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## Carboxyethyltin and transition metal co-functionalized tungstoantimonates composited with polypyrrole for enhanced electrocatalytic methanol oxidation

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Carboxyethyltin and first-row transition metal (TM) were firstly introduced into trivacant Keggin-type tungstoantimonate in aqueous solution, leading to the formation of four crystalline organic-inorganic hybrid sandwich-type polyoxometalates, formulated as  $Na_{10-xy}K_yH_x[((TM)(H_2O)_3)_2(Sn(CH_2)_2COO)_2(SbW_9O_{33})_2]\cdotnH_2O$  (SbW<sub>9</sub>-TM-SnR, TM = Mn, Co, Ni, Zn; x = 1, 1, 0, 0; y = 0, 5, 5, 2; n = 18, 24, 24, 22, respectively). SbW<sub>9</sub>-TM-SnR exhibit high catalytic ability for the oxidation of cyclohexanol. Meanwhile, SbW<sub>9</sub>-TM-SnR was composited with polypyrrole (PPy) through an electropolymerization process, forming PPy-SbW<sub>9</sub>-TM-SnR, on which platinum (Pt) was further electro-deposited to prepare PPy-SbW<sub>9</sub>-TM-SnR/Pt for electrocatalytic methanol (CH<sub>3</sub>OH) oxidation in acid solution. The composition and morphology of PPy-SbW<sub>9</sub>-TM-SnR/Pt were determined by IR, scanning electron microscope (SEM), energy disperse spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The electrochemical experiment results show that SbW<sub>9</sub>-TM-SnR and PPy obviously enhance the electrocatalytic and anti-intoxication abilities of Pt, and the highest peak current density of 0.87 mA cm<sup>-2</sup>, corresponding to 1.85 and 1.43 times higher than those of pure Pt and PPy/Pt electrodes separately, is acquired for PPy-SbW<sub>9</sub>-Ni-SnR/Pt composite electrode. These findings may enlarge the application of PPy and POMs in electrocatalytic field.

#### Introduction

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Methanol oxidation reaction (MOR) is the anodic half-reaction in direct methanol fuel cells (DMFCs),<sup>1</sup> and the performance of anode catalysts is a determinant of the overall efficiency of fuel cells.<sup>2</sup> At present, Pt-based materials are still necessary anodic electrocatalysts in acidic medium for CH<sub>3</sub>OH electrooxidation,<sup>3</sup> although some Pt-free materials such as CeO<sub>2</sub>/Nano-ZSM-5, SnO<sub>2</sub>/m-ZSM-5 and Pd/C(PDA) have been proved to be active to CH<sub>3</sub>OH electrooxidation in alkaline solution.<sup>4-6</sup> However, Pt has the disadvantage of high cost, and the more prominent is that the active sites on pure Pt are easily adsorbed and blocked by CO<sub>ads</sub>-like intermediate products, causing the delay of further reactions, and this poisoning phenomenon is particularly obvious in an acidic electrolyte,7 which limits its practical use. Therefore, many strategies have been implemented for modification of Pt to further improve its catalytic activity and stability.<sup>8,9</sup>

Polyoxometalates (POMs) are a class of anionic nano-sized metal-oxygen clusters and can transfer electrons and protons

property and high stability.<sup>10</sup> In recent years, POMs have been broadly used in a variety of electronic devices such as solar cells, lithium-ion batteries, capacitors, liquid-flow cells and fuel cells.<sup>11–16</sup> For CH<sub>3</sub>OH electrooxidation, Keggin-type POMs  $([PM_{12}O_{40}]^{3-}, M = W, Mo)$  have been applied to increase the performance of Pt by acting as a kind of electron mediators and stabilizers.<sup>17,18</sup> Moreover, POMs could effectively promote the electrochemical oxidation of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>) in an aqueous solution.<sup>19</sup> It has been reported that sandwich-type ruthenium-containing POM  $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-SiW}_{10}O_{36})_2]^{10-}$ shows efficient electrocatalytic activity towards oxidation of ethanol and CH<sub>3</sub>OH, yielding aldehydes and acids with total faradaic efficiencies exceeding 94%.<sup>20</sup> As a result, the main merit of POMs in MOR is that the physicochemical properties of POMs can be easily adjusted by structure and composition modifications.

without structure changes owing to their excellent redox

Carboxyethyltin decorated POMs are a new class of unique POM-based organic-inorganic hybrids. In our recent work, it is found that the functionalities of POMs, such as photoelectric, electrocatalytic and oxidation catalytic activities, can be enhanced by introducing carboxyethyltin group.<sup>21–25</sup> Furthermore, the composites of POM-estertin derivatives with titanium dioxide (TiO<sub>2</sub>), *e.g.* TiO<sub>2</sub>/P<sub>2</sub>W<sub>15</sub>-Co-SnR and TiO<sub>2</sub>/PW<sub>9</sub>-Co-SnR, exhibit photoelectrocatalytic activity for oxidation of CH<sub>3</sub>OH.<sup>26</sup> Unfortunately, good electrocatalytic performance was not got in this system, which may be due to the poor

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<sup>&</sup>lt;sup>+</sup> Electronic Supplementary Information (ESI) available: ORTEP views and packing arrangement of **SbWg-TM-SnR (TM = Mn/Co/Ni/Zn)**; IR, XRPD, TG, Solid diffuse reflection absorption spectra, XPS, catalytic oxidation and electrocatalytic CH<sub>3</sub>OH oxidation results. CCDC reference numbers: 1885004 – 1885007.

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conductivity and low catalytic activity. Herein, considering the excellent modification effect of carboxyethyltin group on POMs, as an extension of our work, four cases of carboxyethyltin and TM co-functionalized tungstoantimonates  $Na_{10-x-y}K_yH_x[((TM)(H_2O)_3)_2(Sn(CH_2)_2COO)_2(SbW_9O_{33})_2]\cdot nH_2O$ 

(SbW<sub>9</sub>-TM-SnR, TM = Mn, Co, Ni, Zn; x = 1, 1, 0, 0; y = 0, 5, 5, 2; n = 18, 24, 24, 22, respectively) were designed and synthesized. Moreover, PPy-SbW<sub>9</sub>-TM-SnR composites were prepared through an electropolymerization process, and were further used to fabricate PPy-SbW<sub>9</sub>-TM-SnR/Pt composite electrodes with electro-deposition method. Their electrocatalytic activity towards oxidation of CH<sub>3</sub>OH was explored.

### Experimental

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#### Materials and methods

Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>, parent POMs Na<sub>9</sub>[B- $\alpha$ -SbW<sub>9</sub>O<sub>33</sub>]·19.5H<sub>2</sub>O  $(Na-SbW_9)$  and  $Na_{10}[Co_2(WO_2)_2(B-\beta-SbW_9O_{33})_2(H_2O)_6]\cdot40H_2O$ (Co-SbW<sub>9</sub>) were synthesized according to the literature methods.<sup>27,28</sup> H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and Pyrrole were purchased from Aladdin. All other reagents were of analytical grade and were not further purified before use. FTO conductive glass was purchased from HEPTACHROMA and used as substrate for electrochemical tests. The experimental water was doubledistilled water with the resistivity of 16 – 18 M $\Omega$  cm<sup>-1</sup>. C and H elemental analysis was performed with a Vario Elcube elemental analyzer, and Na, K, Sb, Sn, Mn, Co, Ni, Zn and W were analyzed with a Prodigy XP emission spectrometer. Single crystal X-ray diffraction data were collected on a Bruker Smart APEX X-diffractometer equipped with graphitemonochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). IR spectra (KBr pellets) were recorded on a Bruker AXS TENSOR-27 FTIR spectrometer in the range of 4000 – 400 cm<sup>-1</sup>. TG analysis was performed on a Pyris Diamond TG-DTA thermal analyzer at the heating rate of 10 °C min<sup>-1</sup> in air atmosphere. The solid diffuse reflectivity spectra were collected on a Cary series UV-Vis spectrophotometer in absorption mode, which was measured from 200 to 800 nm using  $BaSO_4$  as a standard with 100% reflectance. Field emission scanning electron microscopy (FESEM) was performed on Hitachi SU-8010. XRPD data were collected on a Bruker AXS D8 Advance diffractometer using Cu  $K\alpha$  radiation ( $\lambda$  = 1.5418 Å) in the 2 $\vartheta$  range of 5 – 50° with a step size of 0.02 °. XPS was operated on a VG ESCALAB MKII spectrometer using Mg Ka (1253.6 eV) achromatic X-ray source. All electrochemical experiments were performed with a CHI604B electrochemical workstation (Shanghai Chenhua Instrument Corp, China) at room temperature. A threeelectrode system was employed with a platinum wire as the counter electrode, an Ag/AgCl electrode as the reference electrode and the hybrids films electro-deposition on FTO electrode with an effective area of 1.0×1.0 cm<sup>2</sup> as the working electrode. For CO stripping experiments, first of all, CO was adsorbed on the prepared Pt-based catalysts by purging CO in the solution at the potential of 0.2 V for 15 min. Then, the dissolved CO was removed from the electrolyte by purging N<sub>2</sub>

for 30 min. Finally, the measurements were conducted in the potential range from 0 to 1.0 V at a scan rබዊቂ ቆቶ 50 ክናያ መንካሪያ መን

Synthesis of  $Na_4K_5H[(Co(H_2O)_3)_2(Sn(CH_2)_2COO)_2(SbW_9O_{33})_2]$ . 24H<sub>2</sub>O (SbW<sub>9</sub>-Co-SnR). A Parent POM Na-SbW<sub>9</sub> (0.286 g, 0.1 mmol), Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub> (0.062 g, 0.2 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.087 g, 0.3 mmol) were dissolved respectively in 10.0 mL of 0.4 mol L<sup>-1</sup> NaAc-HAc buffer solution (pH  $\approx$  5.0) to form solution A, B and C, respectively. Then solution B was slowly added to solution A, and stirred at 80 °C for 1 h, and then solution C was added dropwise to the above solution, and stirred for another 2 h. After cooling to room temperature, a certain amount of guanidine hydrochloride (C(NH<sub>2</sub>)<sub>3</sub>Cl) aqueous solution and KCl (s) were added to the obtained solution. Slow evaporation of the aqueous solution at 50 °C resulted in purple block crystals (yield: ca. 68.9% based on W) of SbW<sub>9</sub>-Co-SnR after about three days. Anal. calcd for  $C_6H_{69}K_5Na_4O_{100}Sb_2Co_2Sn_2W_{18}$  (SbW<sub>9</sub>-Co-SnR): C 1.21, H 1.17, K 3.29, Na 1.55, Sb 4.10, Co 1.99, Sn 4.00, W 55.74%; found: C 1.26, H 1.13, K 3.30, Na 1.51, Sb 4.05, Co 2.04, Sn 4.06, W 55.67%.

Synthesis of SbW<sub>9</sub>-TM-SnR (TM = Mn, Ni, Zn). The synthetic methods of  $Na_9H[(Mn(H_2O)_3)_2(Sn(CH_2)_2COO)_2(SbW_9O_{33})_2]$ ·18  $H_2O$  (SbW<sub>9</sub>-Mn-SnR),  $Na_5K_5[(Ni(H_2O)_3)_2(Sn(CH_2)_2COO)_2(SbW_9)]$  $O_{33}_{2}$ ]·24H<sub>2</sub>O (SbW<sub>9</sub>-Ni-SnR) and Na<sub>8</sub>K<sub>2</sub>[(Zn(H<sub>2</sub>O)<sub>3</sub>)<sub>2</sub>(Sn(CH<sub>2</sub>)<sub>2</sub>) COO)<sub>2</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·22H<sub>2</sub>O (SbW<sub>9</sub>-Zn-SnR) are similar to that of SbW<sub>9</sub>-Co-SnR by only replacing Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.087 g, 0.3 mmol) with MnCl<sub>2</sub>·4H<sub>2</sub>O (0.059 g, 0.25 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.088 g, 0.3 mmol), ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.086 g, 0.3 mmol) (yield: *ca*. 68.7%, 69.0% and 68.8% based on W), respectively. Anal. calcd for C<sub>6</sub>H<sub>57</sub>Na<sub>9</sub>O<sub>94</sub>Sb<sub>2</sub>Mn<sub>2</sub>Sn<sub>2</sub>W<sub>18</sub> (SbW<sub>9</sub>-Mn-SnR): C 1.26, H 1.00, Na 3.61, Sb 4.24, Mn 1.91, Sn 4.14, W 57.65%; found: C 1.30, H 1.05, Na 3.58, Sb 4.20, Mn 1.89, Sn 4.18, W 57.61%. C<sub>6</sub>H<sub>68</sub>K<sub>5</sub>Na<sub>5</sub>O<sub>100</sub>Sb<sub>2</sub>Ni<sub>2</sub>Sn<sub>2</sub>W<sub>18</sub> (SbW<sub>9</sub>-Ni-SnR): C 1.21, H 1.14, K 3.28, Na 1.93, Sb 4.09, Ni 1.97, Sn 3.98, W 55.53%; found: C 1.24, H 1.17, K 3.31, Na 1.97, Sb 4.11, Ni 2.00, Sn 4.02, W 55.41%. C<sub>6</sub>H<sub>64</sub>K<sub>2</sub>Na<sub>8</sub>O<sub>98</sub>Sb<sub>2</sub>Zn<sub>2</sub>Sn<sub>2</sub>W<sub>18</sub> (SbW<sub>9</sub>-Zn-SnR): C 1.22, H 1.09, K 1.33, Na 3.12, Sb 4.14, Zn 2.22, Sn 4.03, W 56.20%; found: C 1.26, H 1.06, K 1.39, Na 3.05, Sb 4.10, Zn 2.28, Sn 3.95, W 56.26%.

#### X-ray crystallography

The structures were solved by direct methods and refined on  $F^2$  by full- matrix least-squares fitting using SHELXTL-2014.<sup>29</sup> An empirical absorption correction was applied by using the SADABS program. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Hydrogen atoms on C atoms were added in calculated positions. Crystal data and structure refinement parameters of **SbW<sub>9</sub>-TM-SnR** are listed in Table 1. Selected bond lengths, angles and hydrogen bonds are listed in Tables S1–S8 (ESI<sup>†</sup>). CCDC reference numbers: 1885004–1885007.<sup>†</sup>

#### Catalytic oxidation of cyclohexanol to cyclohexanone

The catalytic experement refers to the method described in our previous work.<sup>30</sup> In a typical experiment, cyclohexanol (9.6 mL), catalyst (**SbW<sub>9</sub>-TM-SnR** or parent compounds, 0.03 mmol)

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Table 1 Crystal and refinement data for SbWg-TM-SnR (TM = Mn, Co, Ni, Zn)

Compound	SbW₀-Mn-SnR	SbW <sub>9</sub> -Co-SnR	SbW₀-Ni-SnR	SbW₀-Zn-SnR
Formula	$C_6H_{57}Na_9O_{94}Sb_2Mn_2Sn_2W_{18}$	$C_6H_{69}K_5Na_4O_{100}Sb_2Co_2Sn_2W_{18}$	$C_6H_{68}K_5Na_5O_{100}Sb_2Ni_2Sn_2W_{18}$	$C_6H_{64}K_2Na_8O_{98}Sb_2Zn_2Sn_2W_{18}$
Formula weight	5740.48	5937.11	5958.65	5887.61
<i>т/</i> к	296(2)	296(2)	296(2)	296(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	Pī	Pī	Pī	Pī
a/Å	12.621(3)	12.4391(12)	12.4828(18)	12.4709(19)
b/Å	12.751(2)	12.6196(12)	12.6293(17)	12.6542(18)
c/Å	16.797(3)	16.3813(16)	16.440(2)	16.428(2)
α/°	93.553(3)	94.581(2)	94.595(2)	94.899(2)
β/°	110.782(3)	109.896(2)	109.959(2)	109.885(3)
γ/°	99.534(3)	101.759(2)	101.665(2)	101.197(3)
V/Å ³ , Z	2470.8(8)	2335.9(4)	2354.3(6)	2359.0(6)
Dc/g cm $^{-3}$ , F $_{000}$	3.858, 2528	4.220, 2632	4.203, 2644	4.144, 2604
GOF	1.031	0.979	1.037	1.093
Reflections collected	12707	12118	12005	11121
R <sub>int</sub>	0.0288	0.0329	0.0389	0.0471
ϑ Range (°)	1.633-25.000	1.340-25.000	1.335-24.999	1.336-25.000
R <sub>1</sub> (I > 2σ(I)) <sup>a</sup>	0.0417	0.0365	0.0419	0.0955
$wR_2$ (all data) <sup>a</sup>	0.1192	0.0788	0.0977	0.3894

and acetonitrile (10.0 mL) were added into 100 mL threenecked round-bottom flask with water condenser, and 30% of  $H_2O_2$  (20.0 mL) as oxidant was slowly added dropwise to the mixture over 3 h with the reaction temperature of about 88 °C. After completing the reaction, the solvent acetonitrile was removed by distillation, and thus organic and inorganic phases could be separated by separatory funnel extraction method, and the catalyst was remained in the reaction vessel. The reaction products were characterized by gas chromatography. **Preparation of PPy-POM/Pt composite films** 

Primarily, FTO glasses were ultrasonically cleaned with detergent solution, double-distilled water, acetone and ethanol successively. Then it was processed with piranha solution for 30 minutes, and rinsed with double-distilled water and dried under a stream of N<sub>2</sub>, standby for application. First of all, PPy-POM composite films were prepared by potentiostatic electropolymerization under + 0.65 V in a threeelectrode system consisting of the cleaned FTO glass as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The electrolyte solution was composed of 0.1 mol L<sup>-1</sup> pyrrole, 1.0 mmol L<sup>-1</sup> POM (SbW<sub>9</sub>-TM-SnR) and 0.02 mol L<sup>-1</sup> tetrabutylammonium bromide. The prepared films were rinsed with double-distilled water and dried under a stream of N2. Subsequently, Pt particles were deposited on the surface of PPy-POM composite film-modified FTO electrodes in situ by potentiostatic electrodeposition at -0.2 V in a 0.5 mol  $L^{-1}\ H_2SO_4$  solution containing 1.0 mmol  $L^{-1}$  $H_2PtCl_6$ , and the polymerization time was 150 s, followed by rinsing with double-distilled water and drying under N<sub>2</sub> atmosphere.

#### **Results and discussion**

#### Synthesis

By using Na-SbW<sub>9</sub> as an inorganic building block, estertin Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub> as an organic precursor, and TM ions as modified components, new POM-based organic-inorganic hybrids are successfully constructed by carefully adjusting the synthetic conditions. As seen from Scheme 1, step I, when selecting double-distilled water as a solvent, only powders were obtained as the molar ratio range of Na-SbW<sub>9</sub>:estertin:TM was from 1:2:2 to 1:4:4. Considering the sensitivity of lacunary POM to pH in aqueous solution, a buffer solution of 0.4 mol L<sup>-1</sup> NaAc-HAc (pH  $\approx$  5.0) was selected as a solvent with refer to the stable pH value of  $[SbW_9O_{33}]^{9-}$  (SbW<sub>9</sub>) subunit, and the influence of the molar ratio of the reactants on the formation of crystalline products was investigated. As shown in Scheme 1, step II, when the molar ratio was 1:2:2, 1:3.5:3.5 and 1:4:4, respectively, no crystal was obtained. While, at the same pH (5.0), the molar ratio was changed to 1:(2.5-3):(2.5-3), four new crystalline Keggin sandwich-type tungstoantimonates (SbW<sub>9</sub>-TM-SnR, TM = Mn, Co, Ni, Zn) were successfully obtained (Scheme 1, step IIIa). It is found that these four tungstoantimonates are isostructural although containing different TM ions. And it is worth noting that the POM unit  $B-\alpha$ -**SbW** has converted to  $B-\beta$ -**SbW** (Scheme 1, furthermore, the Step IIIb). original estertin [Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>]<sup>3+</sup> group has hydrolyzed into carboxyethyltin [Sn(CH<sub>2</sub>)<sub>2</sub>COO]<sup>2+</sup> group during this synthetic process (Scheme 1, Step IIIc). As can be seen from our synthetic strategies for





Scheme 1 Schematic representation of the formation of SbW9-TM-SnR (TM = Mn/Co/Ni/Zn).



Fig. 1 Single crystal structure of SbW<sub>9</sub>-TM-SnR (TM = Mn, Co, Ni, Zn), the polyhedral and ball-and-stick representation of the isostructural polyoxoanions (a); the ball-and-stick representation of the central belt (b) (H atoms, K and Na cations, and free water molecules have been omitted for clarity).

**SbW**<sub>9</sub>-**TM-SnR**, through controlling pH and molar ratio of the reactants, the carboxyethyltin and TM ions co-functionalized Keggin sandwich-type organic-inorganic hybrids based on trivacant **SbW**<sub>9</sub> POM can be prepared after crystallization process.

#### Structural analysis

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Single crystal X-ray structure analysis indicates that the polyoxoanions of SbW9-TM-SnR display the well-known Keggin sandwich-type structures (Fig. 1). In the four compounds, the  $B-\beta$ -**SbW**<sub>9</sub> unit can be regarded as an isomer of  $B\text{-}\alpha\text{-}\textbf{SbW}_{9}\text{,}$  in other words, the in-plane rotation of one edge-shared  $\{W_3O_{13}\}$  fragment in B- $\alpha$ -**SbW**<sub>9</sub> by 60° yields the above B-β-SbW<sub>9</sub> unit. Estertin precursor [Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>]<sup>3+</sup> was found to be hydrolyzed into carboxyethyltin [Sn(CH<sub>2</sub>)<sub>2</sub>COO]<sup>2+</sup> during the reaction process. In SbW<sub>9</sub>-TM-SnR, each symmetrical unit consists of a B-β-SbW<sub>9</sub> subunit modified by one Mn/Co/Ni/Zn ion and one carboxyethyltin group (Fig. S1, ESI<sup>+</sup>). The polyoxoanion structures in SbW<sub>9</sub>-TM-SnR are isostructural, and the central belt contains two symmetrical inner organotin groups, and two (TM)O<sub>6</sub> (i.e. MnO<sub>6</sub>/CoO<sub>6</sub>/NiO<sub>6</sub>/ZnO<sub>6</sub>) fragments located in the outer opposite positions (Fig. 1a). As shown in Fig. 1b, each Mn/Co/Ni/Zn ion was matched with three terminal oxygen

atoms (O11, O20, O24) in three WO<sub>6</sub> octahedra and three water molecules (O1W, O2W, O3W). Each Sn1/Sn1' atom coordinates with four terminal oxygen atoms (O4, O6, O22, O23) from four  $WO_6$  octahedra and a carbon atom C1 and an oxygen atom O34 from a [Sn(CH<sub>2</sub>)<sub>2</sub>COO]<sup>2+</sup>. Sn1, Sn1', W1 and W1' form a close ring through sharing-briged atoms O4, O4', O6 and O6'. The bond lengths of Sn-O and Sb-O are in the range of 2.02(4) - 2.188(10) Å and 1.991(9) - 2.034(10) Å, separately. The Sn-C bond lengths are 2.113(16) - 2.148(12) Å. The W–O and TM–O distances are in the range of 1.66(4) – 2.38(4) Å and 2.00(8) – 2.240(13) Å, respectively (Tables S1–S4, ESI<sup>†</sup>). In **SbW**<sub>9</sub>-**TM-SnR**, the sandwich-type polyoxoanions and Na<sup>+</sup>/K<sup>+</sup> cations, free water molecules are accumulated to form 3D supramolecular frameworks by OW-H…O/OW hydrogen bonds (2.24(4) - 3.369(16) Å) (Tables S5-S8, ESI<sup>†</sup>) between water molecules and the polyoxoanions or among water molecules, as well as the electrostatic forces between Na<sup>+</sup>/K<sup>+</sup> cations and polyoxoanions (Fig. S2, ESI<sup>†</sup>).

#### Characterization

IR spectra. IR spectra of SbW<sub>9</sub>-TM-SnR (TM = Mn, Co, Ni, Zn) (Fig. S3, ESI<sup>†</sup>) are similar. As shown in Fig. S3 (ESI<sup>†</sup>), the vibration peaks between 950 and 670 cm<sup>-1</sup> are attributed to v(W=O<sub>t</sub>), v(Sb–O<sub>a</sub>), v(W, TM–O<sub>c</sub>) and v(W–O<sub>b</sub>) (O<sub>t</sub>, O<sub>a</sub>, O<sub>b</sub> and O<sub>c</sub> are terminal, tetrahedral, edge- and corner-sharing oxygen atoms).<sup>31,32</sup> The peaks at 503-509 cm<sup>-1</sup> are assigned to the antisymmetric and symmetric vibrations of Sn-C bonds, and the stretching vibrations of Sn–O bond are at 467–495 cm<sup>-1.33</sup> The bands at 1648–1571 cm<sup>-1</sup> and 1345–1360 cm<sup>-1</sup> correspond to  $v_{as}(COO)$ and *v*<sub>s</sub>(COO) vibrations, respectively.<sup>34</sup> The broad bands of lattice water molecules are located at 3400-3424 cm<sup>-1</sup>. The peaks at 2917-2924 and 2849-2861 cm<sup>-1</sup> are attributed to the characteristic vibrations of the organic group (-CH<sub>2</sub>).<sup>24</sup> IR spectra indicate that carboxyethyltin group and POM framework exist in SbW<sub>9</sub>-TM-SnR, which are in good agreement with the singlecrystal structural analysis.

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Thermal gravimetric (TG) analysis. The thermal stability of SbW9-TM-SnR was investigated by TG curves in the range from room temperature to 1000 °C (Fig. S4, ESI<sup>+</sup>). As shown in Fig. S4 (ESI<sup>+</sup>), the four compounds exhibit similar threestep continuous weight loss processes. The first weight loss in the ranges of 36-366, 36-388, 36-254 and 36-399 °C is 5.95, 7.13, 7.46 and 6.22%, respectively (corresponding to the calculated values of 5.64, 7.28, 7.28 and 6.73%), owing to the loss of crystal water molecules in SbW9-Mn-SnR, SbW9-Co-SnR, SbW<sub>9</sub>-Ni-SnR and SbW<sub>9</sub>-Zn-SnR, respectively. The last two step weight losses of 4.22% at 268-913 °C for SbWg-Ni-SnR meet the theoretical value (4.23%) of loss of coordination water molecules and (CH<sub>2</sub>)<sub>2</sub>COO groups. While for SbW9-Mn-SnR, SbW9-Co-SnR and SbW9-Zn-SnR, the last two weight losses of 2.98, 2.89 and 2.29% at 355-823 °C, 388-863 °C and 388-887 °C respectively are all lower than the calculated values (4.39, 4.25 and 4.28%), which means that SbW9-TM-SnR (TM = Mn, Co, Zn) only lose coordination water molecules and part of (CH<sub>2</sub>)<sub>2</sub>COO groups. The above analytical results show that the carboxyethyltin and TM cofunctionalized sandwich-type tungstoantimonates have higher thermal stability, which are also verified by IR spectra of SbW<sub>9</sub>-TM-SnR samples burned at different temperatures in air (Fig. S5, ESI<sup>†</sup>). As seen from Fig. S5 (ESI<sup>†</sup>), at 380, 520, and 800 °C, the characteristic peaks of POM and CH<sub>2</sub> group are still retained and up to 800 °C, meanwhile the characteristic peaks of  $v_{as}(COO)$  and  $v_s(COO)$  are also maintained in spite of a little blue shifts.

Solid diffuse reflection absorption spectra. The optical absorption behavior of SbW<sub>9</sub>-TM-SnR was studied by solid diffuse reflection absorption spectroscopy. It can be seen that SbW<sub>9</sub>-TM-SnR (TM = Mn, Co, Ni, Zn) display a strong absorption band emerging in the  $\lambda$  range from 200 to 400 nm (Fig. S6, ESI†), and the max absorbance is at 318, 315, 325 and 316 nm, respectively, which should be attributed to oxygen to metal (O<sub>bridging</sub>->W) charge transfer transition.<sup>35</sup> Moreover, SbW<sub>9</sub>-Co-SnR shows an extra absorption band from 450 to 650 nm, and SbW<sub>9</sub>-Ni-SnR shows two extra absorption bands from 370 to 800 nm in the visible region, which can be attributed to *d*-*d* transition of Co/Ni ions.

**NMR analysis.** The structures of **SbW**<sub>9</sub>**-TM-SnR** (TM = Mn, Co, Ni, Zn) were further confirmed by <sup>119</sup>Sn NMR spectrum (Fig. 2). From the results shown in Fig. 2a–c, it is found that the chemical shifts ( $\delta$ ) at – 519.06, – 491.75 and – 509.32 ppm of <sup>119</sup>Sn for **SbW**<sub>9</sub>-**Co-SnR**, **SbW**<sub>9</sub>-**Ni-SnR** and **SbW**<sub>9</sub>-**Zn-SnR** have shifted to high field compared with the <sup>119</sup>Sn NMR peak of precursor Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub> ( $\delta$  = – 115.51 ppm),<sup>36</sup> which is due to the increased electron density on Sn atom. The result shows that the organotin group has been successfully incorporated into the POM system. While <sup>119</sup>Sn NMR signal of **SbW**<sub>9</sub>-**Mn-SnR** was not detected under our experiment condition because of its low solubility and paramagnetism of Mn<sup>2+</sup>.

X-ray powder diffraction (XRPD). The XRPD spectra of  $SbW_9$ -TM-SnR are used to test the purity of these compounds (Fig. S7, ESI<sup>+</sup>). It can be seen from the graphs in

Fig. S7 (ESI†) that the experimental values of the four the work samples match well with the simulated values of the PSIA  $18^{\circ}$ 



Fig. 2 <sup>119</sup>Sn NMR spectra of  $SbW_9$ -Co-SnR (a),  $SbW_9$ -Ni-SnR (b) and  $SbW_9$ -Zn-SnR (c) in D<sub>2</sub>O.



Fig. 3 CV curves of  $SbW_9$ -Mn-SnR (a),  $SbW_9$ -Co-SnR (b),  $SbW_9$ -Ni-SnR (c), and  $SbW_9$ -Zn- SnR (d) in 0.4 mol L<sup>-1</sup> NaAc-HAc solution (pH = 5).

crystals, indicating that the four compounds are pure phase. The difference of peak strength may be due to the different orientation of samples, the destruction of crystal water during the test and the change of specimen shape.

**Cyclic voltammetry (CV).** In order to study the electrochemical behavior of **SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn), the CV curves of four compounds in 0.4 mol L<sup>-1</sup> NaAc-HAc buffer solution (pH = 5.0) were obtained at the scan rate of 50 mV s<sup>-1</sup> (Fig. 3). As shown in Fig. 3, in the voltage range from 0 to – 1.0 V *vs* Ag/AgCl, **SbW**<sub>9</sub>-**TM-SnR** all exhibit one pair of redox peaks (I-I') located at – 0.777 and – 0.644 V, – 0.760 and – 0.630 V, – 0.786 and – 0.630 V, – 0.755 and – 0.647 V, respectively, which are assigned to the redox process of W centers.<sup>35</sup> Meanwhile, there are also another

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reduction peak (II) for **SbW<sub>9</sub>-TM-SnR** (TM = Mn, Co, Ni, Zn) at -0.542, -0.516, -0.531 and -0.510 V, respectively. To



Fig. 4 Influence of reaction time (a) and catalyst dosage (*n*(cyclohexanol)/*n*(W)) (b) on cyclohexanol conversion using **SbW**<sub>3</sub>-**Ni-SnR** as a catalyst.

attribute this, the CV curves of precursor estertin and **Na-SbW**<sub>9</sub> were recorded. For estertin, it has one irreversible reduction peak located at -0.662 V (Fig. S8, ESI<sup>†</sup>). **Na-SbW**<sub>9</sub> has one pair of peaks (I-I') located at -0.679 and -0.594 V (Fig. S9, ESI<sup>†</sup>), corresponding to the redox process of W center. In comparison with **Na-SbW**<sub>9</sub>, the redox peaks of W centers for **SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn) show negative shifts, which is manifested in the previous work.<sup>37,38</sup> Comprehensive comparison of these CV results, the peak (II) in CVs of **SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn) belongs to the signal of Sn center. Moreover, from Fig. 3a, we can see one pair of redox peaks (III-III') located at 0.632 and 0.924 V, which are due to the redox process of Mn ion.<sup>39</sup>

#### Catalytic oxidation performance

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In this paper, the oxidation of cyclohexanol to cyclohexanone by  $H_2O_2$  was selected as a model reaction to study the oxidation catalytic performance of **SbW<sub>9</sub>-TM-SnR** (TM = Mn, Co, Ni, Zn). Using **SbW<sub>9</sub>-TM-SnR** as a catalyst and  $H_2O_2$  as an oxidant with the molar ratio of 1:2.2 for cyclohexanol to  $H_2O_2$ ,<sup>28</sup> the effects of catalyst dosage and reaction time on the conversion of cyclohexanol were explored.

Taking SbW<sub>9</sub>-Ni-SnR as an example, the catalytic oxidation of cyclohexanol was carried as the follows: 0.030 mmol SbW<sub>9</sub>-Ni-SnR, 20.0 mL of 30% H<sub>2</sub>O<sub>2</sub>, 9.6 mL of cyclohexanol and 10.0 mL of acetonitrile were added into the reaction system, and the reaction temperature was about 88 °C (Fig. 4). As can be seen from Fig. 4a, the conversion of cyclohexanol reaches 94.6% at 3 h, and further increasing reaction time results in a little increase of conversion, so, the best reaction time is determined to be 3 h. Under the reaction time of 3 h and the other reaction conditions remaining unchanged, when the molar ratio of W/cyclohexanol is 1:200, that is, the dosage of SbWg-Ni-SnR is 0.030 mmol, the cyclohexanol conversion reaches the maximum (94.6%) (Fig. 4b). Moreover, when the catalyst dosage is 0.017 mmol, the conversion rate of cyclohexanol can still reach up to about 85%, which shows that the catalyst shows good catalytic oxidation activity.

Subsequently, under the above determined optimum reaction conditions, that the reaction time is 3 h and the dosage of the catalyst is 0.030 mmol, the catalytic oxidation activity of four new compounds, their parent POM **Na-SbW**<sub>9</sub>,

simple TM salts (MnCl<sub>2</sub>·4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NQ<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>Q and ZnSO<sub>4</sub>·7H<sub>2</sub>O) and the precursor ester th have been TO5118F



Fig. 5 IR spectra of PPy-SbWg-TM-SnR (TM = Mn, Co, Ni, Zn).



Fig. 6 SEM images of PPy-SbW<sub>9</sub>-Mn-SnR/Pt (a), PPy-SbW<sub>9</sub>-Co-SnR/Pt (b), PPy-SbW<sub>9</sub>-Ni-SnR/Pt (c), PPy-SbW<sub>9</sub>-Zn-SnR/Pt (d) composite films, Pt microparticles (e) on FTO and EDS of PPy-SbW<sub>9</sub>-Ni-SnR/Pt composite (f).

evaluated. The conversions of cyclohexanol are listed in Table S9 (ESI<sup>†</sup>), from which it can be seen that the catalytic performance of **SbW**<sub>9</sub>-**TM-SnR** is obviously higher than those of **Na-SbW**<sub>9</sub>, TM salts and estertin. The conversions of cyclohexanol are 88.7, 92.1 94.6 and 91.2% for **SbW**<sub>9</sub>-**Mn-SnR**, **SbW**<sub>9</sub>-**Co-SnR**, **SbW**<sub>9</sub>-**Ni-SnR** and **SbW**<sub>9</sub>-**Zn-SnR**, respectively. As a result, **SbW**<sub>9</sub>-**TM-SnR** is proved to be a good kind of oxidation catalysts. The introduction of SnR group and TM ions is able to obviously enhance the catalytic oxidation activity of the sandwich-type tungstoantimonate. **Characterization of PPy-SbW**<sub>9</sub>-**TM-SnR/Pt composite film** 

In viewing of good redox property, **SbW**<sub>9</sub>-**TM-SnR** was used for assistant electropolymerization of pyrrole, forming PPy-**SbW**<sub>9</sub>-**TM-SnR** composite on the FTO substrate, on which Pt was further deposited to prepare PPy-**SbW**<sub>9</sub>-**TM-SnR**/Pt composite. Here, PPy can improve electrical conductivity as a conductive polymer, and **SbW**<sub>9</sub>-**TM-SnR** is expected to modulate the catalytic activity of Pt.

IR spectra of PPy-**SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn) composite materials all contain four absorption bands between 1000 and 600 cm<sup>-1</sup>, which are assigned to the characteristic peaks of  $v(W=O_t)$ ,  $v(Sb-O_a)$ ,  $v(W, TM-O_c)$  and  $v(W-O_b)$  in **SbW**<sub>9</sub>-**TM-SnR** (Fig. 5). Besides, the absorption

bands at 1620 and 1570  $\rm cm^{-1}$  correspond to the pyrrole ring stretching vibrations in PPy.  $^{40}$  Hence, IR spectra verify the



Fig. 7 XPS spectra of Sn 3d (a), C 1s (b), N 1s (c), O 1s (d), W 4f (e) of PPy-SbW<sub>9</sub>-Co-SnR/Pt, Pt 4f of PPy/Pt (f) and PPy-SbW<sub>9</sub>-Co-SnR/Pt (g) on FTO electrodes.

successful incorporation of  $SbW_9$ -TM-SnR in PPy during electropolymerization, which can be attributed to the strong interaction between pyrrole cations and POM anions. Moreover, the structures of  $SbW_9$ -TM-SnR are stable in the composites.

Fig. 6 shows SEM images of PPy-SbWg-TM-SnR/Pt (TM = Mn, Co, Ni, Zn) composites on FTO substrate. As shown in Fig. 6e, in situ electrodeposition of pure Pt on FTO produces the sub-micron spherical particles of Pt with an average diameter of 350 nm, and these Pt particles disperse on the surface of FTO composed of tightly packed F-doped SnO<sub>2</sub> particles. The mass loading of Pt particles deposited on the FTO or PPy-SbW9-TM-SnR-modified FTO can be calculated using the following equation<sup>41</sup>:  $m(Pt) = (Q_{dep} \times M) / (F \times n)$ , in which  $Q_{dep}$ is the charge utilized for deposition of Pt particles, M is atomic weight of Pt, F is the faraday constant (96,485.309 C  $mol^{-1}$ ) and *n* is the electron number transferred for formation of Pt. The mass loading of Pt is 9.45, 9.00, 12.13, 10.72, 12.18 and 10.36 µg cm<sup>-2</sup> for Pt, PPy/Pt and PPy-SbW<sub>9</sub>-TM-SnR/Pt (TM = Mn, Co, Ni, Zn), respectively. But attention needs to be paid that under the electrodeposition condition adopted (-0.2 V vs Ag/AgCl), hydrogen generation occurs inevitable, so the mass loading of Pt calculated by Coulomb charge is very likely to be overestimated. Because of this, afterwards the catalytic current is normalized to electroactive surface area (EAS) of Pt. In addition, it is clearly seen from Fig. 6a-d that the as-obtained PPy-**SbW**<sub>9</sub>-**TM-SnR**/Pt composites<sub>e o</sub> are covered onto the FTO surface, and Pt<sup>P</sup>MicPo<sup>A</sup>A<sup>A</sup>/<sup>6</sup>C<sup>A</sup>USters with similar diameters to that of pure Pt are incorporated homogeneously in PPy. As illustrated in Fig. 6a–d, particles of **SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn) are not observed in the SEM images, which is inferred that **SbW**<sub>9</sub>-**TM-SnR** anions are homogeneously dispersed in PPy. Fig. 6f shows the EDS data of PPy-**SbW**<sub>9</sub>-**Ni-SnR**/Pt composite, which proves that C, N, Ni, W, Pt, Sb, Sn elements are present.

The XPS spectroscopy of PPy-SbW<sub>9</sub>-Co-SnR/Pt composite is given in Fig. 7. As shown in Fig. 7a, the Sn 3d spectrum splits into two peaks and their binding energies are respectively located at 494.5 and 486.1 eV.<sup>22</sup> From Fig. 7e, the two strong peaks with binding energies of 36.9 eV and 34.8 eV, respectively, are ascribed to the W<sup>VI</sup> oxidation state.<sup>22</sup> The above results suggest that SbW9-Co-SnR in the film exists in its oxidized form. In Fig. 7b-c, the presence of carbon (C 1s) and nitrogen (N 1s) are located at 284.5 and 399.6 eV in the sample, which are derived from PPy, and the N 1s peak observed at 399.6 eV is assigned to pyrrole nitrogen.42 The peaks with binding energies of 530.3 and 531.9 eV in Fig. 7d are attributed to O 1s.<sup>22</sup> Fig. 7f-g shows XPS spectra of Pt for PPy/Pt and PPy-SbWg-Co-SnR/Pt composites, which both have Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> peaks, exhibiting the presence of Pt species.<sup>43</sup> The XPS spectra of Pt in 4f region are decomposed into two groups of peaks: Pt (0) and Pt(II). Significantly, the Pt (0) peak for PPy-SbW<sub>9</sub>-Co-SnR/Pt located at 70.58 eV (4f<sub>7/2</sub>) and 73.93 eV  $(4f_{5/2})$  both shows a slightly positive shift (0.12 eV) in comparison with that for PPy/Pt located at 70.46 eV  $(4f_{7/2})$  and 73.81 eV  $(4f_{5/2})$ . This may be due to an interaction between Pt particles and the PPy-SbW<sub>9</sub>-Co-SnR support.<sup>44</sup> Besides, two peaks appearing at 539.7 and 529.78 eV correspond to Sb 3d<sub>3/2</sub> and Sb 3d<sub>5/2</sub> of Sb<sup>III</sup> center in Fig. S10 (ESI<sup>+</sup>).45

#### Electrocatalysis of PPy-SbW9-TM-SnR/Pt composite films in MOR

The electrocatalytic activity of PPy-SbW9-TM-SnR/Pt hybrids towards CH<sub>3</sub>OH oxidation was determined by CV measurements in an aqueous electrolyte solution containing 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> and 1.0 mol  $L^{-1}$  CH<sub>3</sub>OH (Fig. 8). As can be seen from Fig. 8, there are two oxidation peaks located at about 0.70 V vs Ag/AgCl during the forward scanning and about 0.45 V vs Ag/AgCl during the reverse scanning, respectively, which show a typical feature of CH<sub>3</sub>OH oxidation, and are related to the oxidation of CH<sub>3</sub>OH and intermediates, respectively.<sup>46</sup> The electrocatalytic activity towards CH<sub>3</sub>OH oxidation can be compared by the oxidation current density that is normalized with respect to the EAS. The EAS was estimated by the area of H-desorption of Pt catalysts according to the following equation (Eq. (1)):47  $EAS = Q_H / (210 \times 10^{-6}) \text{ cm}^2$ (1)

where  $Q_{\rm H}$  (C) is the charge transferred during the desorption of hydrogen on the surface of Pt catalyst and a value of  $210 \times 10^{-6}$  (C cm<sup>-2</sup>) is taken as the charge required for oxidizing a monolayer of hydrogen.

As a preliminary test, the effects of amount of both  $SbW_9$ -Co-SnR and PPy on the electrocatalytic performance were

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studied. Fig. 8a shows CV curves of PPy-**SbW**<sub>9</sub>-**Co-SnR**/Pt hybrid electrodes prepared from different concentrations of



**Fig. 8** CV curves that were normalized to EASs of PPy-**SbW**<sub>9</sub>-**Co-SnR**/Pt modified electrode obtained from different concentrations of **SbW**<sub>9</sub>-**Co-SnR** (0.5, 1.0, 3.0, 5.0 mmol L<sup>-1</sup>) at scan rate of 50 mV s<sup>-1</sup> with *Q* of 4×10<sup>4</sup> C (a), obtained from different *Q* (5×10<sup>-6</sup>, 1×10<sup>-5</sup>, 1×10<sup>-4</sup>, 1×10<sup>-3</sup>, 1×10<sup>-2</sup> C) at scan rate of 50 mV s<sup>-1</sup> in 1.0 mmol L<sup>-1</sup> **SbW**<sub>9</sub>-**Co-SnR** (b) in a mixed solution of 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1 mol L<sup>-1</sup> CH<sub>3</sub>OH.

SbW<sub>9</sub>-Co-SnR during electropolymerization of pyrrole. It can be seen that as the concentration of SbW<sub>9</sub>-Co-SnR increases, the oxidation peak current density increases thanks to more efficiently facilitating charge transfer in the electrocatalytic process, however, further increasing the concentration of SbW<sub>9</sub>-Co-SnR, it leads to a decrease in the oxidation current density, which may be because the reduction of electrical conductivity caused by excess SbWg-Co-SnR. As a whole, it is proved that 1.0 mmol L<sup>-1</sup> SbW<sub>9</sub>-Co-SnR results in the highest current of CH<sub>3</sub>OH oxidation. Furthermore, Fig. 8b displays the CV curves of PPy-SbW<sub>9</sub>-Co-SnR/Pt hybrid electrodes obtained from different electric quantity (Q) consumed during electropolymerization of pyrrole, which reflects the influence of PPy amount on the catalytic activity. It indicates that a moderate amount of PPy can enhance the catalytic oxidation current density, while an excessive amount of PPy reduces the catalytic current, which may be due to the fact that excessive PPy may inhibit the charge transmission to electrode or inhibit the diffusion of electrolyte during the catalytic process. Accordingly, it is clearly seen from Fig. 8b that the composite has the biggest peak current density as the consumed electric quantity is  $1 \times 10^{-5}$  C.

As a consequence, under the optimized electrodeposition condition, that is, in 1.0 mmol L<sup>-1</sup> SbW<sub>9</sub>-TM-SnR with the consumed electric quantity of 1×10<sup>-5</sup> C during potentiostatic electropolymerization, four PPy-SbWg-TM-SnR/Pt (TM = Mn, Co, Ni, Zn) hybrid electrodes were further constructed for electrocatalytic oxidation of CH<sub>3</sub>OH. Meanwhile, pure Pt and PPy/Pt hybrid electrodes were also prepared for comparison. CV data recorded in the potential range of - 0.2 to 1.2 V (vs Ag/AgCl) at scan rate of 50 mV s<sup>-1</sup> was got to estimate the EAS (Figs. S11 and S12, ESI<sup>+</sup>). All catalysts show the standard hydrogen desorption potentials of - 0.09 V (vs Ag/AgCl). The associated EASs for PPy-SbWg-TM-SnR/Pt (TM = Mn, Co, Ni, Zn) hybrid electrodes, PPy/Pt electrode and Pt electrode are 0.84, 1.27, 0.83, 0.84, 0.77 and 0.82 cm<sup>2</sup>, respectively. As shown in Fig. 9, PPy-SbWg-Mn-SnR/Pt, PPy-SbWg-Co-SnR/Pt, hybrid PPy-**SbW**<sub>9</sub>-**Ni-SnR**/Pt and PPy-**SbW**<sub>9</sub>-**Zn-SnR**/Pt electrodes all display higher forward oxidation peak current density (0.80, 0.81, 0.87, 0.84 mA cm<sup>-2</sup>) than Pt electrode (0.47 mA cm<sup>-2</sup>) and PPy/Pt hybrid electrode (0.61 mA cm<sup>-2</sup>).

And PPy-**SbW**<sub>9</sub>-**Ni-SnR**/Pt shows the highest oxidatione peak current density, which is 1.85 and 1.43 times higher than 5118F



Fig. 9 CV curves that were normalized to EASs of different composites modified FTO electrodes: Pt, PPy/Pt, PPy-SbWg-TM-SnR/Pt in 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> and 1.0 mol  $L^{-1}$  CH<sub>3</sub>OH, scan rate is 50 mV s<sup>-1</sup>.

Table 2      The detailed electrochemical parameters of various electrodes									
Sample	EAS (cm <sup>2</sup> )	<i>I</i> <sub>f</sub> (mA cm <sup>-2</sup> )	<i>I</i> <sub>b</sub> (mA cm <sup>-2</sup> )	$I_{\rm f}/I_{\rm b}$					
PPy- <b>SbW₀-Mn-SnR</b> /Pt	0.84	0.80	0.18	4.40					
PPy- <b>SbW₀-Co-SnR</b> /Pt	1.27	0.81	0.27	3.03					
PPy- <b>SbW₀-Ni-SnR/</b> Pt	0.83	0.87	0.19	4.55					
PPy- <b>SbW₃-Zn-SnR/</b> Pt	0.84	0.84	0.17	5.09					
PPy/Pt	0.77	0.61	0.25	2.42					
Pt	0.82	0.47	0.22	2.15					



Fig. 10 EIS of different composites modified FTO electrodes: Pt, PPy/Pt, PPy-SbW<sub>9</sub>-TM-SnR/Pt in 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> and 1.0 mol  $L^{-1}$  CH<sub>3</sub>OH.

those of pure Pt and PPy/Pt electrodes, respectively. This result proves that **SbW**<sub>9</sub>-**TM-SnR** (TM = Mn, Co, Ni, Zn) can effectively improve the electrocatalytic activity of Pt catalyst.

The four carboxyethyltin and TM co-functionalized compounds have different electrocatalytic ability, which may be due to their different redox property caused by TM.



Fig. 11 Chronoamperometric curves of different films modified FTO electrodes: Pt, PPy/Pt, PPy-**SbW<sub>9</sub>-TM-SnR**/Pt in 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> and 1.0 mol  $L^{-1}$  CH<sub>3</sub>OH at 0.65 V for 800 s.

Besides, the higher oxidation current density of PPy/Pt electrode than Pt electrode is attributed to the enhancement of conductivity by PPy. Furthermore, for comparing experiments, simple TM (Mn, Co, Ni, Zn) salts, Na-SbW<sub>9</sub>, Co-SbW<sub>9</sub> as well as Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub> were respectively used to construct PPy/Pt-based hybrid electrodes, and their electrocatalytic results are shown in Figs. S13 and S14 (ESI<sup>+</sup>). It is found that these inorganic or organic precursors do not achieve the matched electrocatalytic effect like SbWg-TM-SnR, inferring that the enhancement effect of SbW<sub>9</sub>-TM-SnR is resulted from the co-functionalization of carboxyethyltin and TM. The ratio of the forward peak current density  $(I_f)$  to the reverse anodic peak current density  $(I_b)$ ,  $I_f/I_b$ , can be used to describe the catalyst tolerance to carbonaceous species accumulation. A high  $I_{\rm f}/I_{\rm b}$  ratio indicates that it can remove the poisoning species more effectively from the catalyst surface. From Table 2, it thus indicates that plenty of intermediate carbonaceous species are oxidized to carbon dioxide for PPy-SbWg-TM-SnR/Pt compared to that of PPy/Pt or Pt in the forward scan. At the same time, the CO stripping experiments were conducted for confirming the capability of all the samples towards the methanol oxidation. As shown in Fig. S15 (ESI<sup>+</sup>), for PPy-SbW<sub>9</sub>-TM-SnR/Pt (TM=Mn, Co, Ni, Zn), the CO oxidation peak is observed at 0.750, 0.693, 0.737, and 0.759 V vs. Ag/AgCl, respectively, and they are negatively shifted compared with the oxidation peak for Pt (0.838 V) and PPy/Pt (0.811 V), indicating the adsorbed CO at the surface of PPy-SbWg-TM-SnR/Pt catalyst is more easily removed in comparison to Pt and PPy/Pt. Besides, for all catalysts, CO oxidation peak disappears in the second scan, confirming the complete removal of the adsorbed CO species from the catalyst surface.

Furthermore, the charge transfer resistance at the interface between electrode and electrolyte was

characterized by electrochemical impedance spectrum (EIS) in Fig. 10. As can be seen, the semicircle diameter is related to the charge-transfer resistance ( $R_{ct}$ ). Compared with Pt and PPy/Pt electrodes, PPy-**SbW**<sub>9</sub>-**TM-SnR**/Pt displays smaller  $R_{ct}$ , which demonstrates that **SbW**<sub>9</sub>-**TM-SnR** can facilitate the electron transfer process during the catalytic oxidation.

To further evaluate the electrocatalytic stability of different films modified electrodes in MOR, chronoamperometry tests were carried out at 0.65 V for 800 s. As shown in Fig. 11, the current intensity of all catalysts decreases rapidly at the beginning of the test, afterwards, it diminish much more slowly and reach a platform within 800 s. In the beginning, the active sites on the catalysts are occupied by intermediate product of CH<sub>3</sub>OH oxidation, causing the rapid decline in current. The subsequent slow current decrease may be due to the adsorbed anion  $SO_4^{2-}$  on the surface of catalysts during long time stability test.<sup>48</sup> It is evident that PPy-**SbW<sub>9</sub>-TM-SnR**/Pt shows a higher quasi-stationary current and lower decay of current with time than PPy/Pt and Pt, which suggests a better tolerance towards CO.

#### Conclusions

In summary, four new tungstoantimonates co-functionalized by carboxyethyltin and TM have been synthesized by conventional method. They show good catalytic activity towards oxidation of cyclohexanol to cyclohexanone. Furthermore, PPy-SbW9-TM-SnR/Pt composites were successfully prepared through an electropolymerization process and electrodeposition method. SEM images show that PPy-SbWg-TM-SnR/Pt composites have high dispersion and homogeneity. The electrochemical measurements indicate that PPy-SbWg-TM-SnR/Pt composites have high electrocatalytic activity, stability and better anti-poisoning property towards CH<sub>3</sub>OH oxidation than PPy/Pt and Pt, which is attributed to the introduction of conductivity PPy molecules and redox activity SbW<sub>9</sub>-TM-SnR, and it also reflects a synergistic effect of PPy, SbW<sub>9</sub>-TM-SnR and Pt. These SbW<sub>9</sub>-TM-SnR crystalline materials with high electron and proton conduction ability are good redox mediators for the electrochemical oxidation of CH<sub>3</sub>OH.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### Notes and references

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## Graphic Abstract

 $PPy-SbW_9-TM-SnR/Pt$ -based electrocatalysts (TM = Mn, Co, Ni, Zn) were synthesized by electro-deposition method and showed good performance of methanol oxidation reaction.

