

## Supplementary information

# Insights into the solvothermal reaction for synthesizing tin(IV) oxide porous spheres

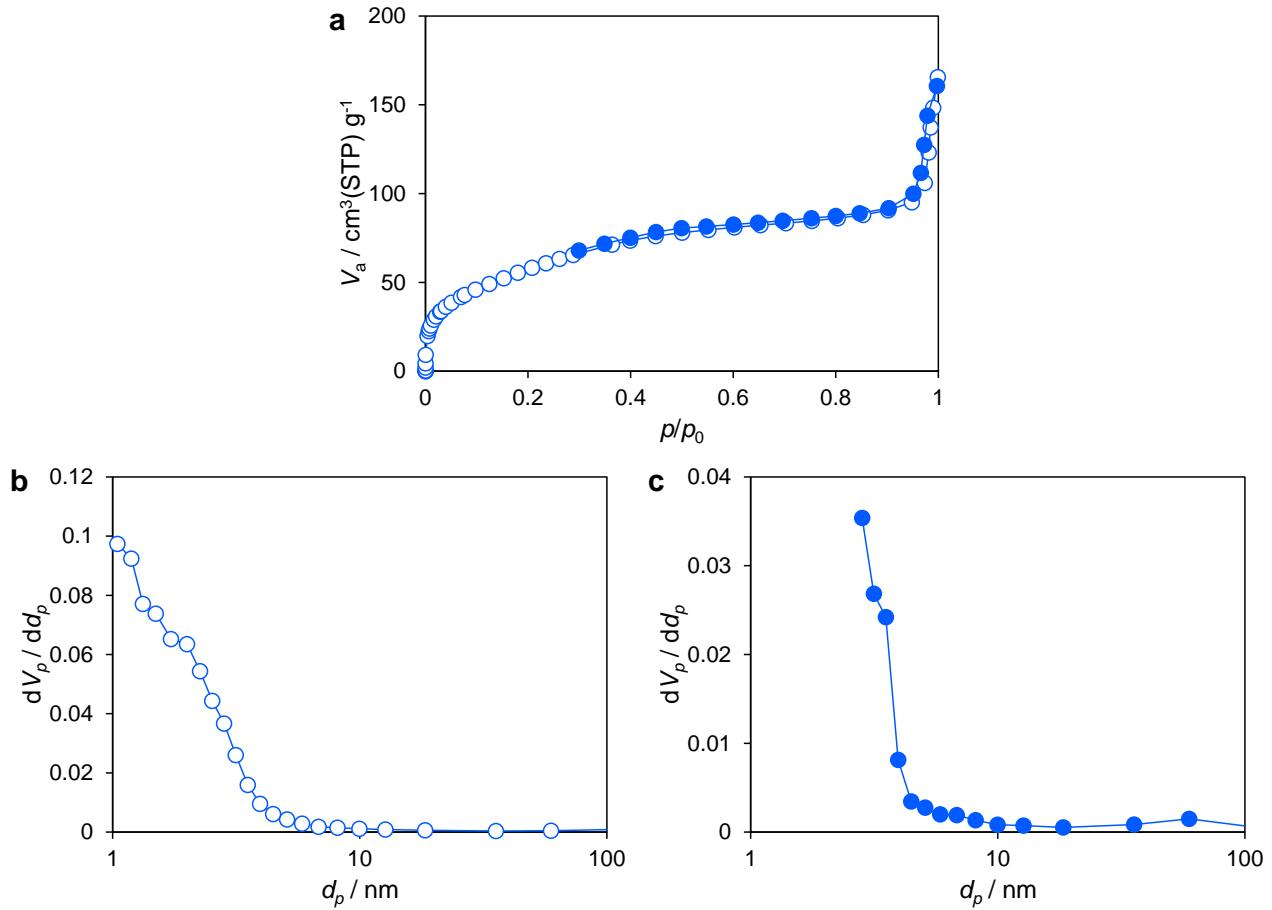
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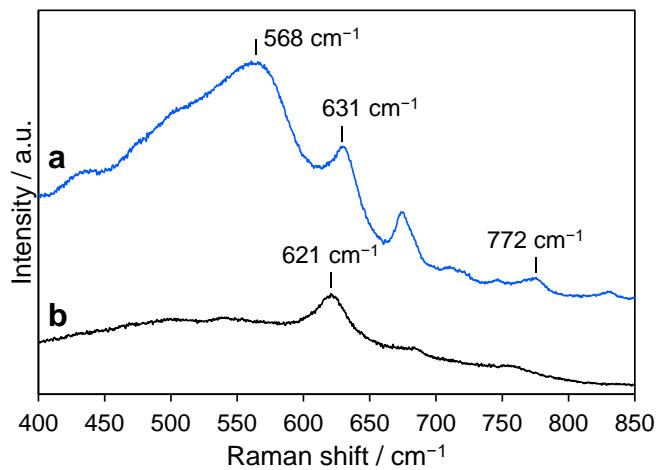
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[ohtani.masataka@kochi-tech.ac.jp](mailto:ohtani.masataka@kochi-tech.ac.jp)

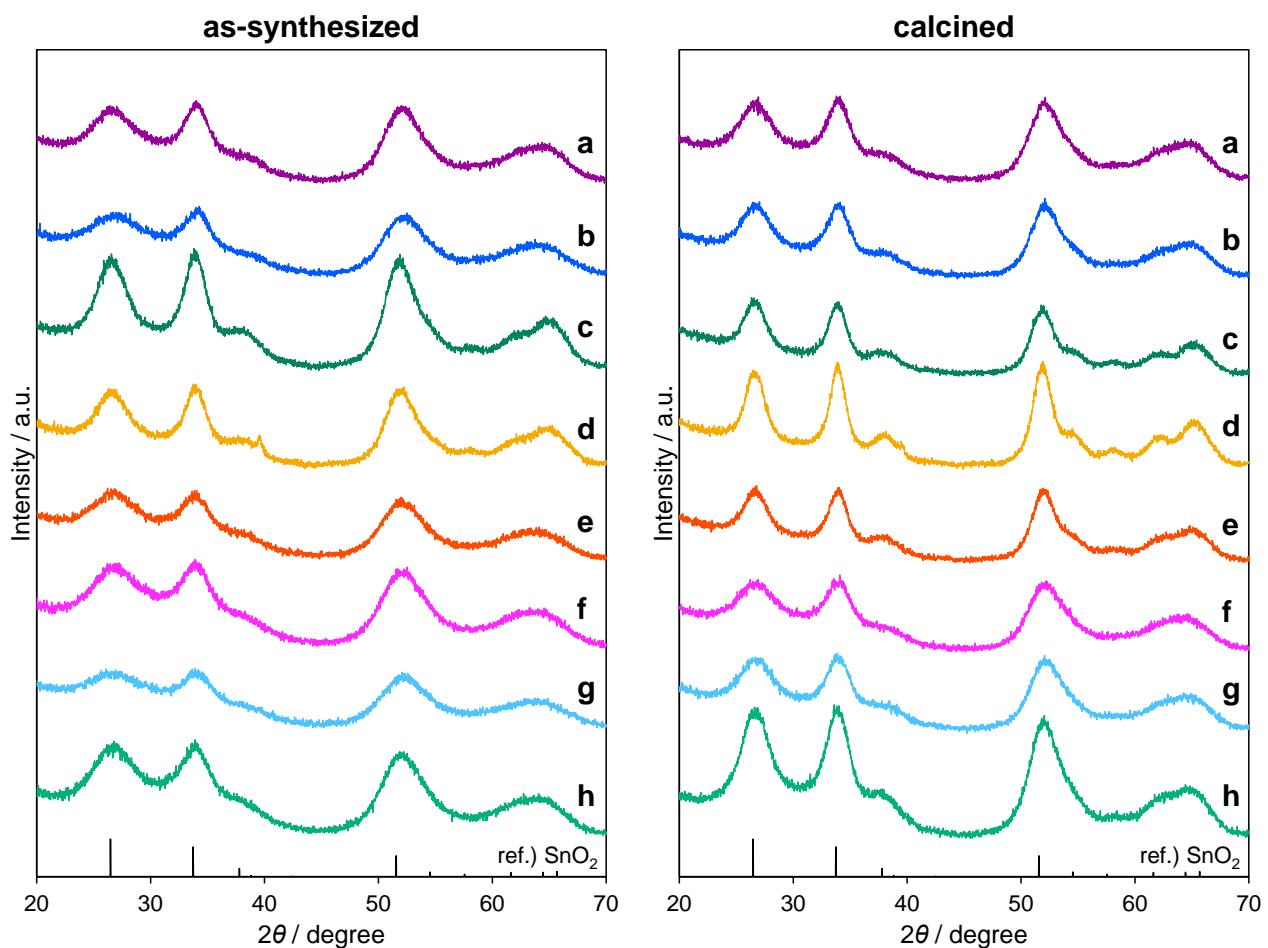
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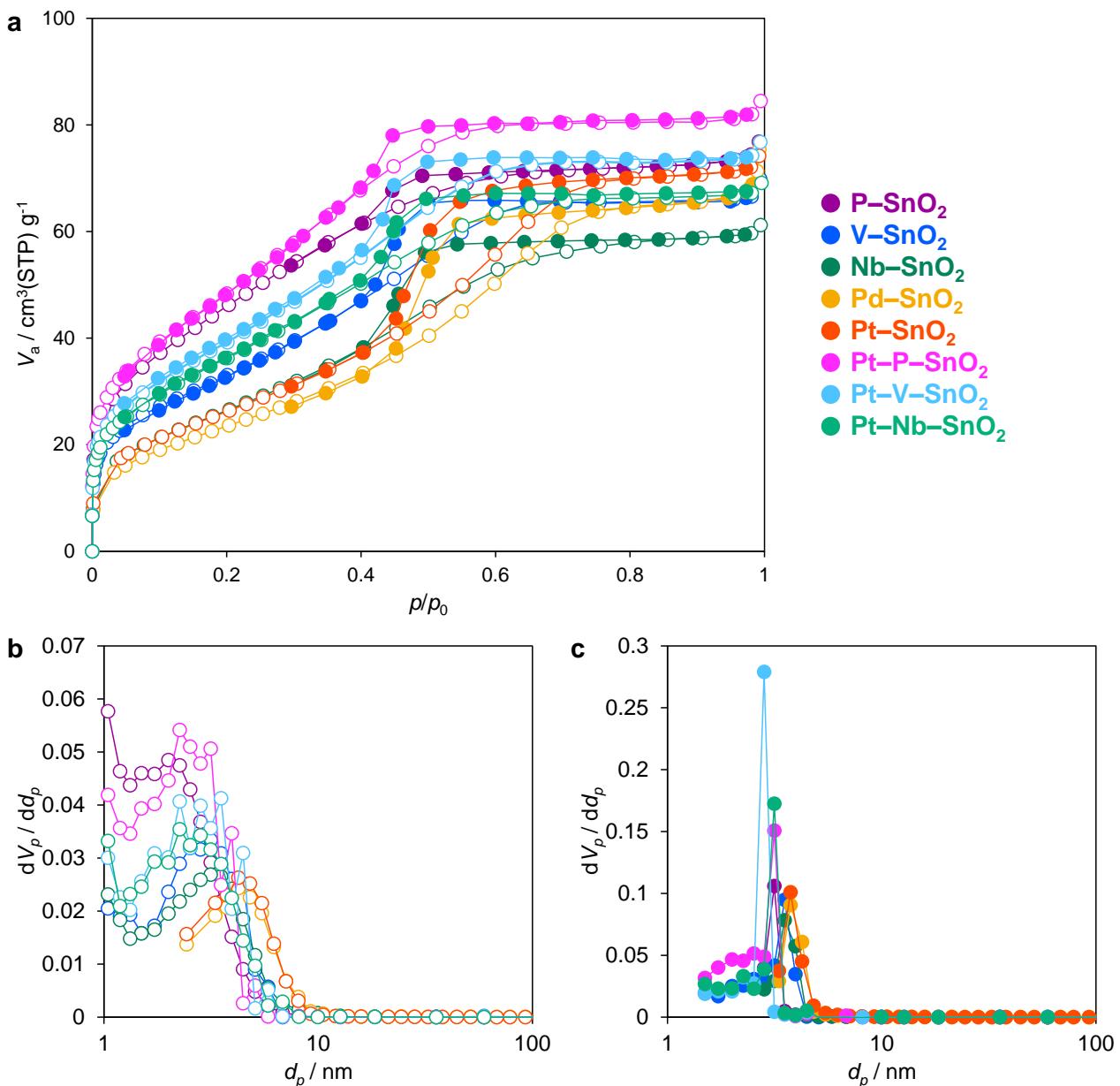
**Fig. S1** Nitrogen adsorption/desorption measurement of porous  $\text{SnO}_2$  obtained through Entry 1 in Table 4. Adsorption/desorption isotherm (a) and pore distributions (BJH plots) analyzed by adsorption (b) and desorption (c) measurement.



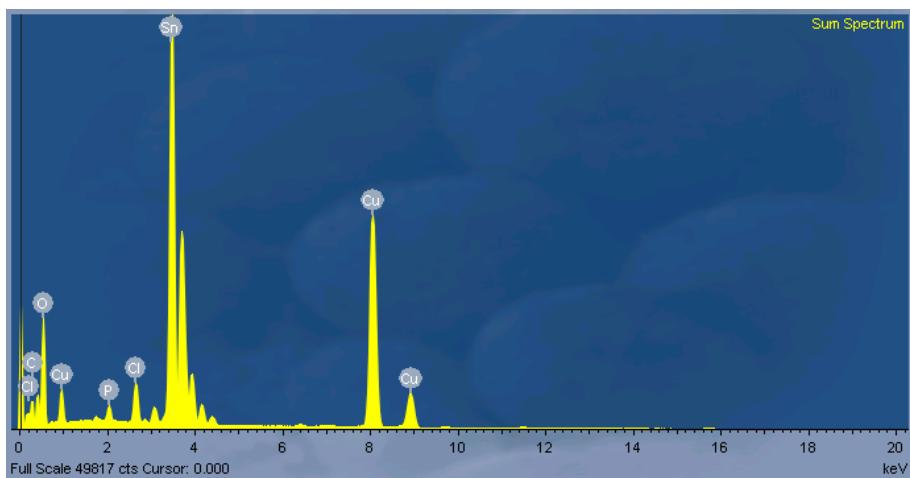
**Fig. S2** Raman spectra of (a) porous SnO<sub>2</sub> obtained through Entry 1 in Table 4 and (b) commercially available SnO<sub>2</sub> (S-2000).



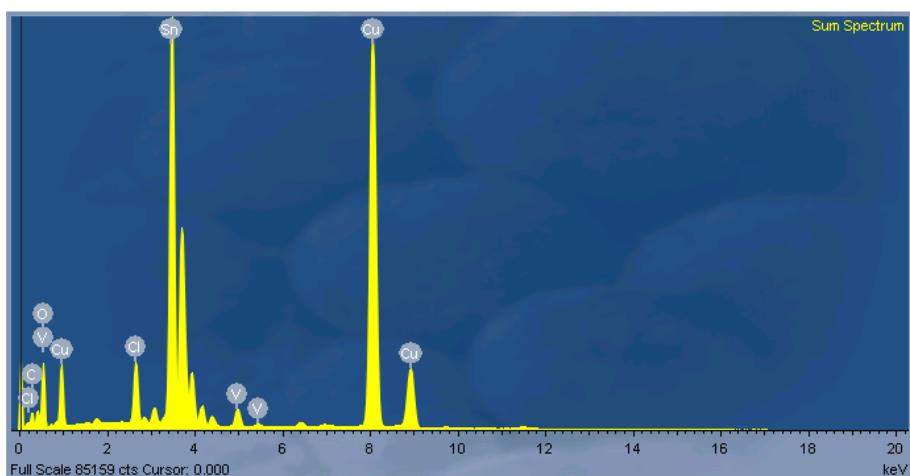
**Fig. S3** XRD patterns of as-synthesized (left) and calcined (right) SnO<sub>2</sub>-based composites. P–SnO<sub>2</sub> (a), V–SnO<sub>2</sub> (b), Nb–SnO<sub>2</sub> (c), Pd–SnO<sub>2</sub> (d), Pt–SnO<sub>2</sub> (e), Pt–P–SnO<sub>2</sub> (f), Pt–V–SnO<sub>2</sub> (g) and Pt–Nb–SnO<sub>2</sub> (h).



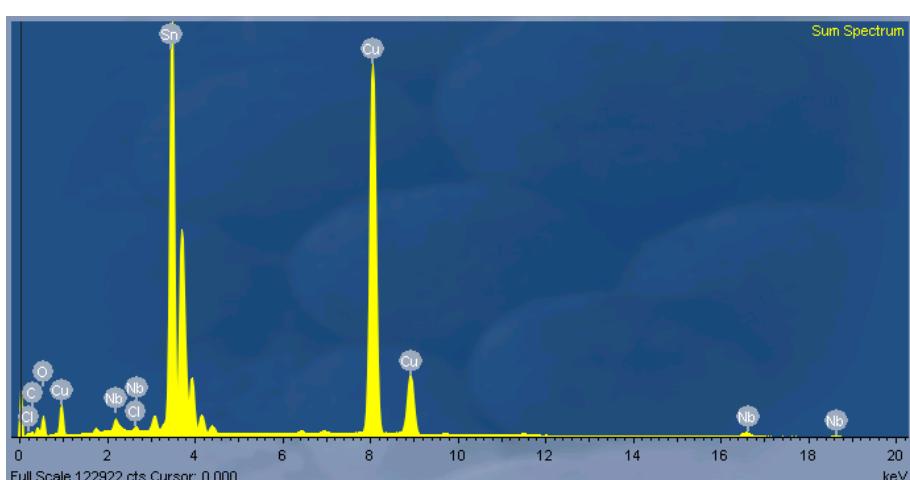
**Fig. S4** Nitrogen adsorption/desorption measurement of porous SnO<sub>2</sub>-based composites obtained through Entries 2–9 in Table 4. Adsorption/desorption isotherm (a) and pore distributions (BJH plots) analyzed by adsorption (b) and desorption (c) measurements. BELSORP-mini X was used for the measurements of P–SnO<sub>2</sub>, V–SnO<sub>2</sub>, Nb–SnO<sub>2</sub>, Pt–P–SnO<sub>2</sub>, Pt–V–SnO<sub>2</sub> and Pt–Nb–SnO<sub>2</sub>. BELSORP-mini II was used for the measurements of Pd–SnO<sub>2</sub> and Pt–SnO<sub>2</sub>.



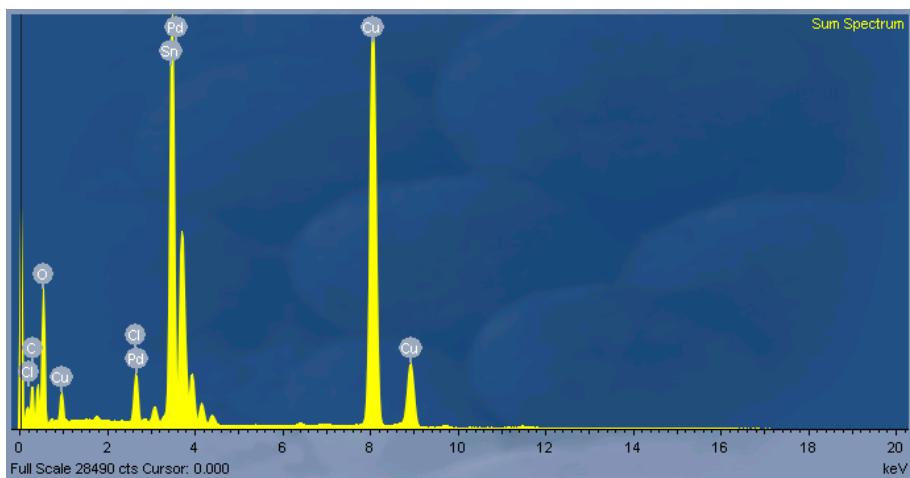
**Fig. S5a** EDX spectrum of P–SnO<sub>2</sub>.



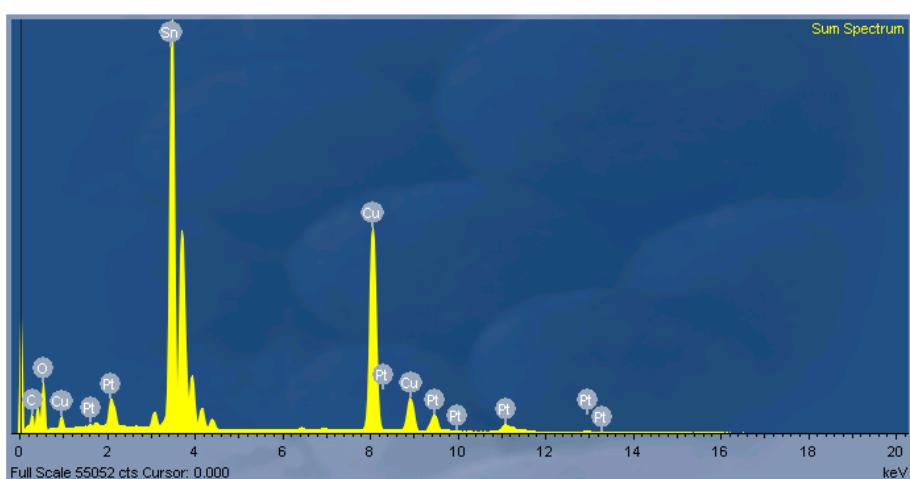
**Fig. S5b** EDX spectrum of V–SnO<sub>2</sub>.



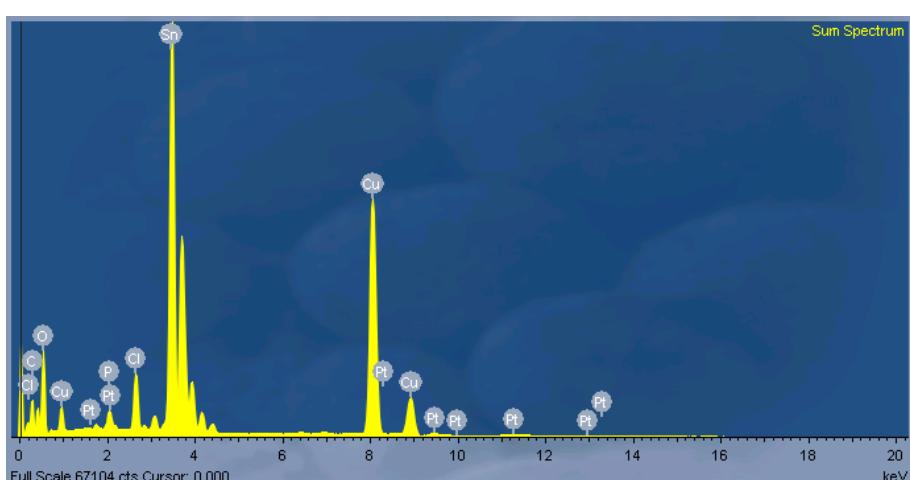
**Fig. S5c** EDX spectrum of Nb–SnO<sub>2</sub>.



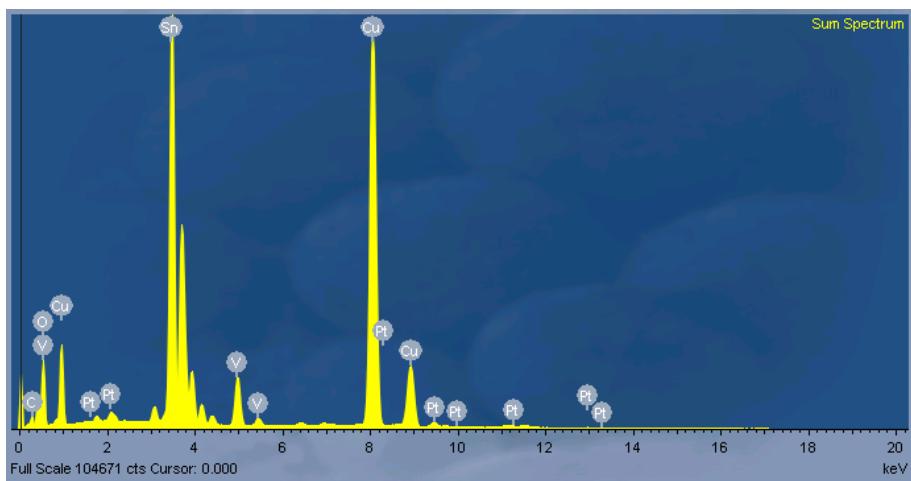
**Fig. S5d** EDX spectrum of Pd–SnO<sub>2</sub>.



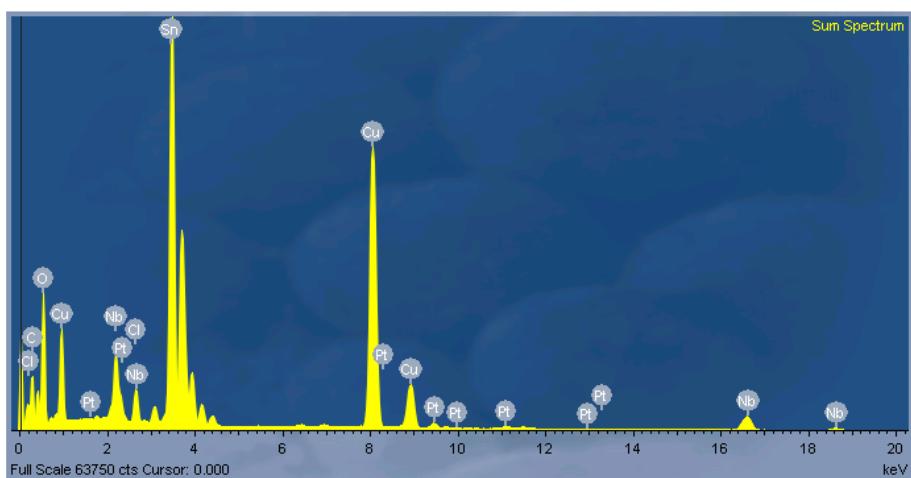
**Fig. S5e** EDX spectrum of Pt–SnO<sub>2</sub>.



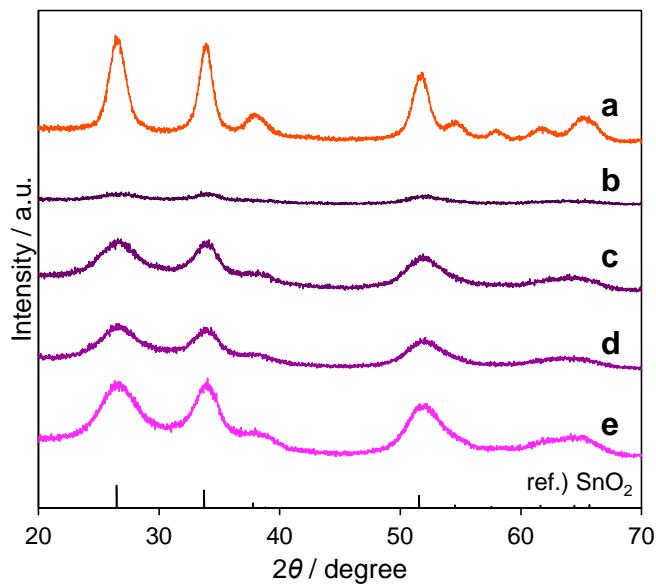
**Fig. S5f** EDX spectrum of Pt–P–SnO<sub>2</sub>.



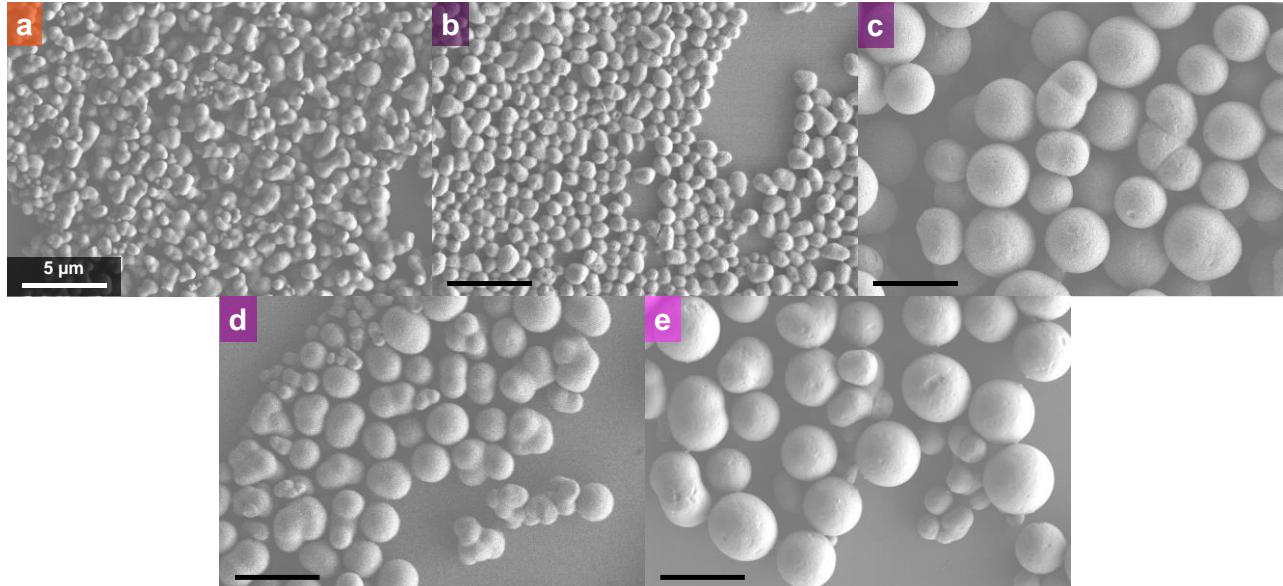
**Fig. S5g** EDX spectrum of Pt–V–SnO<sub>2</sub>.



**Fig. S5h** EDX spectrum of Pt–Nb–SnO<sub>2</sub>.

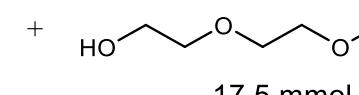


**Fig. S6** XRD patterns of Rh–SnO<sub>2</sub> and Ru–SnO<sub>2</sub> corresponding to Entries 5 (a), 6 (b), 7 (c), 8 (d) and 9 (e) in Table S1.



**Fig. S7** SEM images of Rh–SnO<sub>2</sub> and Ru–SnO<sub>2</sub> corresponding to Entries 5 (a), 6 (b), 7 (c), 8 (d) and 9 (e) in Table S1.

**Table S1** Solvothermal reaction of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  with different element source.<sup>a</sup>

		$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ 866 $\mu\text{mol}$	+	different element source 8.75 $\mu\text{mol}$	+	 17.5 mmol	+	additive	$\xrightarrow[\text{MeOH}\ 8.75\text{mL}]{\Delta}$	product
Entry	Amount of reactant	Heating conditions				Product				
	Different element source	Additive (amount)	Temp. / °C	Time / min	Sample <sup>a</sup>	Yield / %	2 <sup>nd</sup> element <sup>c</sup> / at%			
1	$\text{Rh}(\text{acac})_3$	-	200	60	$\text{Rh-SnO}_2$	0.15	<sup>d</sup>			
2	$\text{Rh}(\text{acac})_3$	HCOOH (4.38 $\mu\text{mol}$ )	200	60	$\text{Rh-SnO}_2$	0.15	<sup>d</sup>			
3	$\text{Rh}(\text{acac})_3$	-	220	60	$\text{Rh-SnO}_2$	-	<sup>d</sup>			
4	$\text{Rh}(\text{acac})_3$	-	200	120	$\text{Rh-SnO}_2$	3.5	<sup>d</sup>			
5	$\text{Rh}(\text{acac})_3$	$\text{H}_2\text{O}$ (1.0 mL)	200	60	$\text{Rh-SnO}_2$	85	1.1 (Rh)			
6	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	-	200	60	$\text{Ru-SnO}_2$	89	<0.2 (Ru)			
7	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ <sup>b</sup>	-	200	60	$\text{Ru-SnO}_2$	89	<0.2 (Ru)			
8	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	-	220	60	$\text{Ru-SnO}_2$	75	<0.2 (Ru)			
9	$\text{Ru}(\text{acac})_3$	-	200	60	$\text{Ru-SnO}_2$	89	<0.2 (Ru)			

<sup>a</sup> Concentration of hetero-element (Rh or Pt) in precursor solutions is 1 at%. <sup>b</sup> Amount of triethylene glycol is 8.75 mmol. <sup>c</sup> Determined by XRF (Entries 5 and 6) and ICP-OES (Entries 7–9). <sup>d</sup> Not enough products to measure.