

Experimental Section

Anhydrous TiCl_4 , toluene and glacial acetic acid were acquired from Sigma Aldrich chemical company. All analytical and spectroscopic samples were prepared inside a Saffron Scientific (type β) glovebox, equipped with a closed loop recirculation system for the removal of moisture and oxygen (operating at ca. 2.1-2.5 vppm O_2).

IR spectra were recorded using a Nicolet 6700 spectrometer (Thermo Fisher Nicolet, USA) with KBr pellets. Powder X-ray diffraction (XRD) experiments were performed using a X'Pert Pro diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 40 mA and the scanning angle ranged from 10° to 90° of 2θ . Both carbon and hydrogen analyses were done using a varioMicro Elemental analyzer (Elementar Analysensysteme GmbH, Germany). Scanning electron microscopy (SEM) images were collected using a field emission scanning electron microscope (Hitachi S-4800). Transmission electron microscopy (TEM) was performed with a FEI Tecnai G2 F30 electron microscope operating at an accelerating voltage of 300 kV. The surface composition of sample B were determined by energy dispersive spectroscopy (EDS). EDS data of sample B was collected using an Thermo SCIENTIFIC energy dispersive X-ray spectroscopy system attached to a Hitachi S-4800 SEM, with an acceleration voltage of 15keV. X-ray photoelectron spectra (XPS) was operated on a photoelectron spectrometer (Kratos AXIS Ultra DLD, Shimadzu, Japan).

Synthesis and Characterisation of 1

A mixture of 10.0ml TiCl_4 (91.0 mmol), 20.0ml dry toluene and 20ml glacial acetic acid was stirred under nitrogen at 35°C for 30 minutes. Cooling at 1°C per hour to room temperature (20°C) gave colorless crystals of **1** (8.73g, 39% based on TiCl_4). Anal. Calc. (%) for $\text{C}_8\text{H}_{14}\text{Cl}_4\text{O}_9\text{Ti}_2$: C, 19.54; H, 2.87. Found (%): C, 19.52; H, 2.80. IR data (KBr, cm^{-1}) for **1**: 3270s, 2930w, 1636m, 1587m, 1503s, 1489s, 1313w, 1275m, 1147s, 1112s, 1089s, 941w, 825w, 754m, 698m, 626m, 525m.

Fig. S1 Crystals image of cage **1**



Preparation of A and B

1.4g dried crystals of cage **1** was performed at 500°C for 5 hour in an air flow, a light yellow solid of **A** was obtained.

1.5g dried crystals of cage **1** was performed at 500 °C for 5 hour in a purified nitrogen flow, a black solid of **B** was obtained.

Elemental Analysis of **A** and **B**:

A, C 0.16%, H 0.52%:

B, C 16.69%, H 0.98%

These results can be compared to EDS measurements, which give similar C content, presumably because they overestimate the C content at which is at the surface of the samples.

Fig. S2 Images of **A**



Fig. S3 Images of **B**



Preparation of electrodes

Electrode **A** was prepared by coating a mixture containing 90% powder of **A**, 10% PVDF binder on an Indium-Tin-Oxide glass (Fig 7a) or a Nickel foil (Fig 7b), followed by drying at 60 °C for 24 hour.

Electrode **B** was prepared by coating a mixture containing 90% powder of **B**, 10% PVDF binder on Indium-Tin-Oxide glass (Fig 7a) or a Nickel foil (Fig 7b), followed by drying at 60 °C for 24 hour.

Fig. S4 Colors of Electrode **A** at different potentials



*Calculation of specific capacitance of **B***

The specific capacitance of **B** is calculated according to the following equation:¹⁻²

$$C_B = \frac{Q_B}{\Delta V \times m_B}$$

Where C (F/g) is the specific capacitance, Q (C) is the average charge during the charging and discharging process, ΔV (V) is the potential window, and m (g) is the mass of **B**.

1. J. Yan, E. Khoo, A. Sumboja, P. S. Lee, *ACS Nano*, 2010, **4**, 4247.
2. J. Yan, Z. J. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. P. Song, M. L. Zhang, *J. Power Sources* 2009, **194**, 1202–1207.

Single Crystal X-ray Crystallography

Crystals data were collected on a Bruker Smart Apex CCD diffractometer. The structures were solved by Direct Methods and refined by full-matrix least squares on F^2 . (SHELX, Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112).

Table S1 Details of the structure solutions and refinements of **1**.

Compound	1
Chemical formula	C₈H₁₄Cl₄O₉Ti₂
<i>FW</i>	491.79
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	
<i>a</i> (Å)	12.6154(9)
<i>b</i> (Å)	18.5017(14)
<i>c</i> (Å)	7.6960(5)
<i>V</i> (Å ³)	1796.3(2)
<i>Z</i>	4
ρ_{calc} (Mg/m ³)	1.818
μ (Mo-K α) (mm ⁻¹)	1.520
reflections collected	17798
independent reflections (<i>R_m</i>)	1907 (0.0423)
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0435, 0.1096
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0492, 0.1132

Fig. S5 View down the *c* axis of the crystal packing diagram of **1**

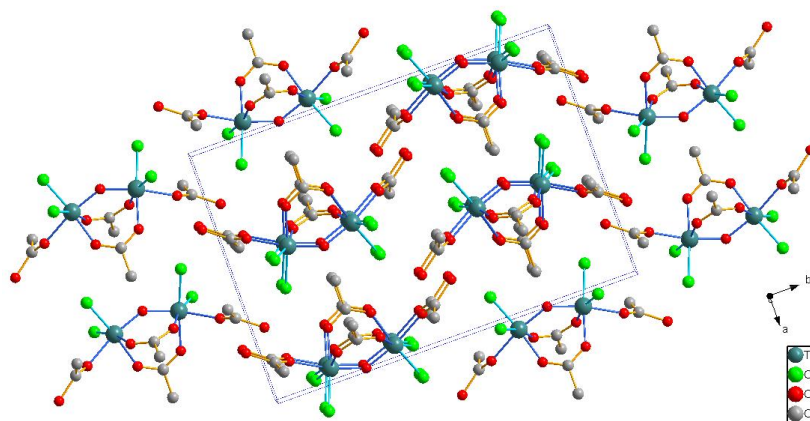
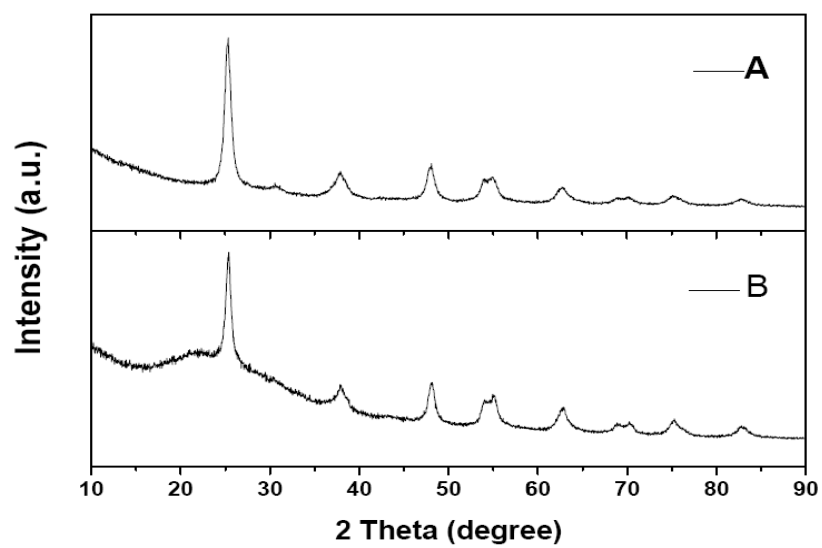


Fig. S6 The powder XRD results of **A** and **B**.



EDS Analysis of A and B

Fig. S7 EDS on sample A.

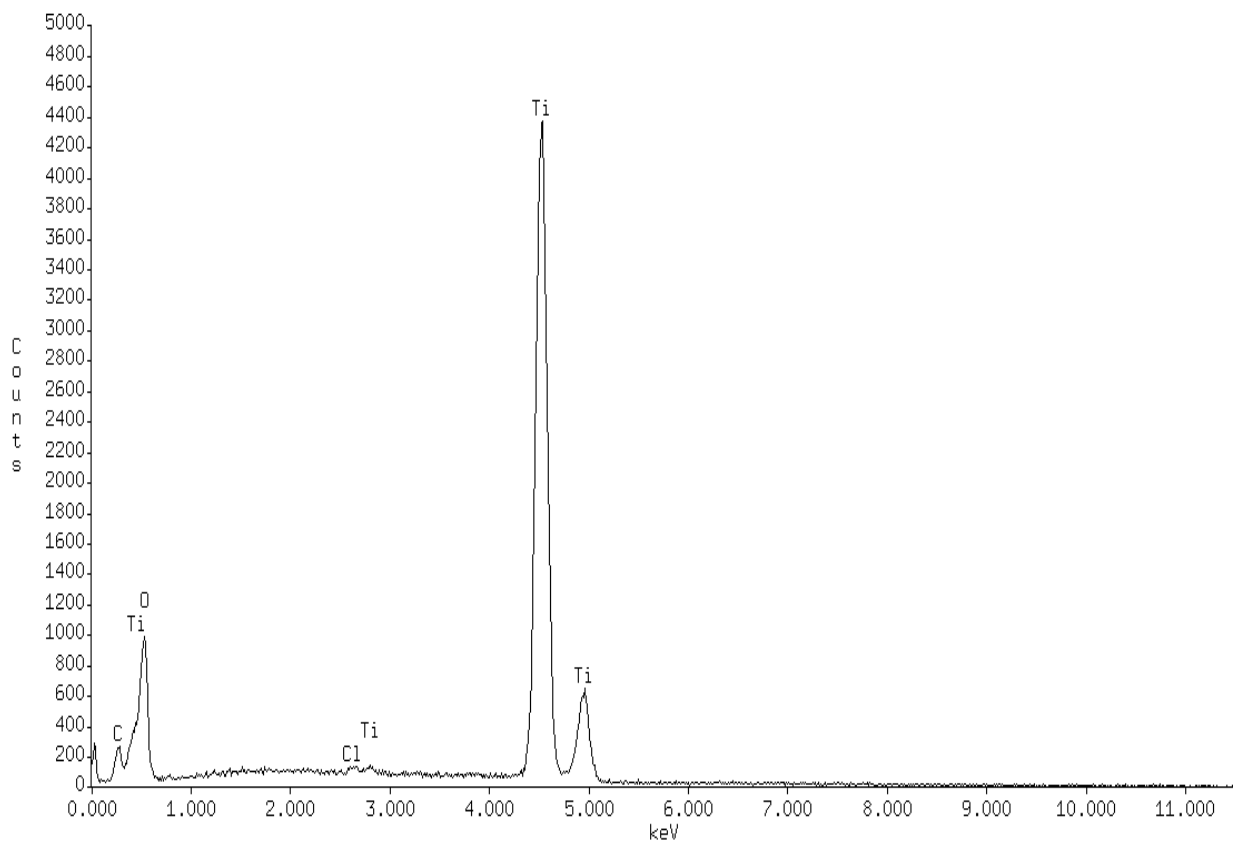


Table S2 EDS on sample A.

Element	Atomic Percentage	Weight Percentage
C	7.53 %	3.48 %
O	60.24 %	37.11%
Cl	0.07 %	0.10 %
Ti	32.16 %	59.31 %

Fig. S8 EDS on sample B.

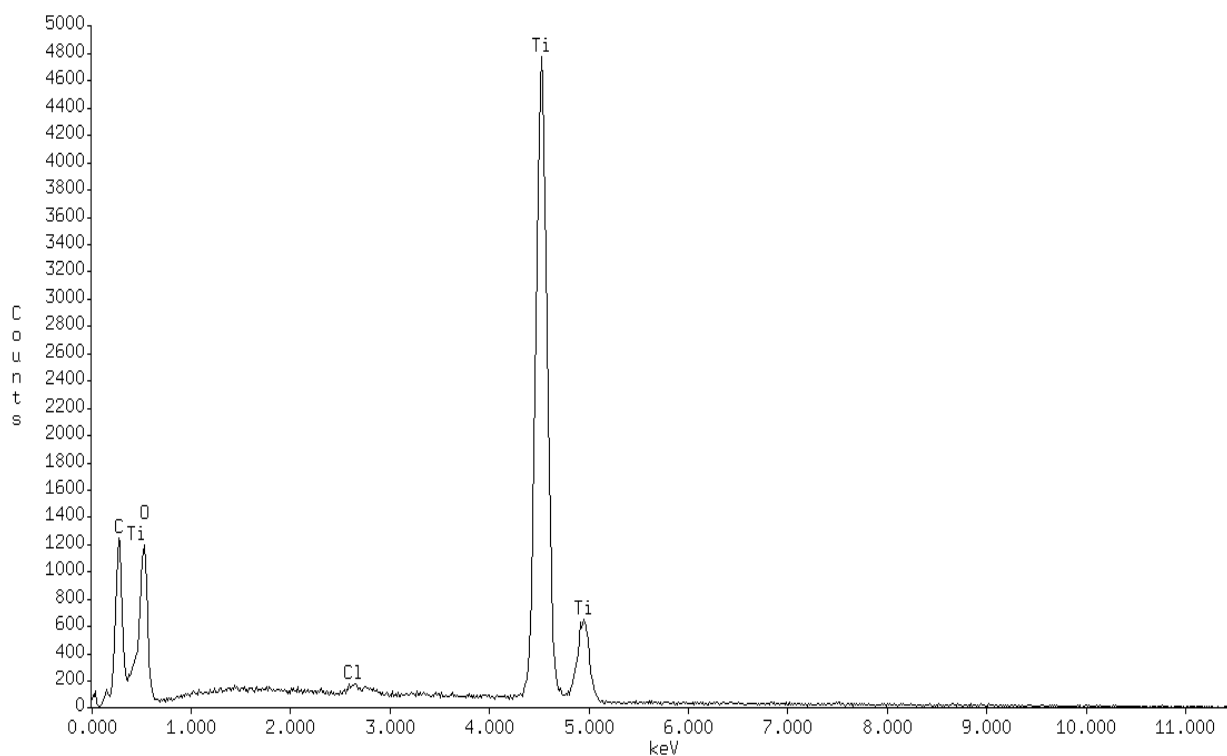


Table S3 EDS on sample B.

Element	Atomic Percentage	Weight Percentage
C	26.81 %	14.64 %
O	51.01 %	37.11 %
Cl	0.12 %	0.19 %
Ti	22.06 %	48.05 %

XPS Analysis of A and B

Fig. S9 XPS signal of A for Ti 2*p* region.

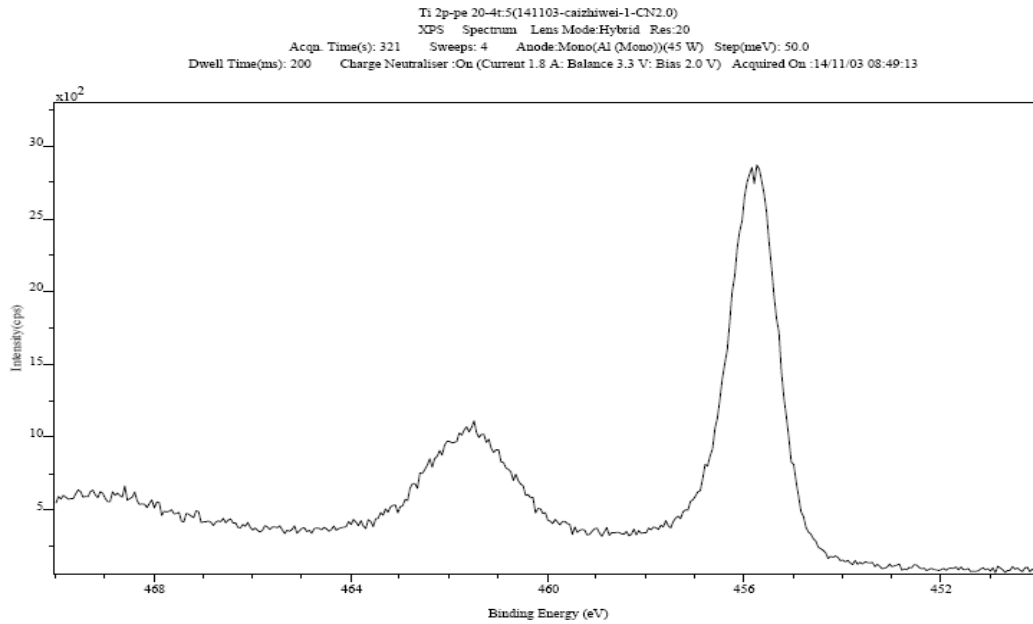


Fig. S10 XPS signal of A for Cl 2*p* region.

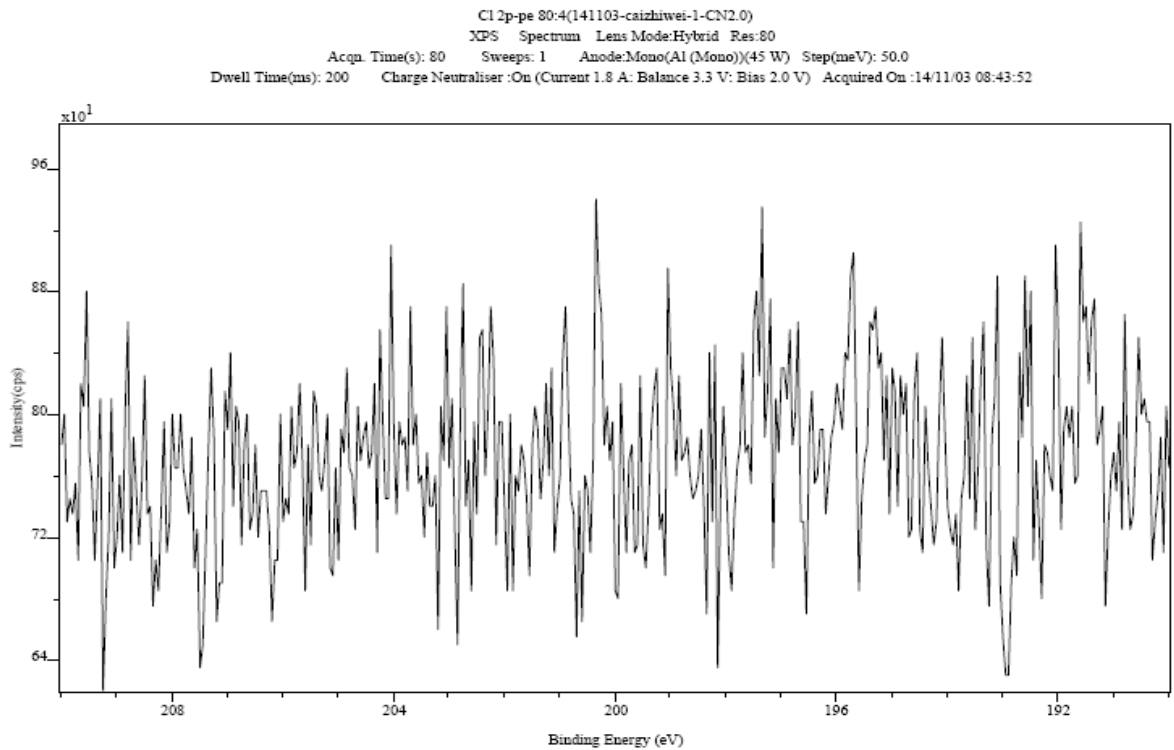


Fig. S11 XPS survey spectra of **A**

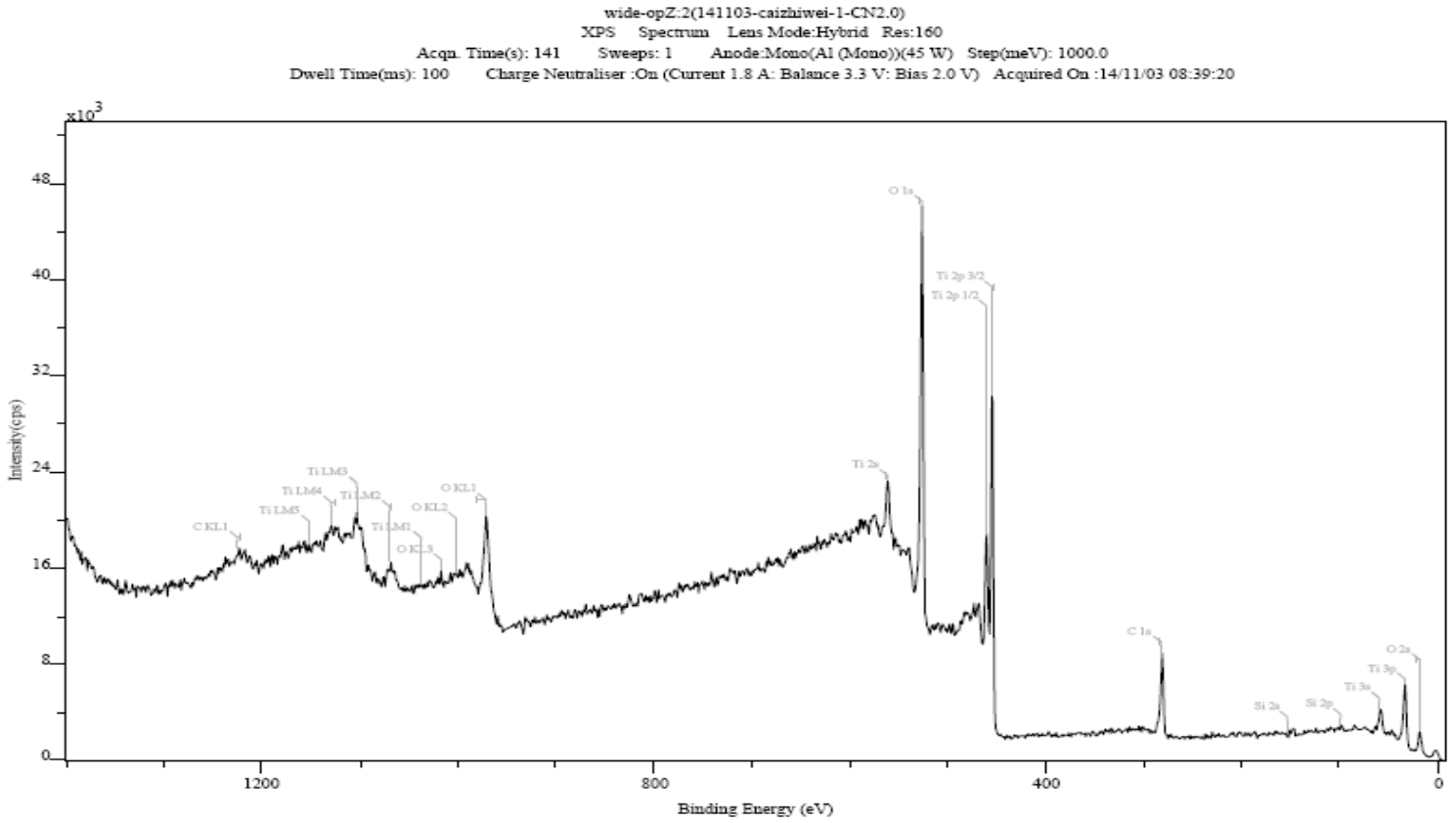


Fig. S12 XPS signal of **B** for Ti *2p* region.

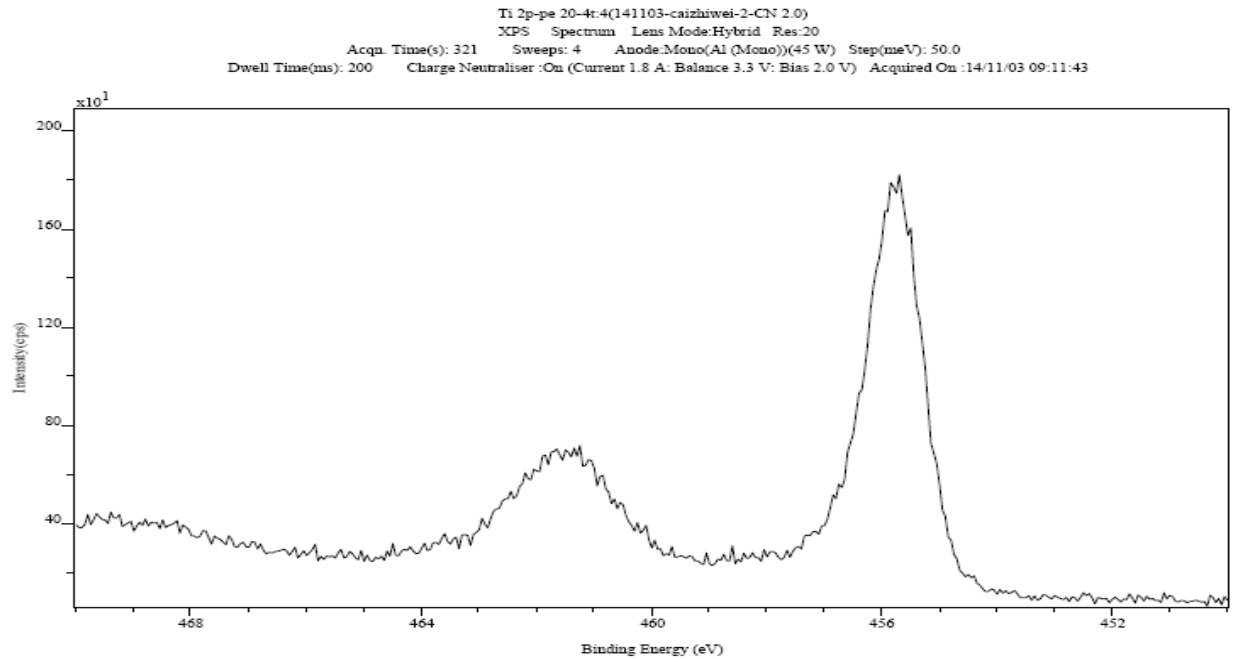


Fig. S13 XPS signal of B for Cl 2p region.

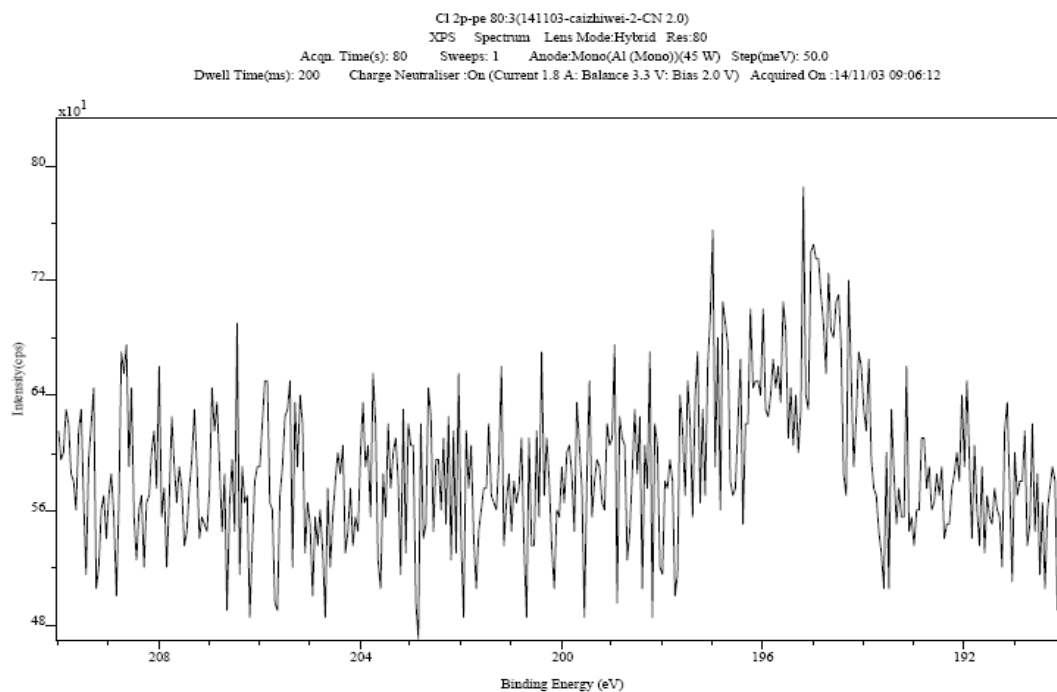


Fig. S14 XPS survey spectra of B

