Materials and chemicals

All chemicals are analytical and can be used without further purification.TC4 titanium alloy plates (Ti-6%Al-4%V) and pure titanium plates purchased from Baoti Group Co., Ltd. (Shaanxi, China) are both for direct use in industrial-grade products.**Table.S1** chemicals and corporation

chemical	
Absolute ethyl alcohol (C_2H_6O),	Aladdin Ltd. (Shanghai, China)
Acetone (C_3H_6O)	Aladdin Ltd. (Shanghai, China)
Ethylene glycol (EG, $(CH_2OH)_2$)	Aladdin Ltd. (Shanghai, China)
Ammonium fluoride (NH_4F)	Aladdin Ltd. (Shanghai, China)
Sulfuric acid (H_2SO_4)	Aladdin Ltd. (Shanghai, China)
Lead nitrate($Pb(NO_3)_2$)	Aladdin Ltd. (Shanghai, China)

Pre-treatment of the titanium sheet

Pure plates and TC4 plates are cut into small pieces in the size of 20 mm x 10 mm x 1 mm. The pre-processing step is divided into two steps. First, the potassium alloy plate is immersed in a mixed solution of HF+HNO_3+H_2O with a volume ratio of 1: 2: 10-15s, and the surface oxide layer is removed by chemical polishing. Then, the titanium alloy tablets use ethanol, the ionic water is removed by ultrasound for 5 mins, the number of times is three, remove the surface oil dirt. Finally, the titanium alloy plate is stored in an ethanol solution for reserve use.

Preparation of ZrO_2-Co_3O_4 Mixed Oxide Powder

ZrO_2-Co_3O_4 compound oxide powder is prepared using the solution-gel method. First, the citric acid (5.6g, 0.03 mol) and the $Zr(NO_3)_4 \cdot 5H_2O$(4.2932 g, 0.01 mol) are dissolved in deionized water and added $Co(NO_3)_2 \cdot 6H_2O$(2.9103 g, 0.01 mol).The resulting solution is heated for 12 hours in a dryer at 160 ° C to obtain a precursor. The black is then transferred to the maffar furnace, in the air, to burn at 700 ° C for 12 hours at a heating rate of 2 ° C/min. Finally, with the use of acrylic, grind, remove impurities, wash, and obtain the target powder.

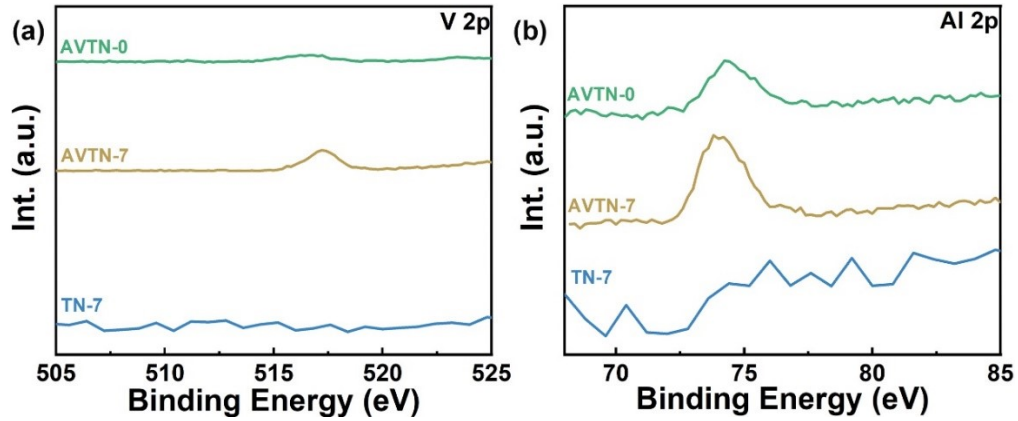

Figure.S1 The XPS spectra of (a) V 2p of AVTN-0,AVTN-7 and TN-7, (b) Al 2p of AVTN-0,AVTN-7 and TN-7

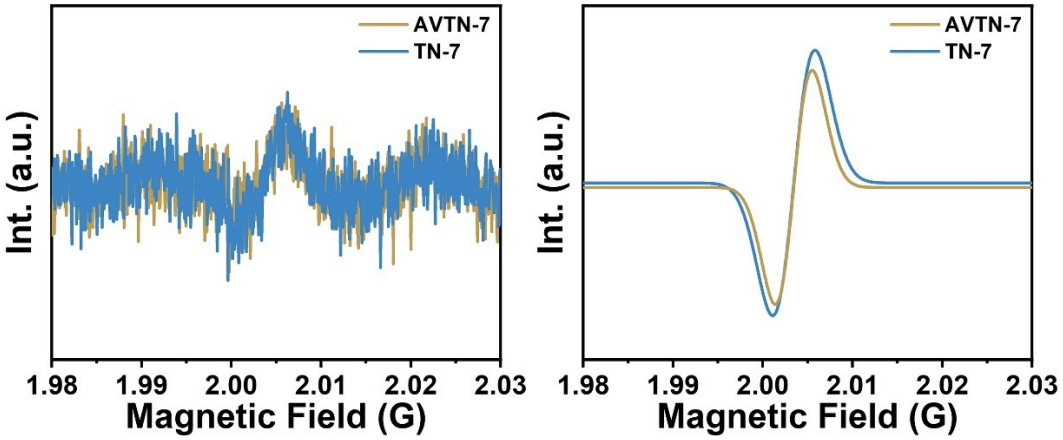

Figure S2 the EPR of AVTN-7and TN-7

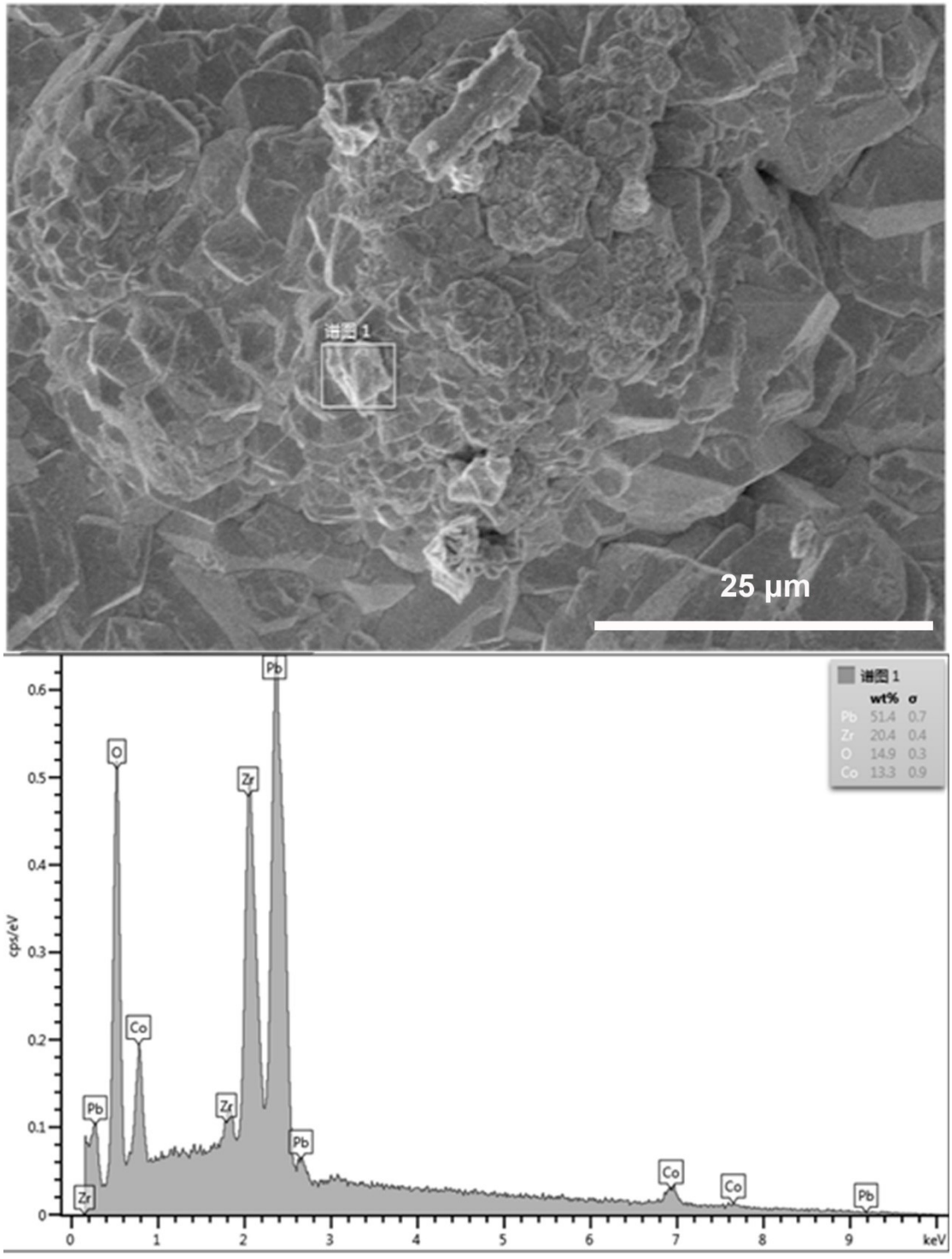

Figure S3 the EDS of TC4/AVTN-7/ZrO_2-Co_3O_4-PbO_2

Table S1 the R_{ct1} and R_{ct2} of different electrodes

Electrode	R_{ct1} (ohm/cm^2)	R_{ct2} (ohm/cm^2)
TC4/AVTN-7/ZrO_2-Co_3O_4-PbO_2	3.004	0.5521
TC4/AVTN-7/PbO_2	20.48	0.7562
TC4/PbO_2	0.07823	22.35
Ti4/PbO_2	123	9.402

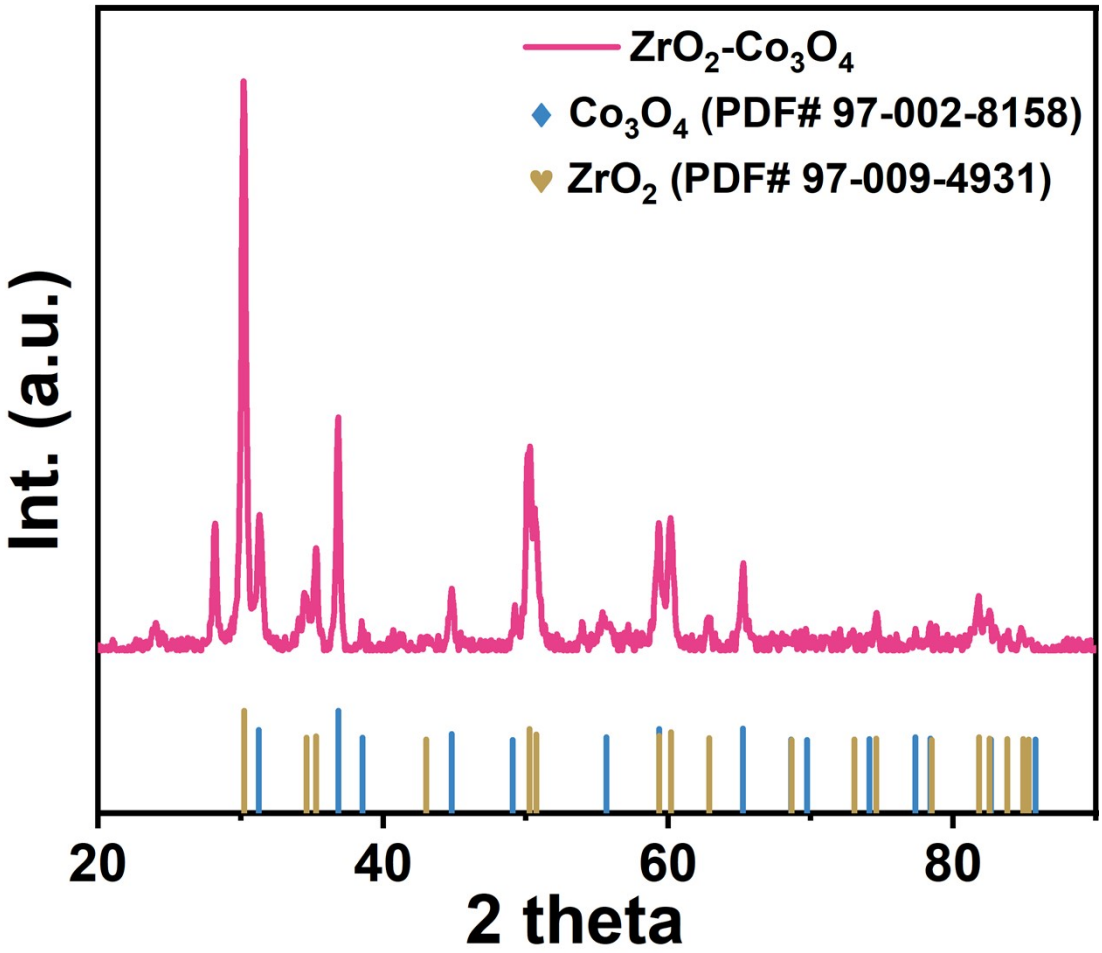

Figure S4 the XRD pattern of ZrO2-Co3O4 powder

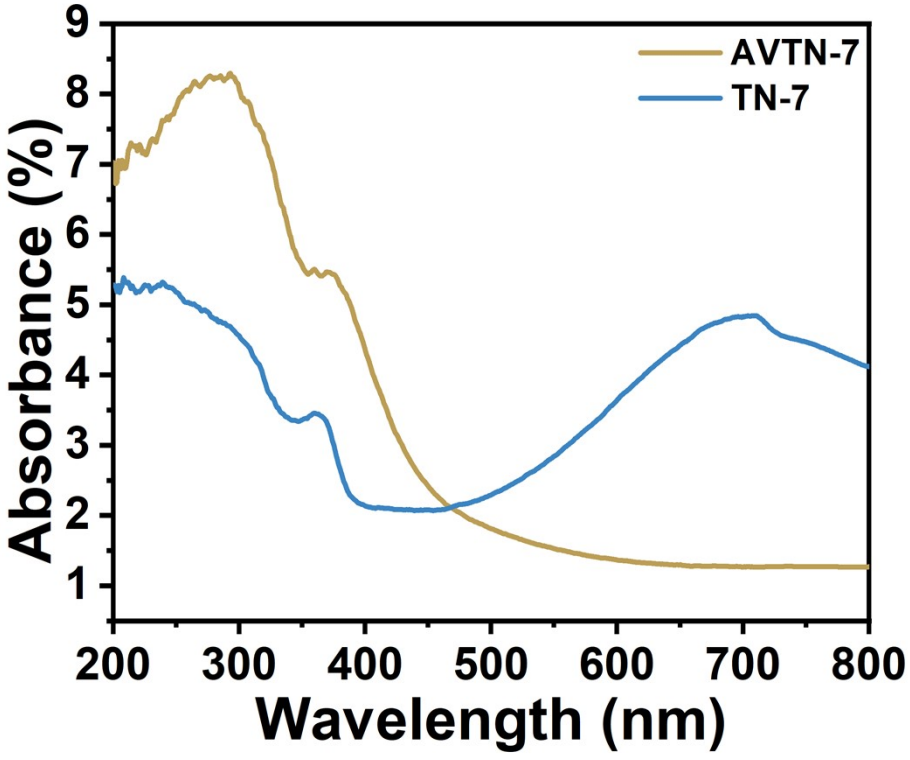

Figure S5 the UV absorption spectroscopy of AVTN-7 and TN-7

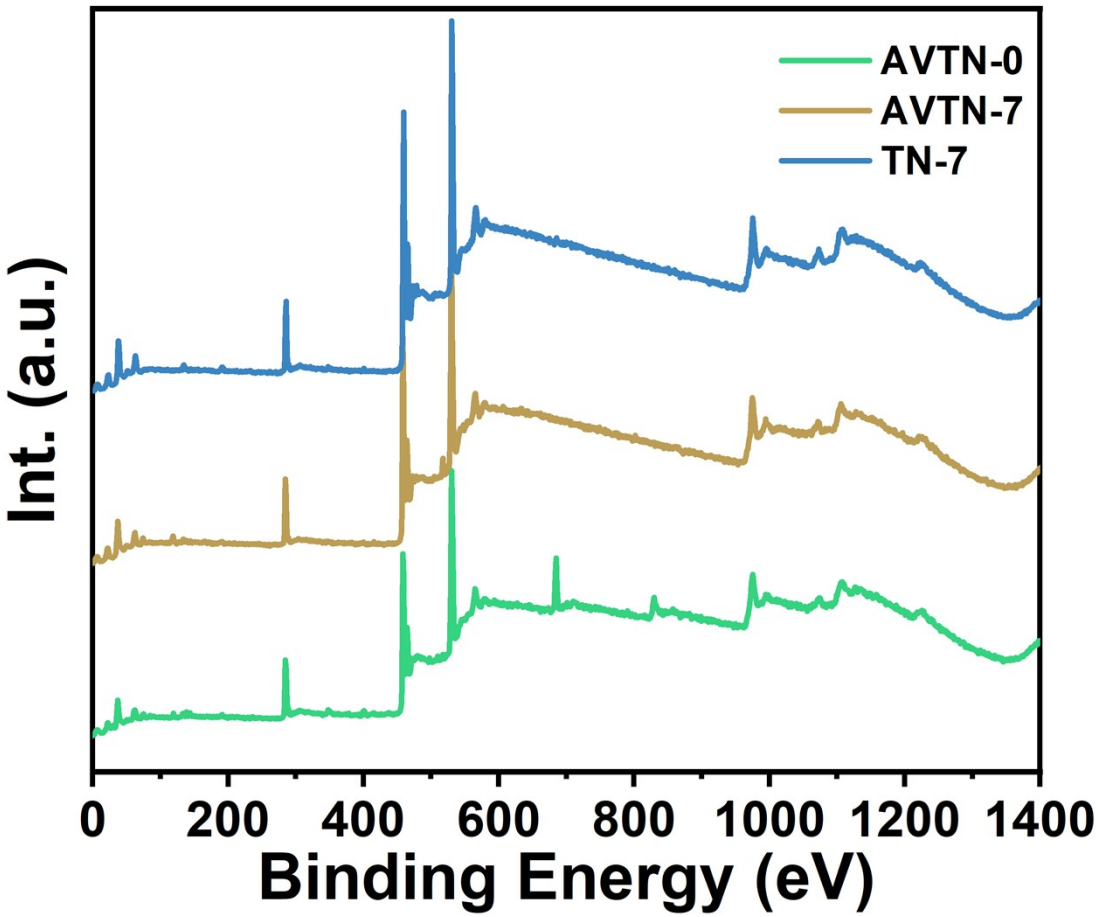

Figure S6 the XPS spectras of AVTN-0, AVTN-7 and TN-7

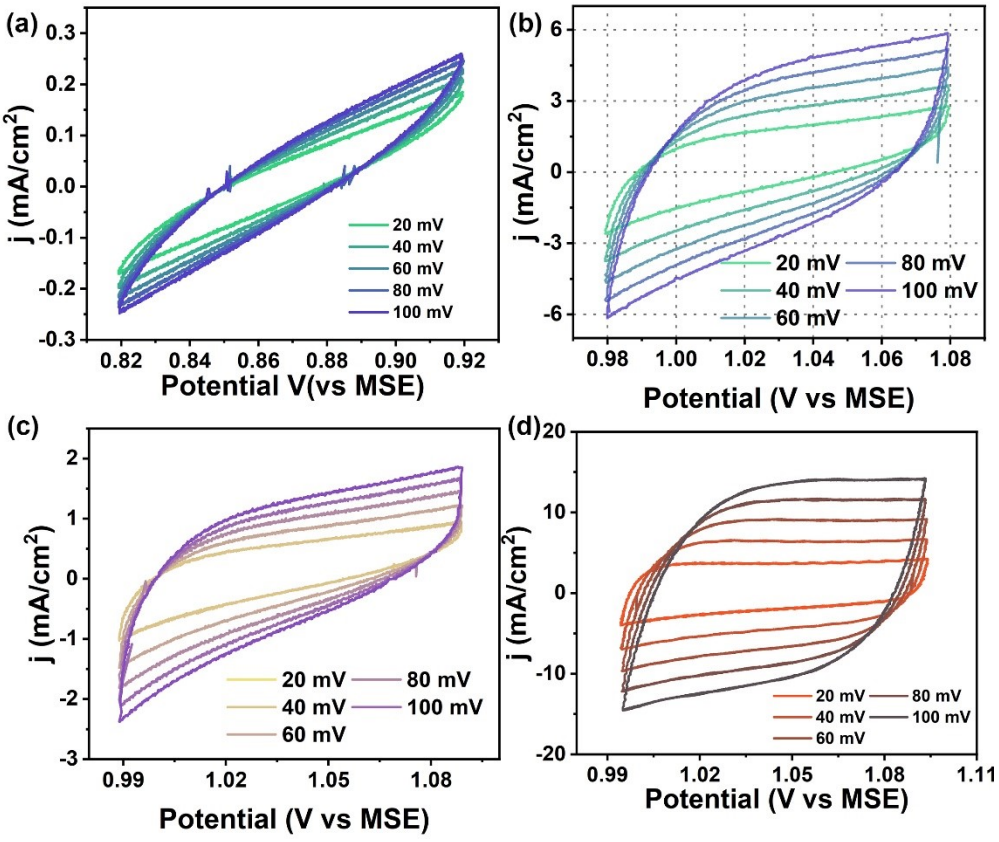

Figure S7 the CV curves of different electrodes

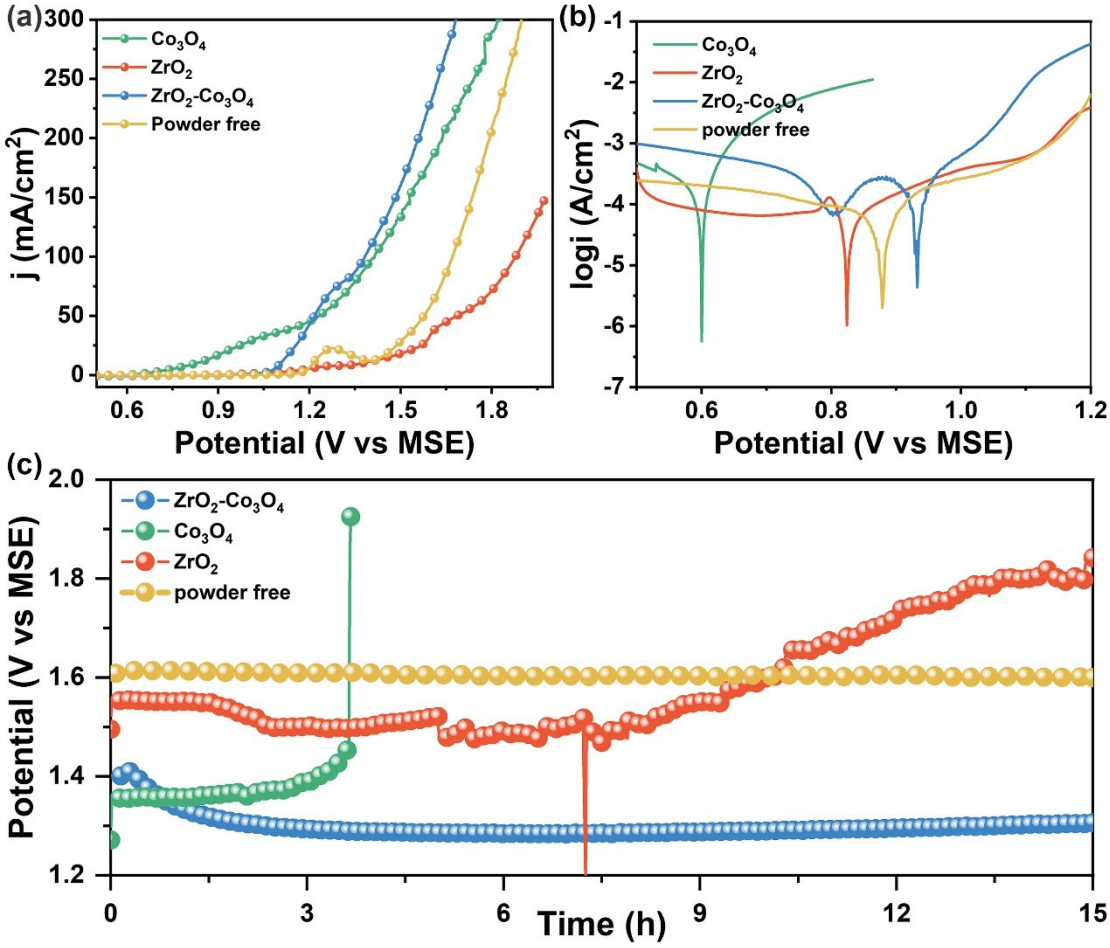

Figure S8 Electrochemical performance testing of the ZrO_2, Co_3O_4, and ZrO_2-Co_3O_4

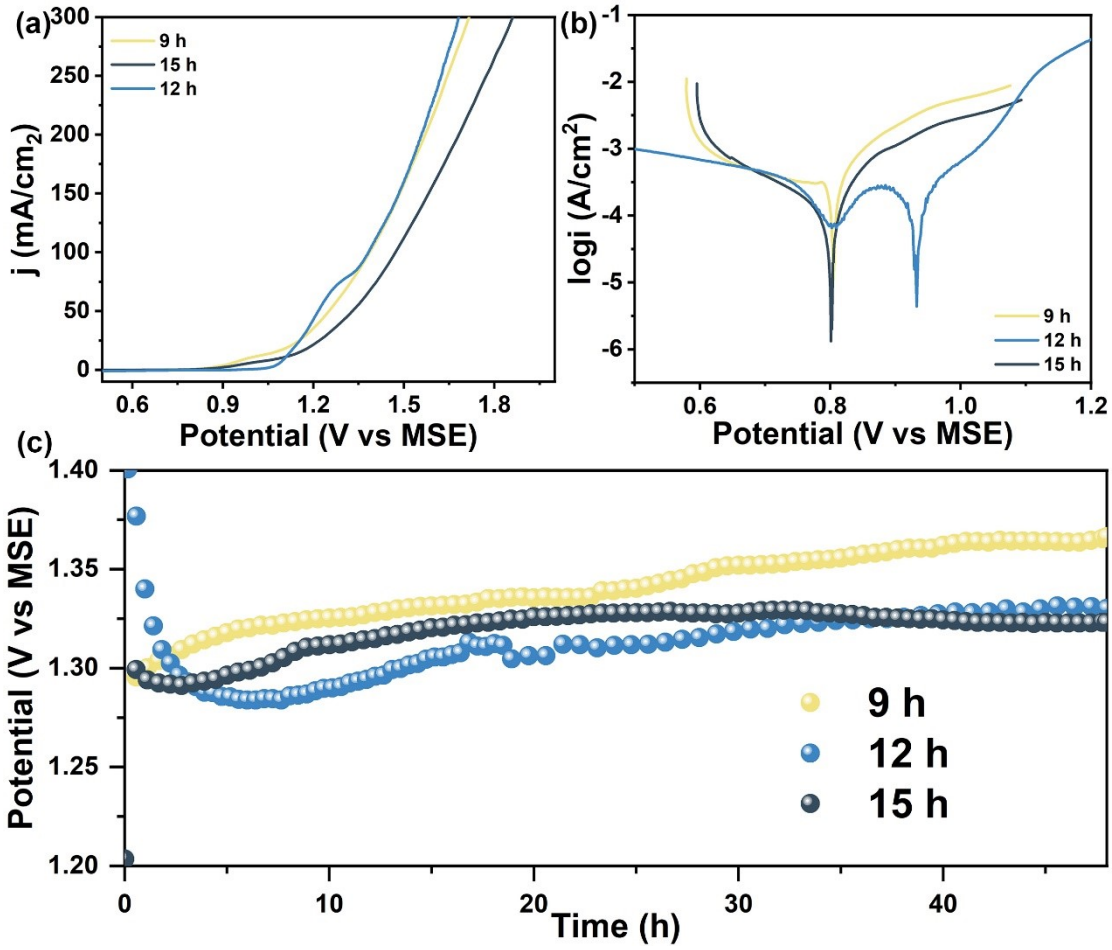

Figure S9 Electrochemical properties of powders annealed over time

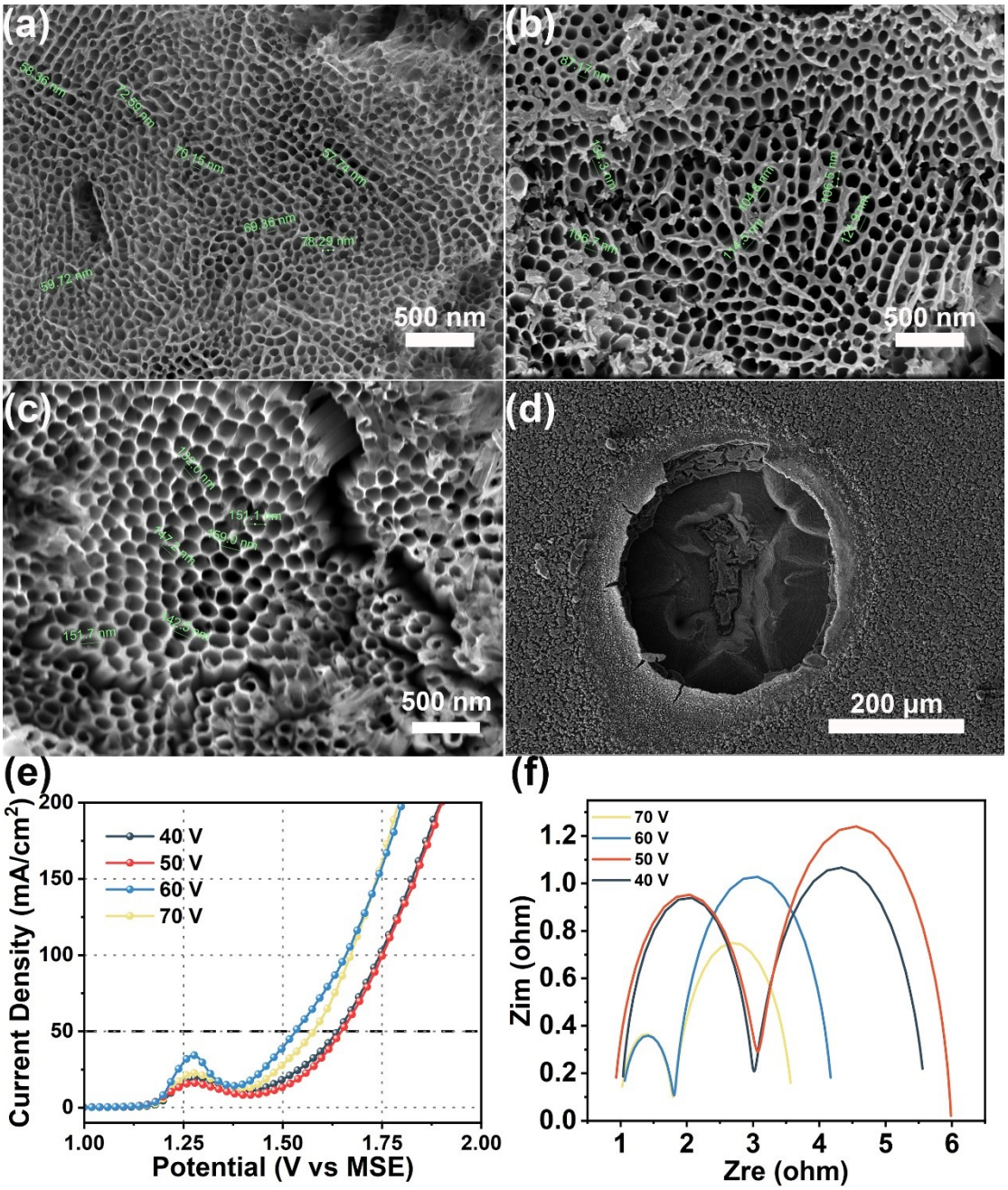

Figure S10 the SEM images of nanotubes at different oxidation voltages (a) 40 V;(b)50 V ;(c)60 V;(d)70 V;(e)(f)The LSV curves and Tafel plot of nanotubes at different oxidation voltages

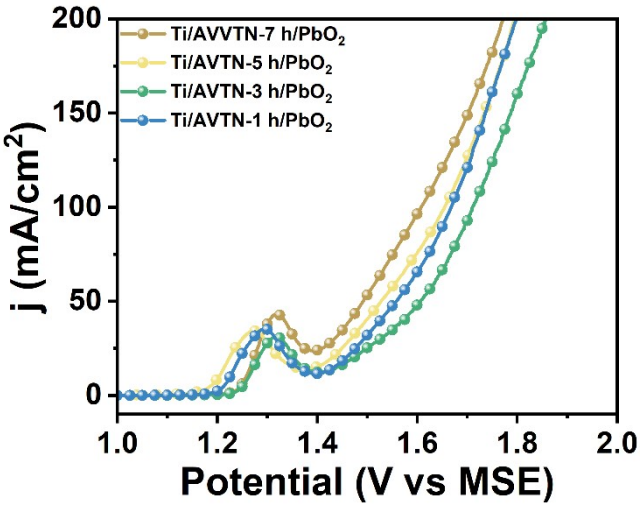

Figure S11 Electrochemical properties of AVTN-1, AVTN-3, AVTN-5 and AVTN-7