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Supporting Information

TePbPt Alloy Nanotube as Electrocatalyst with Enhanced Performances towards Methanol Oxidation Reaction

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Experimental Section

1 Materials

Poly-(N-vinyl-2-pyrrolidone)(PVP-K30, MW:55000), Na_2TeO_3, hydrazine hydrate (50% w/w%), ethylene glycol, aqueous ammonia solution (25% w/w%), chloroplatinic acid (H_2PtCl_6) were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) and used as received without further purification. Ethylenediaminetetraacetic acid (EDTA) was purchased from Aladdin. 5 wt% Nafion ionomer was obtained from Aldrich. Commercial state-of-the-art Pt black (Johnson

Matthey Company, HISPEC^{TM} 3000) was used as the benchmark for comparison and was denoted as Pt black -JM. Unless otherwise stated, other reagents were of analytical grade and were used as received. Ultrapure water (Millipore, 18.2MΩcm) was used throughout all experiments.

2 Synthesis of Te NWs

The Te nanowires were synthesized by the methods previous reports with a little modification.[1] Typically, 775 mg PVP and 71.5 mg Na_2TeO_3 were added in 28mL of double-distilled water to form a homogeneous suspension with vigorous magnetic stirring at room temperature. Then 1.28 mL hydrazine hydrate (50% w/w%) and 2.6 mL ammonia solution (25% w/w%) were added into the above suspension and dissolved to form a homogeneous suspension. The final mixture was transferred into a 40mL Teflon-lined stainless steel autoclave and closed. Then maintained at 180°C to react for 4 hours.

3 Synthesis of TePb NWs

After the above sample cool to the room temperature, the autoclave was opened and added 96.4 mg $Pb(NO_3)_2$ and 2 mL hydrazine hydrate (50% w/w%) with vigorous magnetic stirring at room temperature. Then the autoclave was closed and maintained at 60°C for 24 hours. The sample was washed and centrifuged by acetone and double-distilled water for several times after cooling to room temperature, respectively.

4 Synthesis of TePbPt alloy NTs

A certain amount of TePb nanowires were dispersed in 20 mL of ethylene glycol.

Then 8.5 mg H_2PtCl_6 dissolved in 12.5 mg/ml EDTA solution were added into the TePb nanowires solution. Then the sample was swayed for several seconds and let it react for 24 hours at room temperature. The sample was washed and centrifuged (10 000 rpm, 15min) by double -distilled water for several times, respectively.

5 Synthesis of TePt NTs

The TePt NTs were synthesized by the methods previous reports with a little modification.[1] A certain amount of Te nanowires were dispersed in 20 mL of EG with vigorous magnetic stirring at room temperature. Then, 1.29mL of 77mM H_2PtCl_6 solution in EG was added into the previous solution. The mixed solution was shaken for a moment. Then, the mixture was heated 13 hours under reflux in an oil-bath at 60℃. The products were collected by centrifugation (10 000 rpm, 15min) and washed several times with double-distilled water and absolute ethanol.

6 Physical characterizations

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (STEM) were conducted on a on a Philips TECNAI G2 electron microscope operated at 200 kV.

Energy dispersive X-ray analysis (EDX) and element mapping analysis were conducted on a XL30 ESEM FEG field emission scanning electron microscope (SEM) operating at 20 kV.

X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg Kα radiation source.

X-Ray diffraction (XRD) measurements were performed with a PW1700 diffract meter (Philips Co.) using a Cu Kα (λ=0.15405 nm) radiation source. The obtained XRD patterns were analyzed with Jade 5.0 software to remove the background radiation.

All elemental analyses of catalyst samples were analyzed by ICP-AES-MS (Inductivity Coupled Plasma-Atomic Emission Spectroscopy-Mass Spectroscopy) on a Thermo Elemental IRIS Intrepid.

7 Electrochemical measurements

Electrochemical measurements were carried out with an EG & G PARSTAT 4000 potentiostat/galvanostat (Princeton Applied Research Co., USA) in a conventional three electrode test cell. The catalyst ink was prepared by ultrasonically dispersing a mixture containing a mount of catalyst, 950 μL of ethanol and 50 μL of 5 wt % Nafion solution. Next, 5 μL of the catalyst ink was pipetted onto a pre-cleaned glassy carbon disk (diameter = 5 mm) (polish with 0.3 and 0.05 mm alumina powder, sonicated and rinsed with deionized water) as the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All of the potentials are relative to the SCE electrode, unless otherwise noted. In order to activate and clean the catalyst surface, the working electrodes were potentially cycled from -0.2 V and 0.958 V at a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4 solution until a stable response was obtained. (About 50 cycles) To evaluate the activity of the catalysts for methanol oxidation reaction (MOR), cyclic voltammograms (CVs) measurements were performed at room temperature between -0.2V and 0.958 V in an electrolyte solution containing 1.0 M CH_3OH and 0.5 M H_2SO_4, with scan rates of 50 mV s^{-1}. To investigate the anti-posing ability of the catalysts, 99.99% pure CO was purged to the cells filled with 0.5 M H_2SO_4 electrolyte for 30 min while the working electrode was held at 0.02 V vs. SCE. N_2 was then purged to the system for 30 min to remove non-adsorbed CO before the measurements were made. The CO stripping was performed in the potential range of -0.2~0.958 V at a scan rate of 50 mV s^{-1}. The electrochemical active surface areas (ECSA) and the tolerance to CO poisoning were estimated by the CO stripping test, assuming that the Coulombic charge required for the oxidation of the CO monolayer was 420 μ C cm^{-2}. To estimate the stability of the catalysts, the accelerated durability tests (ADT) experiments were performed in still 0.5 M H_2SO_4 and 1 M CH_3OH solutions. All electrolyte solutions were de-aerated by high-purity nitrogen for at least 20 min prior to each measurement.

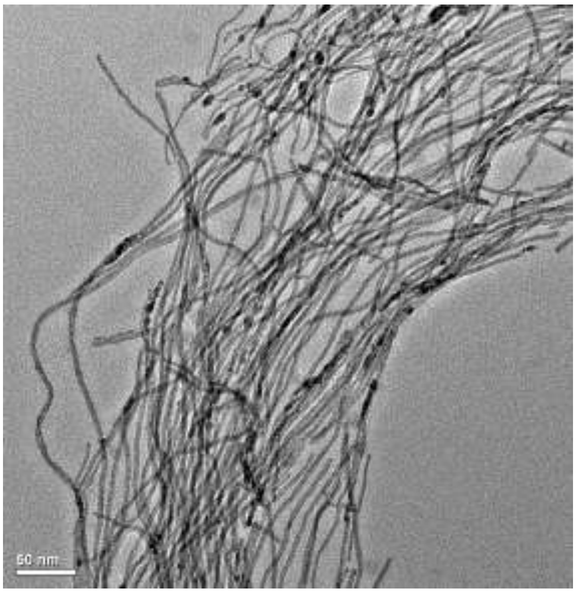

Fig. S1 TEM image of Te NWs.

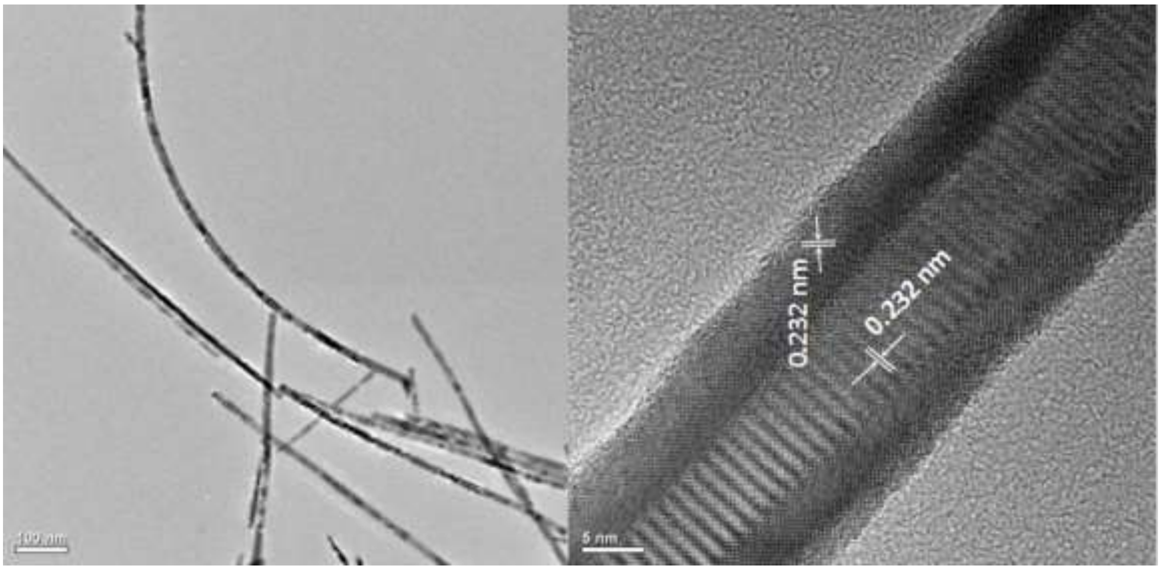

Fig. S2 TEM and HRTEM images of TePb NWs.

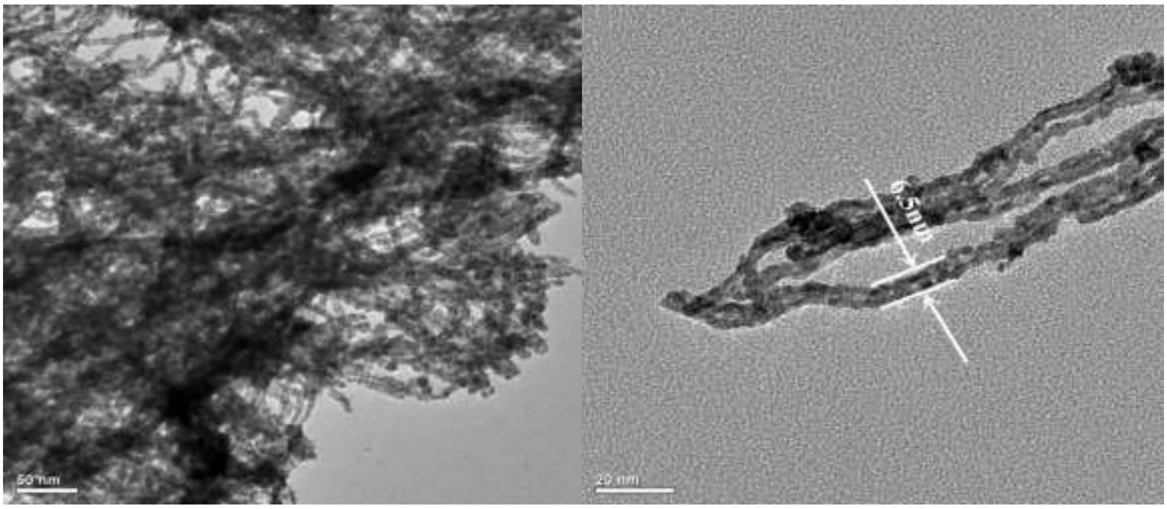

Fig. S3 TEM images of TePt NTs with different scales.

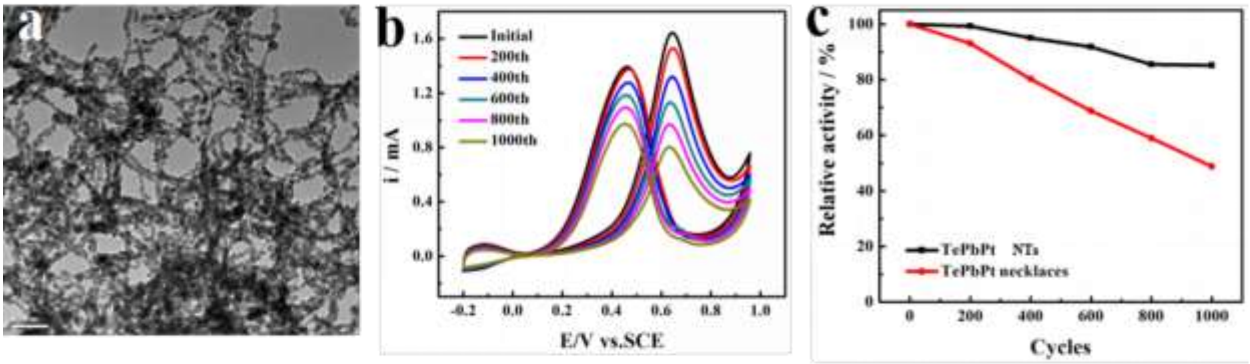

Fig. S4 TEM images of necklaces TePbPt (a), cyclic voltammograms in 1 M CH_3OH + 0.5 M H_2SO_4 solution for necklaces TePbPt during the ADT (b), the attenuation of MOR peak current density with the number of potential cycles (c).

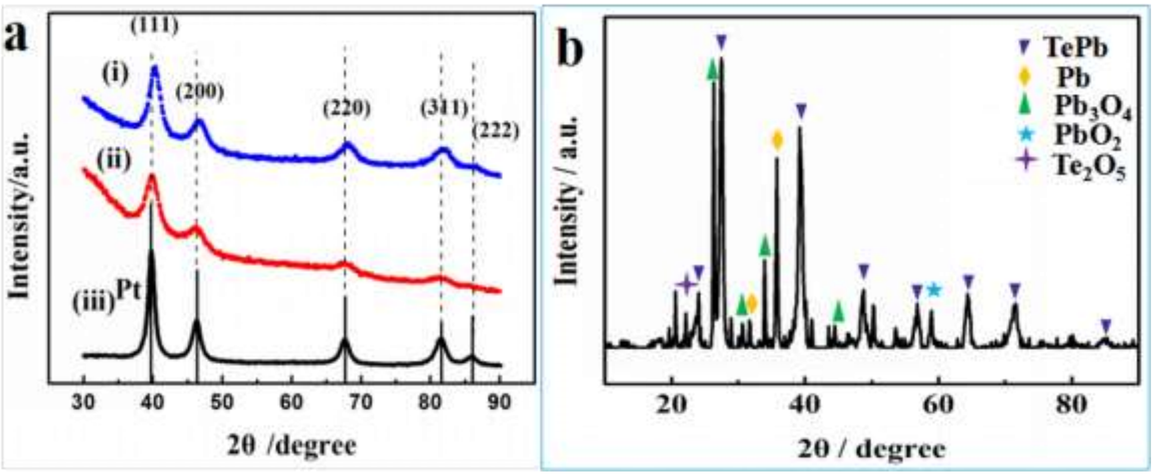

Fig. S5 XRD patterns of the TePbPt alloy NTs catalysts, TePt alloy NTs catalysts, commercial Pt black catalysts (a) and TePb alloy NWs (b).

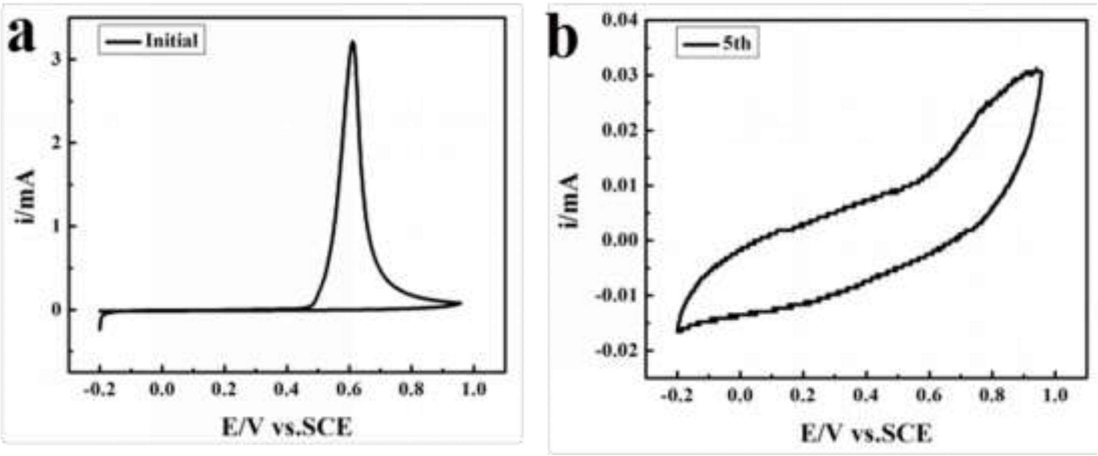

Fig. S6 Cyclic voltammograms in 0.5 M H_2SO_4 solution for Te NWs at the first cycle (a), and after the five cycles (b).

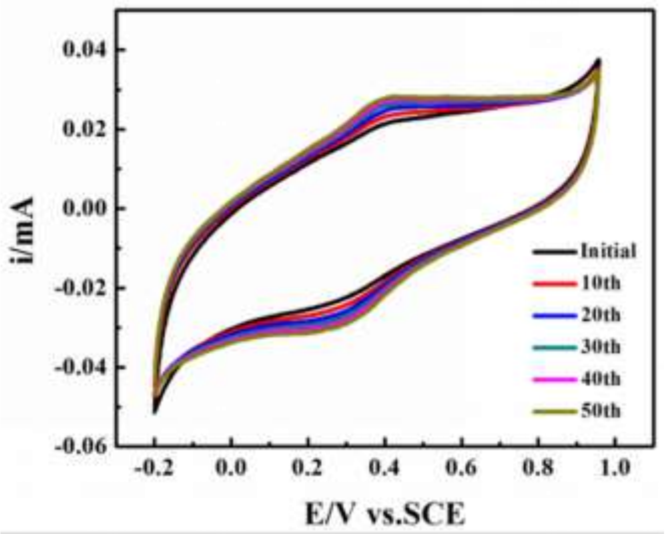

Fig. S7 Cyclic voltammograms in 0.5 M H_2SO_4 solution for Pb nanoparticles.

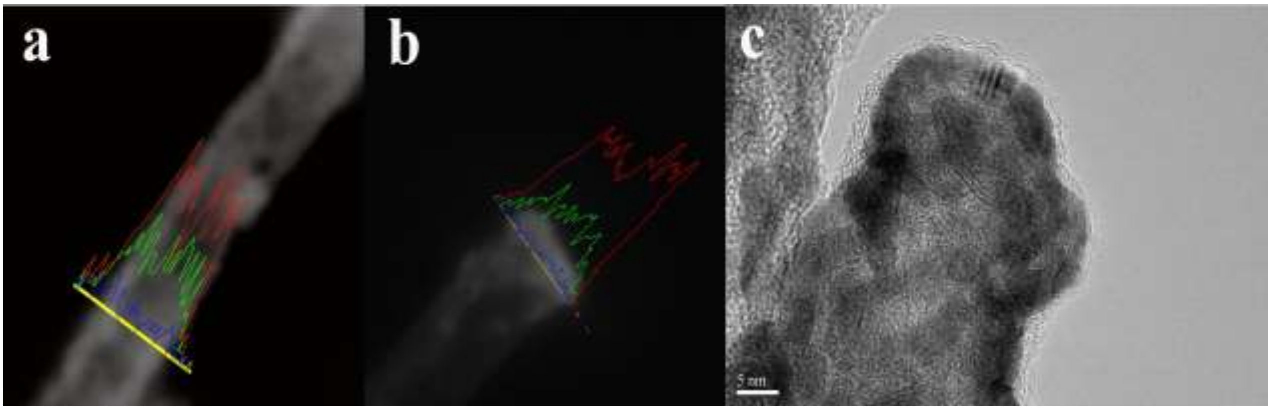

Fig. S8 Line profiles of TePbPt NTs catalyst before activation (a), after cyclic voltammograms test (b) and HRTEM of TePbPt NTs after activation (c) (Pt, the red line, Te, the green line, Pb, the blue line).

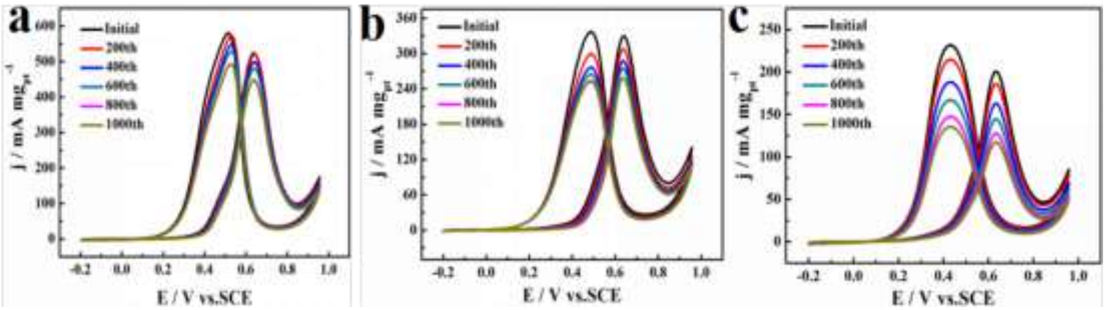

Fig. S9 Cyclic voltammograms in 1 M CH_3OH + 0.5 M H_2SO_4 solution for (a) TePbPt NTs, (b) TePt NTs, (c)commercial Pt black catalyst during the ADT.

Table S1 Electrochemical performance of the catalysts

	CO Stripping/mV		MOR activity		
	Peak potential	**$ECSA_{CO}/m^2/g$**	**Onset potential/mV**	**Mass activity / $mAmg_{Pt}^{-1}$**	**Specific activity / $mAcm^{-2}$**
TePt NTs	**482.5**	**19.75**	**421.6**	**332.5**	**1.68**
TePbPt NTs	**466.5**	**16.67**	**345.1**	**532.4**	**3.20**
Pt black -JM	**534.6**	**17.3**	**422.7**	**200.9**	**1.16**

References

1 H.-W. Liang, S. Liu, J.-Y. Gong, S.-B. Wang, L. Wang and S.-H. Yu, *Advanced Materials*, 2009, 21, 1850-+.