Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

In situ growth of TiO_2/Ti_3C_2 MXene Schottky heterojunction as highly sensitive photoelectrochemical biosensor for DNA detection

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Materials and reagents

Fluorine-doped tin oxide (FTO; 1 cm × 2 cm) thin-film substrate was obtained from Opivit New Energy Technology Co., Ltd. (China). Ti_3AlC_2 powder (approximately 400 mesh) in this work was provided by Jilin 11 Technology Co., Ltd (Jilin, China). Hydrofluoric acid (HF, about 49 wt%), cadmium chloride ($CdCl_2$), and selenium (Se) were purchased from Aladdin Reagent (China). Hydrochloric acid (HCl) was the product of the Xilong Science Corporation. Sodium hydroxide (NaOH) and sodium borohydride ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 1-Ethyl-3-(3-(dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), and Tris(2-carboxyethyl) phosphine hydrochloride (TCEP) were supplied by Sigma-Aldrich. Tris-hydroxymethylamino methane-hydrochloride (Tris) buffer solution was supplied by Shanghai Roche Pharma Co., Ltd. (China). Chloroauric acid ($HAuCl_4$) was supplied by Nanjing XFNANO material Technology Co., Ltd. (China). Ascorbic acid (AA) and mercaptohexanol (MCH) were provided by Solarbio (Beijing, China). A glass cleaner was obtained from Shenzhen Run Ming Tong Technology Co., Ltd. (China). TE buffer with 10 mM Tris-HCl, 0.1 mM EDTA, and pH 8.0 was purchased from Sangon Biotec Co., Ltd. (China). Milli-Q ultrapure water was used in the experiments. The sequences of oligonucleotides fabricated by Sangon Biotec Co., Ltd. (China) are listed in Table S1.

Apparatus

The morphology of samples was characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU8010). Transmission electron microscopy (TEM) images were obtained by TEM (JEOL JEM 2100). The XRD patterns of the as-prepared films were recorded on a Philip X'pert X-ray diffractometer (PANalytical, Almelo, the Netherlands; CuKa irradiation, λ= 0.15418 nm) and performed in an angle range of 3°–80° at a scanning speed of 10°/min. UV-vis absorption spectra were obtained on a UV–vis absorption spectrophotometer (UV-vis, Thermo Fisher Evolution 220). The composition and chemical state were analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu KRATOS, Axis Supra). PEC tests were performed with a homemade PEC system. A xenon lamp (Wavelength range: 200nm–1000 nm, Beijing Ceaulight Technology Co., Ltd., China) served as the irradiation source. Photocurrent was recorded on an electrochemical workstation (Chenhua Technology Co., Ltd., China) by a three-electrode electrochemical system with Ag/AgCl (saturated KCl) reference electrodes and 0.5 cm × 0.5 cm Pt foil as counter electrodes under off–on–off (10 s–10 s–10 s) switching light at 0.0 V in the electrolyte of 0.1 M PBS (containing 0.1 M AA, pH 7.4). EIS was performed on a Bio-Logic electrochemical workstation (France) in 0.1

M KCl solution containing 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) at an open circuit potential over a frequency range of 100 mHz–100 kHz with an AC perturbation of 5 mV.

Table S1 Specific oligonucleotide sequences

Oligonucleotide	Sequences (5'–3')
Probe DNA	NH_2–CGGAGTTCTGCACACCTCTTGACACTCCGTTT–SH
Target DNA	CGGAGTGTCAAGAGGTGTGCAGA
Single-base mismatch	CGGAGTGTCAACAGGTGTGCAGA
Noncomplementary	GCGTAAAGTTTAGGTACAATATT

Table S2 Comparison of different sensors for the detection of target DNA

Biosensors	Dynamic range	Detection limit	References
FL	10 fM–10 nM	3 pM	[1]
FL	1–18 μM	0.47 μM	[2]
EC	5–20 nM	2.39 nM	[3]
EC	1 pM–1 μM	0.15 pM	[4]
PEC	10^5 fM–8 nM	94 fM	[5]
PEC	10 fM–10 nM	6 fM	**This work**

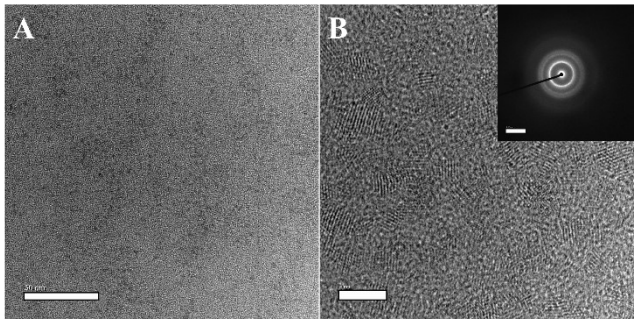

Fig. S1 (A, B, inset) TEM image and SEAD of CdSe QDs.

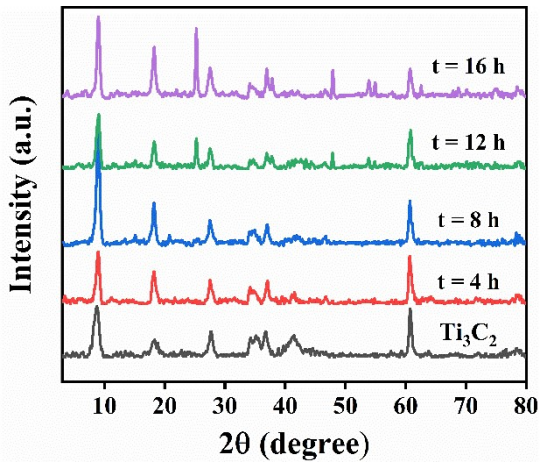

Fig. S2 XRD patterns of TiO_2/Ti_3C_2 prepared for different reaction times.

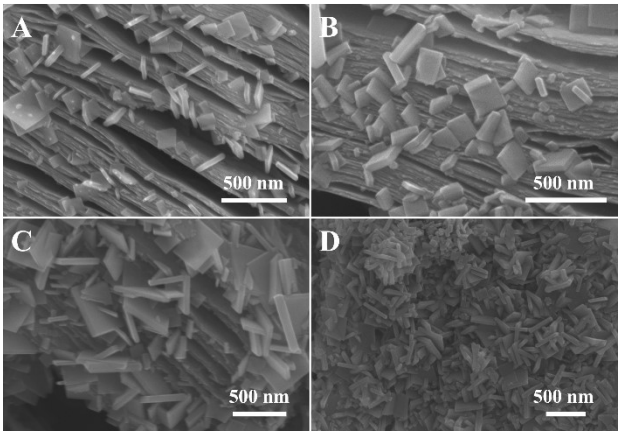

Fig. S3 SEM images of TiO_2/Ti_3C_2 prepared for different reaction times: (A) 4 h, (B) 8 h, (C) 12 h, and (D) 16 h.

References

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