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Single crystalline tantalum oxychloride micro-cubes: controllable synthesis, formation mechanism and enhanced photocatalytic hydrogen production activity

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Electronic supporting information

Synthesis of $TaO_{2.18}Cl_{0.64}$ MCs

In a typical synthesis procedure, 60 mg tantalum chloride ($TaCl_5$, AR, 99.95 %; Ningxia Orient Tantalum Industry Co., Ltd.) was dissolved in 13.3 mL hydrochloric acid ([HCl] is ca. 4M, AR, 38 %; Sinopharm Chemical Reagent Co., Ltd.). Then the solution was mixed with 26.6 mL acetic acid ([CH_3COOH] is ca. 12 M, AR, 99.5 %; Sinopharm Chemical Reagent Co., Ltd.) and transferred into a Teflon-lined autoclave (50 mL), which was subsequently heated at 200 ^{o}C for 10 h in a box furnace. After the autoclave was cooled to room temperature naturally, the white precipitate was separated by suction filtration. The product was placed in a dryer with 3 Å molecular sieves (AR; Tianjin Kemiou Chemical Reagent Co., Ltd.) at room temperature for at least 24 h to obtain the final product.

Characterization of $TaO_{2.18}Cl_{0.64}$ MCs

The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Multilab 2000 XPS system with a monochromatic Mg Kα source and a charge neutralizer; the binding energies were referenced to the C 1s peak at 284.4 eV of the surface adventitious carbon. The element composition was characterized by X-ray energy-dispersive spectrometer (EDX; EX250, Horiba) associated with the FE-SEM and a X-ray fluorescence spectrometer (XRF; AXIOS, PANalytical). The typical sample XRF data indicates that Ta and Cl atom ratio are 11.1 % and 7.1% respectively, for which we can get Ta : Cl = 1 : 0.64. By calculating the O atom ratio according to the charge equilibrium, the chemical composition of the typical sample is Ta : O : Cl = 1 : 2.18 : 0.64. The phase analyses of the samples were performed by powder X-ray diffraction (XRD; RU-200B/D/MAX-RB, Rigaku), using Cu Kα radiation (λ=1.5418 Å) with a resolution of 0.02° of 2θ. The morphologies of the as-synthesized products were characterized by a field emission scanning electron microscope (FE-SEM; S-4800, Hitachi) at an acceleration voltage of 10.0 kV. Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were captured on a high resolution transmission electron microscope (2100F, JEOL) at an acceleration voltage of 200 kV. The typical sample for the SAED was done by cutting the powder embedding bulk into ultrathin slices. Density of the powders was measured to be 6.1 g cm^{-3} by pycnometer test method using acetic acid as the liquid medium. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of the samples were measured from the optical absorption spectra using a UV-Vis spectrophotometer (UV-2550 PC, Shimadzu). Fine $BaSO_4$ powder was used as a standard for baseline and the spectra are recorded in a range 200-500 nm. Photoluminescence (PL) spectra were measured at room temperature on Perkin Elmer, LS 55, Fluorescence Spectrometer with an excitation wavelength of 240 nm.

Photocatalytic Tests

Photocatalytic hydrogen evolution was performed in a closed gas circulation system Labsolar-I (Beijing Perfectlight Co., Ltd., China) with a 300W xenon lamp (PLS-SXE300, Beijing Trusttech Co., Ltd., China) as the light source. A gas chromatograph (GC 7890 II, Techcomp Co., Ltd., China) was connected to the system with a circulating line as the H_2 evolution detector. 20 mg of the samples were dispersed in 30 vol% lactic acid aqueous solution with 5 wt% Pt attached (The platinization was done by in situ photodeposition of $H_2PtCl_6{\cdot}6H_2O$) and then kept in an external irradiation Pyrex cell with a diameter of ~63 mm, almost equal to the facula size of the light source.

Electrochemical measurement

For the preparation of working electrodes for electrochemical measurements, 0.15 g sample powder with 0.05 g PVDF mixed together uniformly, which was subsequently pressed onto a piece of Ni porous foil under 10 MPa pressure for 10 min. This acts as the working electrode with an area of 2 cm^2. The electrolyte is 3 M NaCl aqueous solution. Platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Electrochemical impedance spectra (EIS) and Mott–Schottky plots were both analyzed using an electrochemical analyzer (Autolab PGSTAT302N) in a homemade standard three-compartment cell. The frequency range was 0.1 Hz to 10^5 Hz with ac amplitude of 10 mV.

Structure simulation

Powder XRD simulation was done mainly by manual trial and Rietveld method [1] at a low level. For the measured XRD from the powder of $TaO_{2.18}Cl_{0.64}$ MCs is similar to the pattern of BaTe and TaO_2F (Fig. S2a), we suspect the lattice of $TaO_{2.18}Cl_{0.64}$ contain features of the two structures which is three main points mentioned below. First, peaks at 32.3^o, 46.3^o, 57.7^o, 67.6^o and 76.8^o are so well consistent with corresponding ones of the two standard patterns that $TaO_{2.18}Cl_{0.64}$ should be a cubic lattice just them. Second, in XRD of $TaO_{2.18}Cl_{0.64}$, there is no peaks at the position of (h k l) (h + k + l = odd) corresponding to TaO_2F diffraction pattern and the pattern (> 30^o) of $TaO_{2.18}Cl_{0.64}$ is more similar to BaTe (body-center lattice). Based on the extinction rule, there should be atom at the body-center site of cubic unit cell. Third, at the position of (1 0 0) of TaO_2F, there is arch peak in the XRD of $TaO_{2.18}Cl_{0.64}$ which should be the disorder at the body-center site that make the extinction incomplete. Added with the super structure mentioned in main body text, a 4 × 4 super lattice was modeled by using a ~3.9 Å × 3.9 Å × 3.9 Å cubic lattice as the unit cell. By Rietveld refinement method in Fullprof[2] software with the powder XRD data, the model in Fig. 1d was obtained. The symmetry of the super structure is mainly reflected by the distortion of atom position and occupancy of Ta atom at cation site. As for chlorine atom, because the difference against the XRD of Ta_2O_5 (Fig. S2a) it can exclude the possibility of the emergence of Cl doping. We treat that each Cl atom connecting only one Ta atom according to the coordination of Cl atoms in $TaCl_5$. The density of model is 6.09 g cm^{-3} which is close to the measured value 6.12 g cm^{-3}.

Table S1 Details of the lattice for $TaO_{2.18}Cl_{0.64}$ MCs

symmetry space group name	PM-3M
symmetry Int Tables number	221
symmetry cell setting	cubic
cell length a	15.6876

atom site							
label	type symbol	fract x	fract y	fract z	U iso or equiv	adp type	occupancy
Ta1	Ta	0.000	0.000	0.000	0.0704	Uiso	1.00
O2	O	0.000	0.000	0.099	0.0140	Uiso	1.00
Ta3	Ta	0.239	0.000	0.000	0.0704	Uiso	0.80
O4	O	0.376	0.000	0.000	0.0101	Uiso	1.00
Ta5	Ta	0.500	0.000	0.000	0.0704	Uiso	1.00
O6	O	0.500	0.000	0.118	0.0140	Uiso	1.00
Ta7	Ta	0.285	0.285	0.000	0.0704	Uiso	0.42
O8	O	0.251	0.251	0.119	0.0140	Uiso	1.00
Ta9	Ta	0.381	0.381	0.137	0.0003	Uiso	0.53
Cl10	Cl	0.260	0.260	0.384	0.0140	Uiso	1.00
O11	O	0.367	0.227	0.000	0.0101	Uiso	1.00
Ta12	Ta	0.500	0.245	0.000	0.0704	Uiso	0.62
O13	O	0.500	0.372	0.000	0.0101	Uiso	1.00
O14	O	0.500	0.279	0.127	0.0140	Uiso	1.00
O15	O	0.500	0.239	0.382	0.0140	Uiso	1.00
Ta16	Ta	0.500	0.500	0.000	0.0704	Uiso	0.83
Cl17	Cl	0.500	0.500	0.120	0.0140	Uiso	1.00
Ta18	Ta	0.500	0.500	0.214	0.0704	Uiso	0.21
Cl19	Cl	0.500	0.500	0.374	0.0140	Uiso	1.00
Ta20	Ta	0.380	0.380	0.380	0.0003	Uiso	0.56
Ta21	Ta	0.160	0.160	0.160	0.0000	Uiso	0.84
Ta22	Ta	0.500	0.239	0.239	0.0704	Uiso	0.89

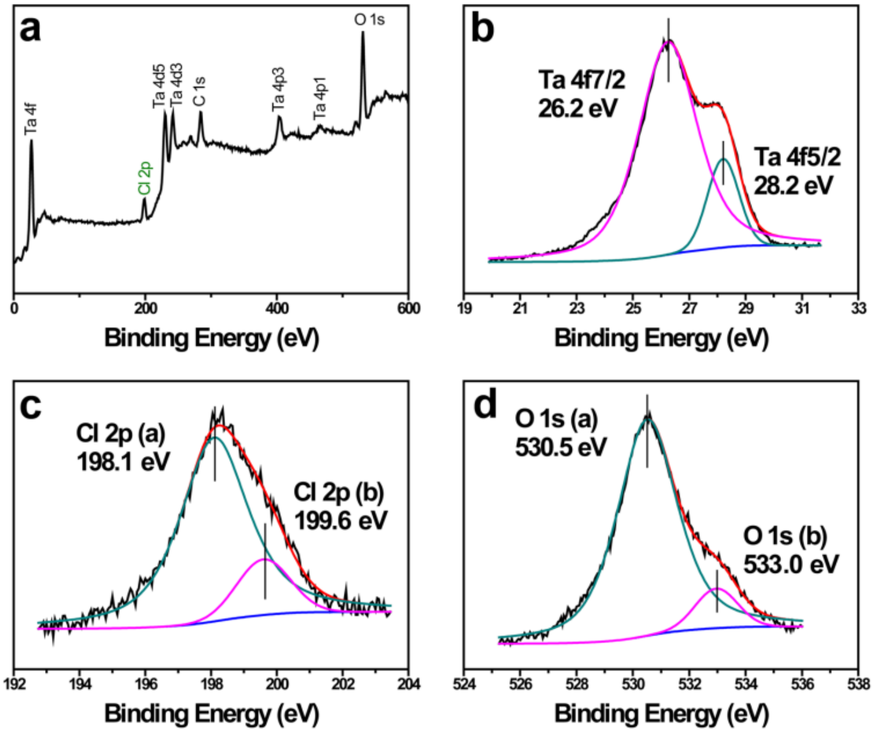

Fig. S1 XPS in full (a), Ta 4f (b), Cl 2p (c) and O 1s (d) of the as-prepared $TaO_{2.18}Cl_{0.64}$ MCs.

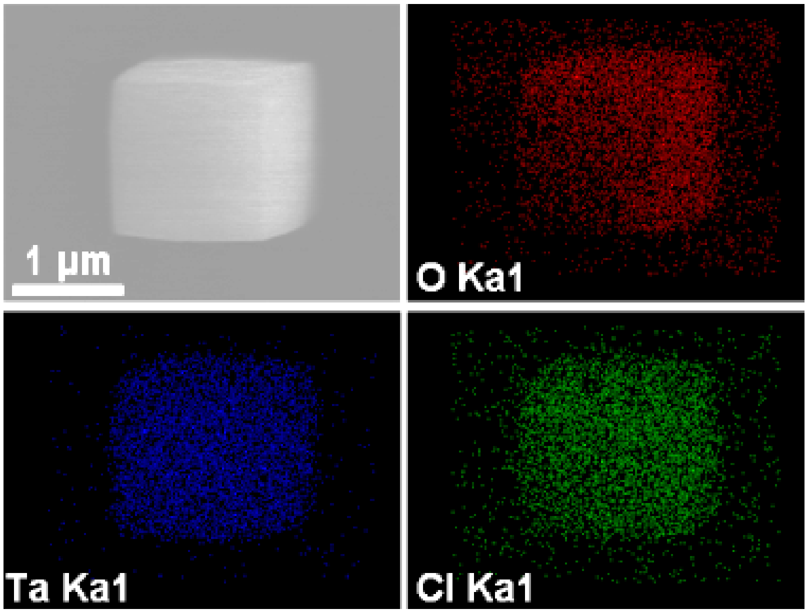

Fig. S2 The SEM and corresponding elemental mapping images of a single crystalline $TaO_{2.18}Cl_{0.64}$ MC.

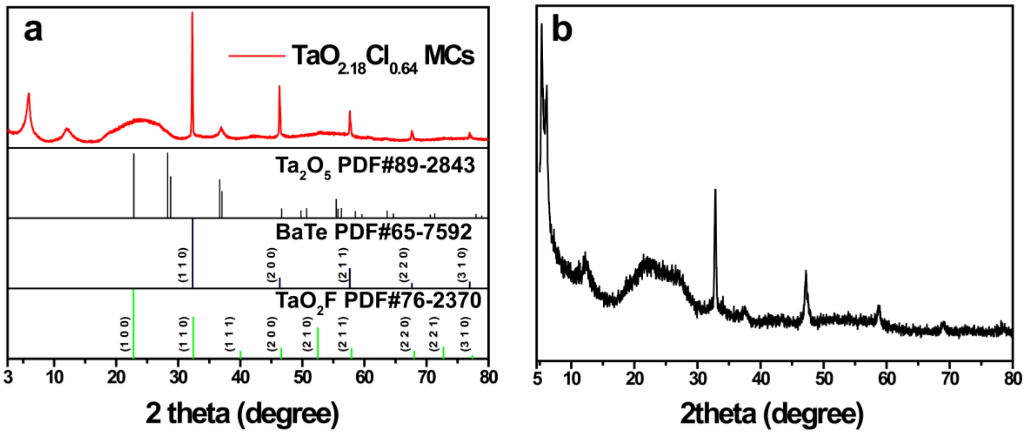

Fig. S3 Standard XRD patterns of Ta_2O_5, TaO_2F and BaTe (a); XRD pattern of $TaO_{2.18}Cl_{0.64}$ MCs placed in liquid nitrogen for 36 h (b).

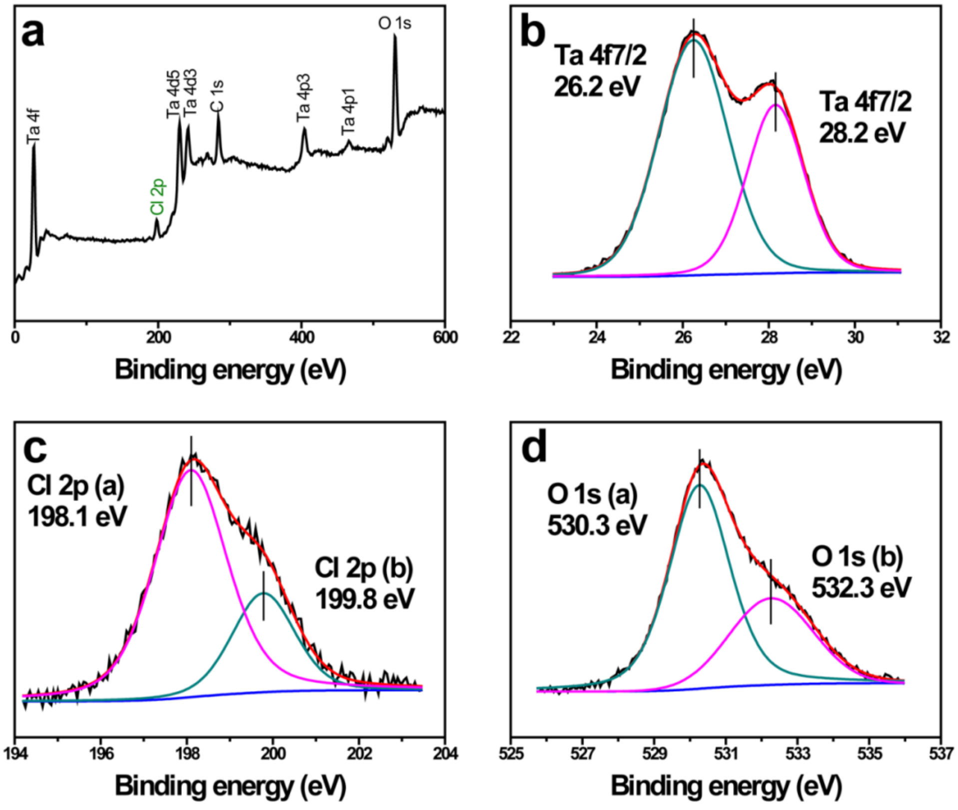

Fig. S4 XPS in full (a), Ta 4f (b), Cl 2p (c) and O 1s (d) of the sample obtained at *t* of 40 min.

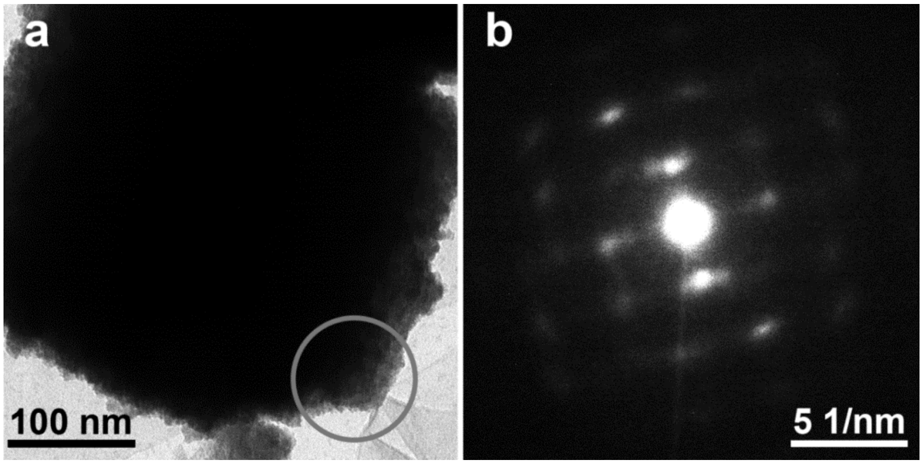

Fig. S5 TEM image (a) and SAED pattern (b) of a cube obtained at *t* of 1 h. The SAED pattern (b) comes from the circled area in (a).

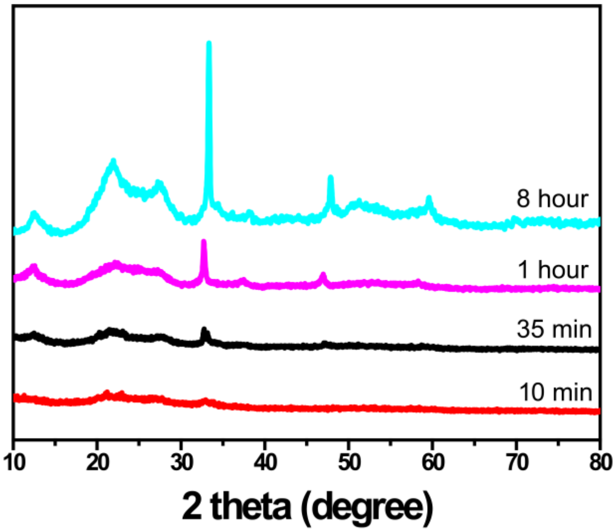

Fig. S6 XRD patterns of the samples obtained at different *t*.

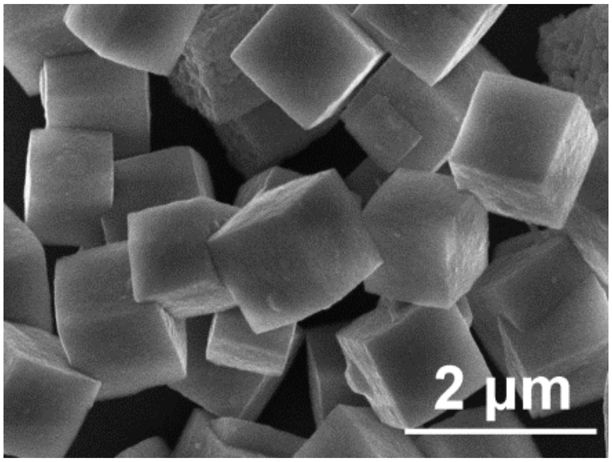

Fig. S7 SEM image of the sample obtained using Ta(OEt)$_5$ instead of TaCl$_5$ in the typical preparation process.

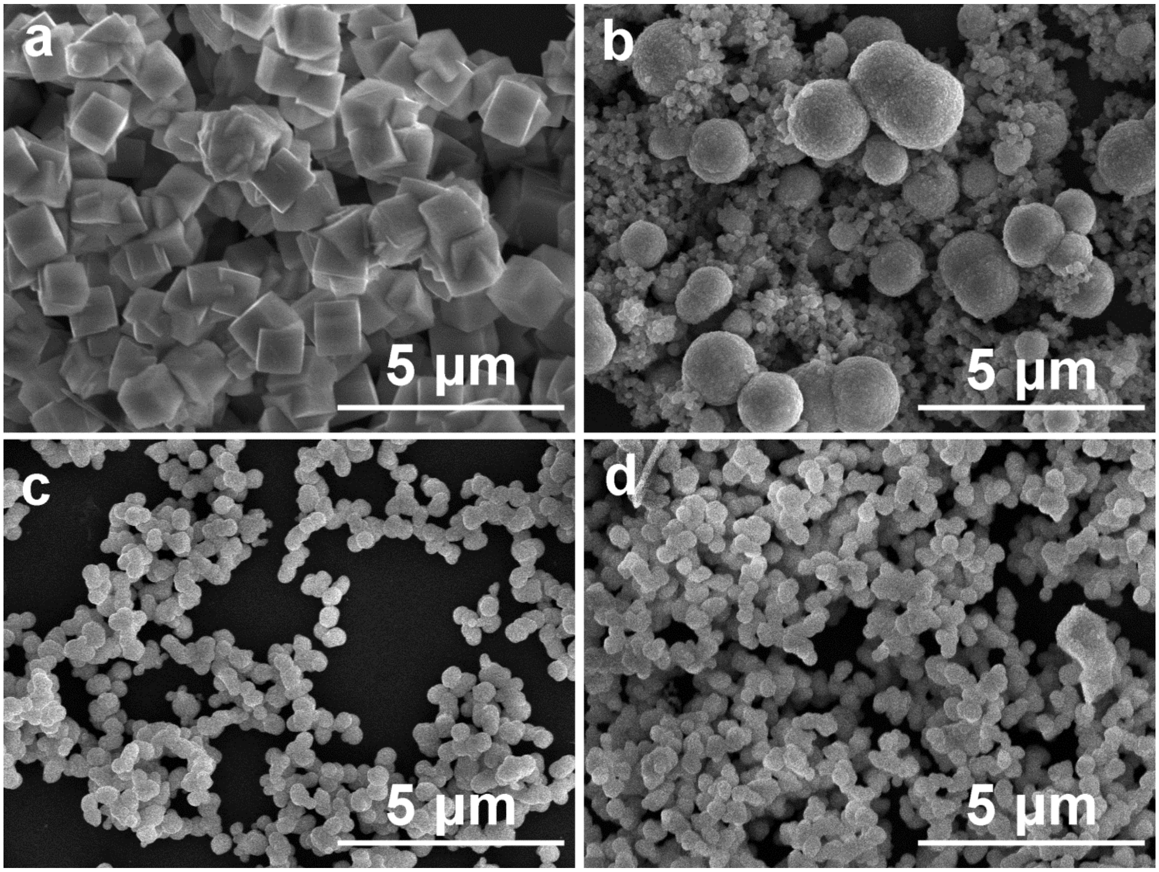

Fig. S8 SEM images of the samples obtained at aqueous solutions containing 12 M acetic acid and different [HCl] of 3.0 M (a), 2.0 M (b), 1.0 M (c) and 0 (d), respectively.

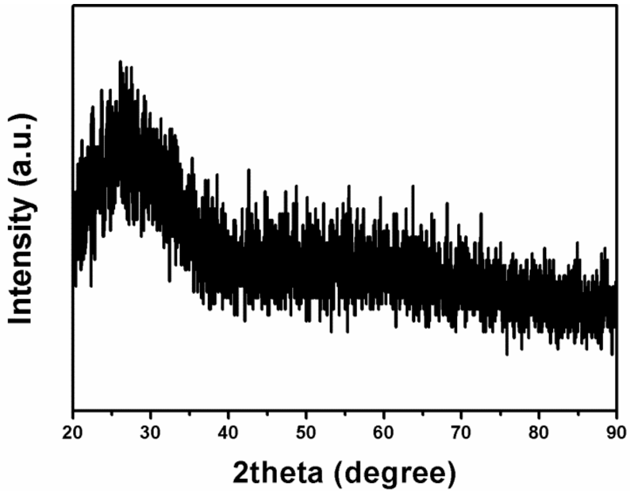

Fig. S9 XRD for the sample imaged in Fig. S8 (d)

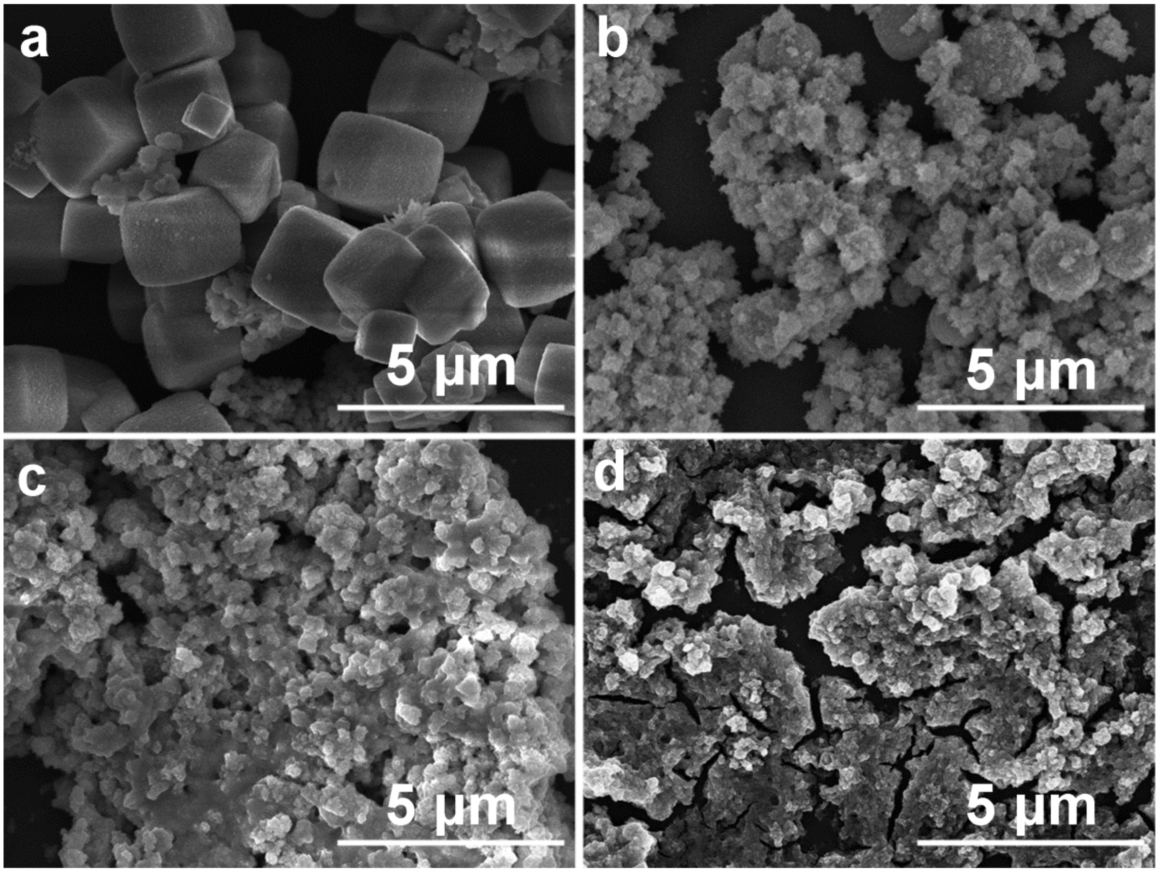

Fig. S10 SEM images of the samples obtained at aqueous solutions containing 4 M HCl and different HAc concentrations of 8.0 M (a), 6.0 M (b), 2.0 M (c) and 0 (d), respectively.

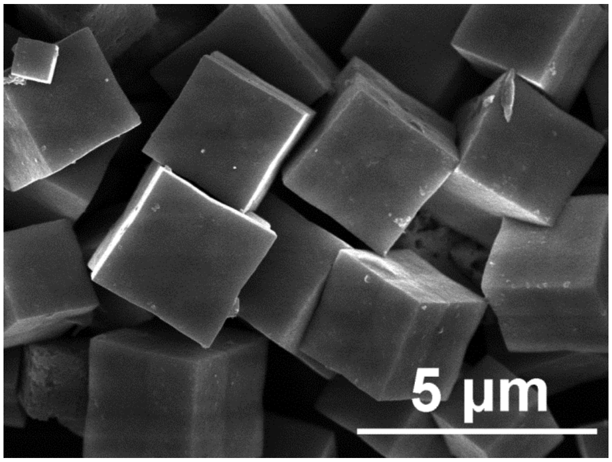

Fig. S11 SEM image of the sample obtained using propionic acid to substitute for acetic acid.

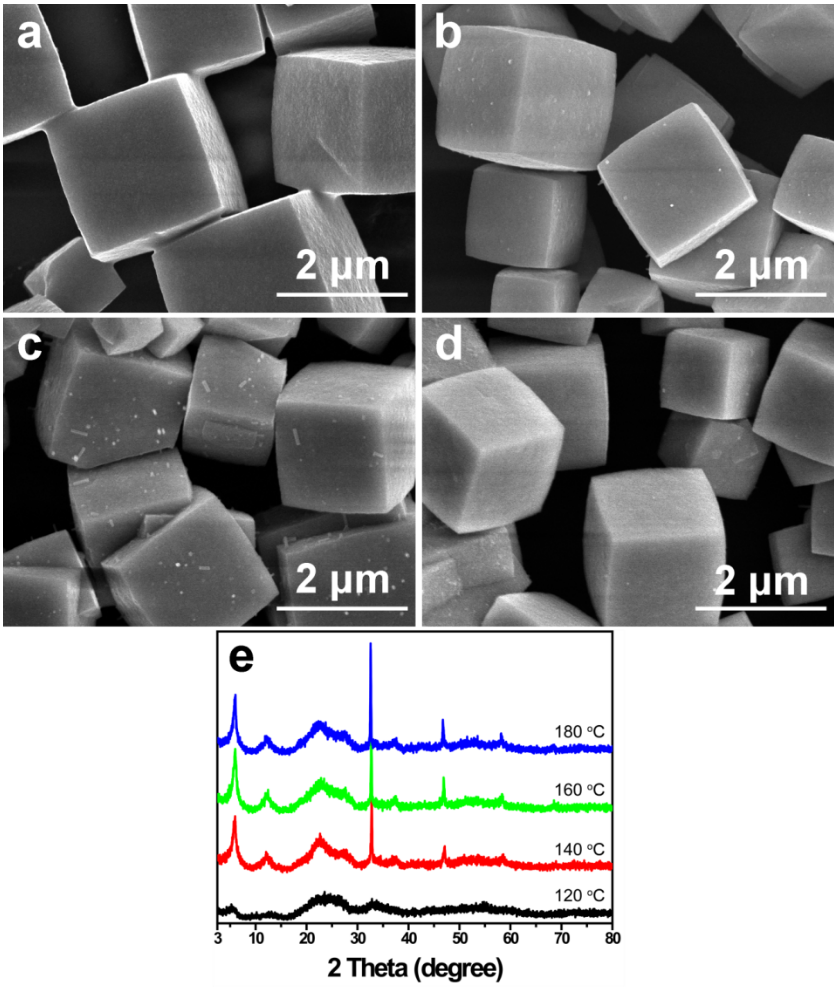

Fig. S12 SEM images (a-d) and XRD patterns (e) of the samples obtained at different solvothermal temperature.

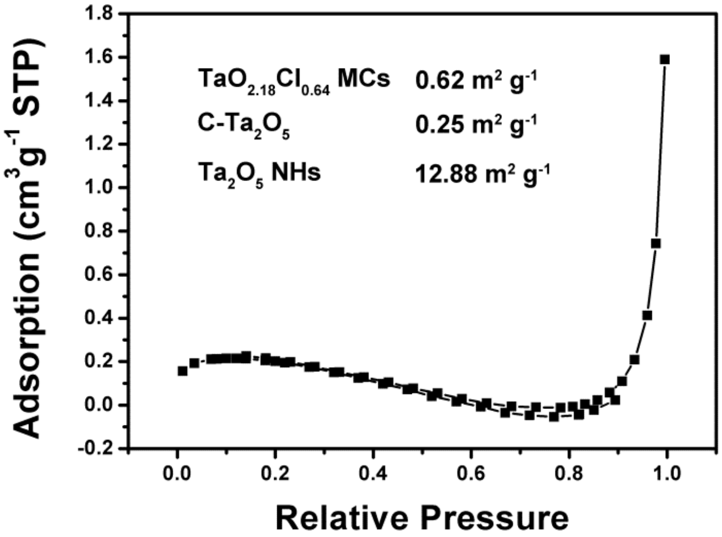

Fig. S13 N_2 absorption-desorption analysis of the as-prepared $TaO_{2.18}Cl_{0.64}$ MCs as well as the surface areas of $C\text{-}Ta_2O_5$ and Ta_2O_5 NHs .[3]

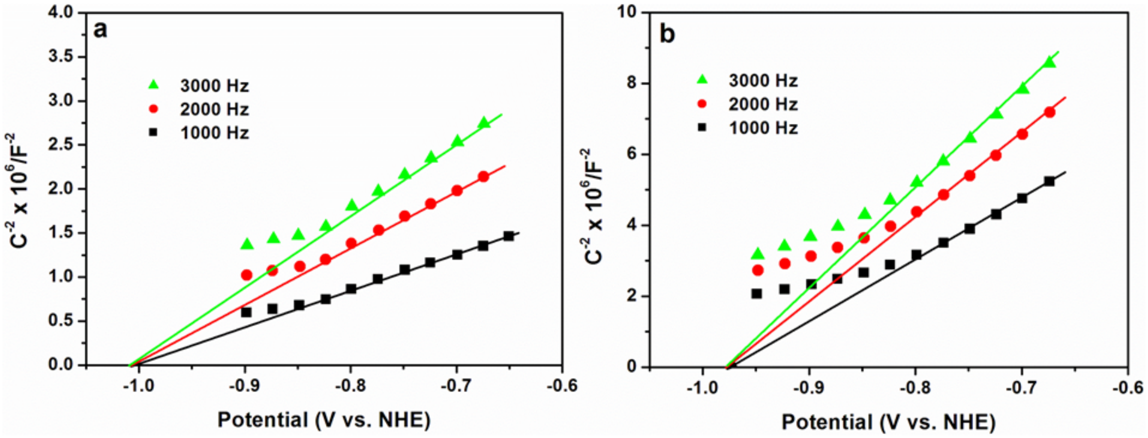

Fig. S14 Mott-Schottky plots of the as-prepared $TaO_{2.18}Cl_{0.64}$ MCs (a) and $C\text{-}Ta_2O_5$ (b).

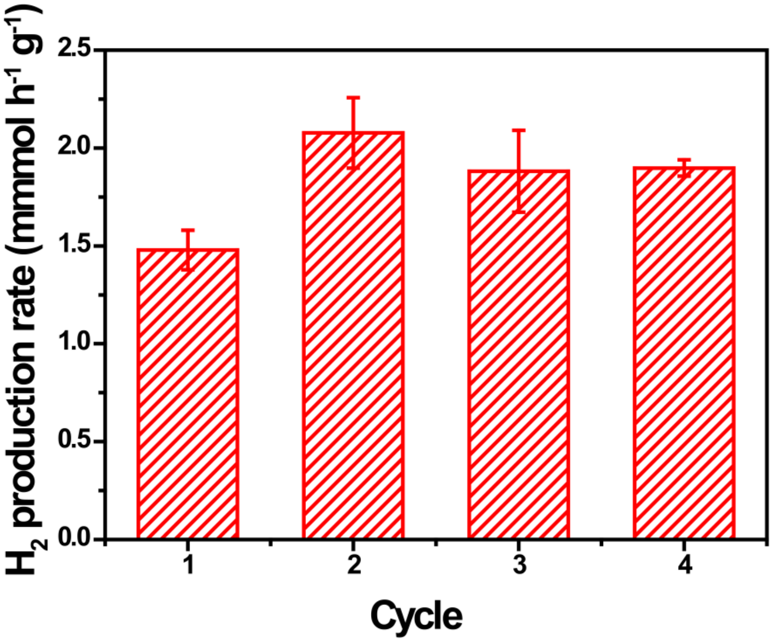

Fig. S15 Repeated cycling of the photocatalytic hydrogen evolution of the as-prepared $TaO_{2.18}Cl_{0.64}$ MCs in 30 vol% lactic acid aqueous solution containing 2M NaCl with 5 wt% Pt attached in each 5 h.

Reference

1. H. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65-71.
2. (a) J. Rodríguez-Carvajal, *Physica B: Condens. Matter*, 1993, **192**, 55-69; (b) J. Rodríguez-Carvajal, *Commission on powder diffraction (IUCr). Newsletter*, 2001, **26**, 12-19; (c) J. Rodriguez-Carvajal and T. Roisnel, *Newsletter*, 1998, **20**, 35; (d) T. Roisnel and J. Rodríquez-Carvajal, in *Mater. Sci. Forum*, Transtec Publications; 1999, 2001, pp. 118-123.
3. J. Y. Duan, W. D. Shi, L. L. Xu, G. Y. Mou, Q. L. Xin and J. G. Guan, *Chem. Commun.*, 2012, **48**, 7301-7303.