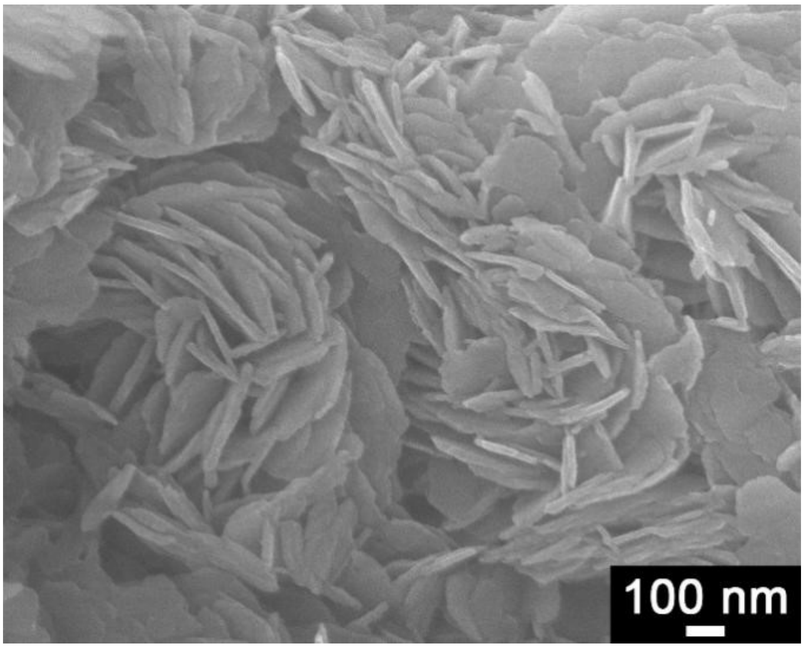

Fig. S2 SEM image of $MnCo_2O_4$ before sintering.

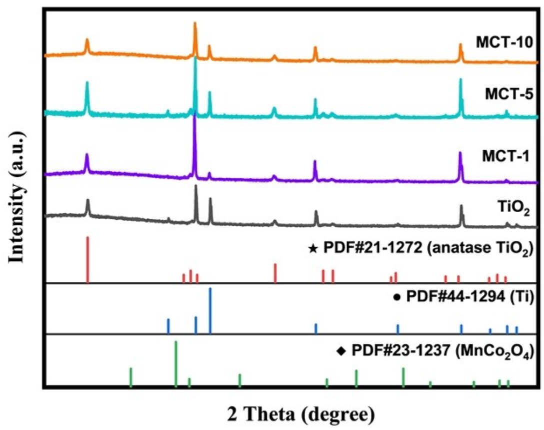

Fig. S3 Pure TiO_2, MCT-1, MCT-5, and MCT-10 XRD patterns.

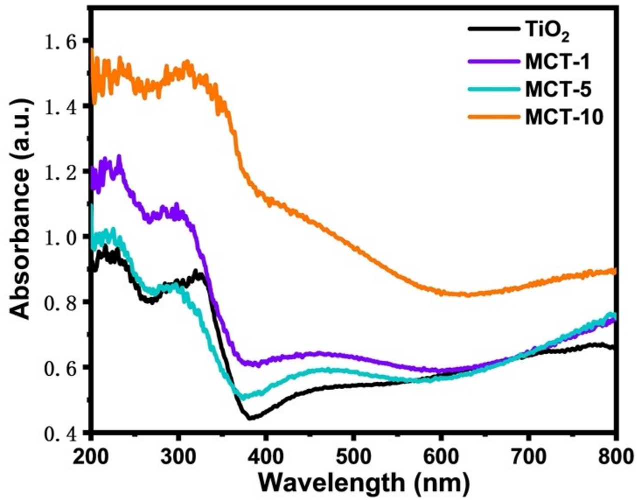

Fig. S4 UV-vis DRS absorption spectra of pure TiO_2, MCT-1, MCT-5 and MCT-10.

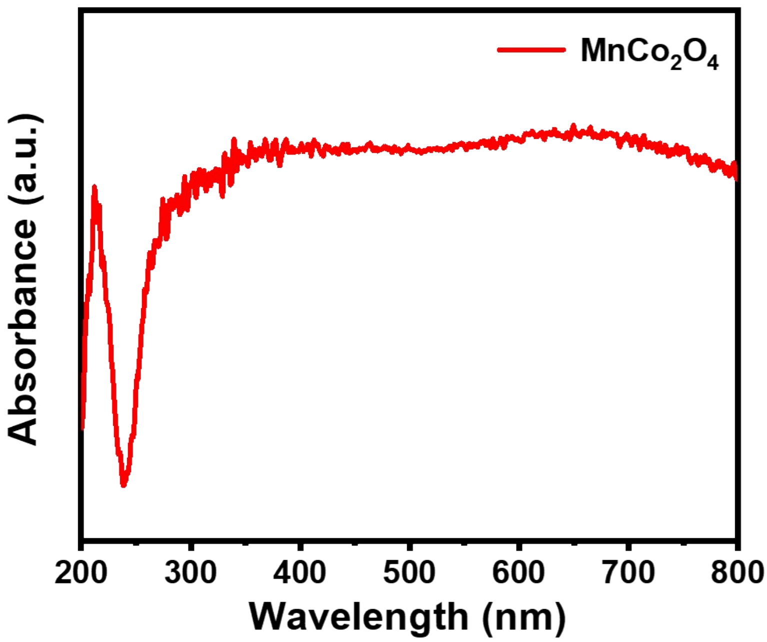

Fig. S5 UV-vis DRS absorption spectra of pure $MnCo_2O_4$.

Note 1

The main reasons for the errors in fluorescence lifetime are divided into the following parts:

(1) The empirical formula is a polynomial, hence the number of undetermined parameters varies.

(2) The graphical representation of the empirical formula, the former is a straight line, while the latter is a parabola.

(3) Under the method of least squares, a system of linear equations regarding the undetermined parameters is obtained, the former being of the second order, and the latter of the third order.

Single-exponential function：

$$I(t) = I_0 \exp\left(-t/\tau\right)$$

$$I(t) = I_0 + A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right)$$

$$\tau = (A_1 {\tau_1}^2 + A_2 {\tau_2}^2)/(A_2 exp(-t/\tau_2)$$

Double-exponential function：

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 exp(-\frac{t}{\tau_2)} + A_3 exp(-\frac{t}{\tau_3)}$$

Triple-exponential function：

$$\tau_{avg} = \frac{A_1 {\tau_1}^2 + A_2 {\tau_2}^2 + A_3 {\tau_3}^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}$$

Table S1 ICP-MS for different MCT

Sample	Element	Mass percentage (%)
	Co	0.723
MCT-1	Mn	0.562
	Ti	67.743
	Co	0.691
MCT-5	Mn	0.623
	Ti	58.671
	Co	0.578
MCT-10	Mn	0.612
	Ti	65.132