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## Pd-incorporated polyoxometalate catalysts for electrochemical CO<sub>2</sub> reduction†

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Polyoxometalates (POMs), representing anionic metal–oxo clusters, display diverse properties depending on their structures, constituent elements, and counteranions. These characteristics position them as promising catalysts or catalyst precursors for electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR). This study synthesized various salts—TBA<sup>+</sup> (tetra-*n*-butylammonium), Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>—of a dipalladium-incorporated POM (Pd<sub>2</sub>, [γ-H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>Pd<sub>2</sub>(OAc)<sub>2</sub>]<sup>4-</sup>) immobilized on a carbon support (Pd<sub>2</sub>/C). The synthesized catalysts—TBAPd<sub>2</sub>/C, CsPd<sub>2</sub>/C, SrPd<sub>2</sub>/C, and BaPd<sub>2</sub>/C—were deposited on a gas-diffusion carbon electrode, and the CO<sub>2</sub>RR performance was subsequently evaluated using a gas-diffusion flow electrolysis cell. Among the catalysts tested, BaPd<sub>2</sub>/C exhibited high selectivity toward carbon monoxide (CO) production (ca. 90%), while TBAPd<sub>2</sub>/C produced CO and hydrogen (H<sub>2</sub>) with moderate selectivity (ca. 40% for CO and ca. 60% for H<sub>2</sub>). Moreover, BaPd<sub>2</sub>/C exhibited high selectivity toward CO production over 12 h, while palladium acetate, a precursor of Pd<sub>2</sub>, showed a significant decline in CO selectivity during the CO<sub>2</sub>RR. Although both BaPd<sub>2</sub>/C and TBAPd<sub>2</sub>/C transformed into Pd nanoparticles and WO<sub>x</sub> nanospecies during the CO<sub>2</sub>RR, the influence of counteranions on their product selectivity was significant. These results highlight that POMs and their counteranions can effectively modulate the catalytic performance of POM-based electrocatalysts in CO<sub>2</sub>RR.

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## Introduction

Anthropogenic carbon dioxide (CO<sub>2</sub>) emissions are widely recognized as major contributors to recent global warming, requiring prompt and effective mitigation strategies.<sup>1</sup> In this context, the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) stands out as a promising solution, attracting considerable attention from both academia and industry.<sup>2</sup> Utilizing multiple electrons and protons, the CO<sub>2</sub>RR process electrochemically converts CO<sub>2</sub> into numerous valuable chemicals and fuels, such as carbon monoxide (CO), methanol, and ethylene (C<sub>2</sub>H<sub>4</sub>).<sup>3</sup> Among these products, CO holds particular importance as a component of syngas, a vital feedstock for hydrocarbon synthesis *via* methanol or Fischer–Tropsch processes.<sup>4</sup> Notably, the selectivity of the CO<sub>2</sub>RR is significantly influenced by the metals used in the electrocatalysts, with Au, Ag, and Zn demonstrating high selectivity toward CO production.<sup>5</sup> In addition to these, Pd can also produce CO with high selectivity;

however, its efficiency is considerably influenced by the applied potential and the state of the Pd catalyst. For instance, with increasing overpotential, the primary CO<sub>2</sub>RR product of Pd changes from formate (HCOO<sup>-</sup>) to CO, and smaller Pd nanoparticles (NPs) produce CO with greater selectivity.<sup>6,7</sup> However, given the widespread use of aqueous electrolytes for the CO<sub>2</sub>RR, the competing hydrogen evolution reaction (HER) is inevitable,<sup>8</sup> and the resulting degradation in catalytic performance emerges as a significant concern.<sup>4</sup> Hence, developing robust CO<sub>2</sub>RR catalysts capable of selectively producing specific products is critical.

Previous studies have extensively investigated the effects of alkali metal cations in electrolytes on the CO<sub>2</sub>RR. Based on their findings, these cations have been widely recognized to play critical roles in driving the CO<sub>2</sub>RR,<sup>9</sup> with larger cations such as K<sup>+</sup> and Cs<sup>+</sup> demonstrating greater productivity for CO, HCOO<sup>-</sup>, and C<sub>2</sub>H<sub>4</sub> compared to smaller cations such as Li<sup>+</sup>.<sup>9–19</sup> Conversely, studies conducted by Schizodimou and Kyriacou have demonstrated higher CO<sub>2</sub>RR activity for electrolytes containing multivalent cations, particularly at low overpotentials.<sup>20</sup> Meanwhile, other reports have suggested that multivalent cations, such as alkaline earth metal cations, enhance the partial current density of CO.<sup>14</sup> Notably, electrolytes with small amounts of Ba<sup>2+</sup> have been observed to reduce HER activity while increasing CO<sub>2</sub>RR activity at high overpotentials.<sup>17</sup> Conversely, Bhargava *et al.* have reported that electrolytes

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containing substantial amounts of  $\text{CaCl}_2$  and  $\text{BaCl}_2$  compromise the  $\text{CO}_2\text{RR}$  performance of Ag.<sup>16</sup> This diminished performance is attributed to the coverage of active sites by the deposited oxides, hydroxides, and other compounds of alkaline earth metals. Beyond these factors, the practical application of alkaline earth metal salts as electrolytes is further constrained by their lower solubility in water,<sup>12</sup> often necessitating excessive quantities for effective use, and their higher cost compared to corresponding alkali metal salts. Consequently, developing systems that minimize the use of alkaline earth metal salts while demonstrating optimal  $\text{CO}_2\text{RR}$  performance is essential.

Polyoxometalates (POMs), representing anionic metal-oxo clusters comprising multiple  $\{\text{MO}_x\}$  units ( $M = \text{W}, \text{Mo}, \text{V}, \text{etc.}$ ), exhibit diverse properties depending on their structures and constituent elements.<sup>21–32</sup> These attributes position POMs as promising catalysts and catalyst precursors for various electrochemical and photochemical reactions including  $\text{CO}_2\text{RR}$ .<sup>30,33–38</sup> Among the known varieties of POMs, particularly noteworthy are lacunary POMs, which lack one or more  $\{\text{MO}_x\}$  units and possess reactive oxygen atoms, thus functioning as inorganic multidentate ligands.<sup>39,40</sup> Our research group has pioneered techniques for synthesizing well-defined multinuclear metal-incorporated POMs by reacting tetra-*n*-butylammonium ( $\text{TBA}^+$ ) salts of lacunary POMs with metal ions in organic solvents.<sup>40–43</sup> These metal-incorporated POMs have been demonstrated to serve as promising catalysts<sup>44–48</sup> or catalyst precursors<sup>49</sup> for various reactions. For instance, we utilized a  $\text{TBA}^+$  salt of a diiron-incorporated POM ( $\text{TBAFe}_2$ ,  $\text{TBA}_8[\text{H}_4(\text{SiW}_{10}\text{O}_{36})_2\text{Fe}_2\text{O}]$ ) supported on silica ( $\text{TBAFe}_2/\text{SiO}_2$ ) as a catalyst precursor for methane oxidation, selectively obtaining formaldehyde and  $\text{CO}$ .<sup>49</sup> Interestingly, tungsten-oxide nanoclusters derived from  $\text{TBAFe}_2$  protected *in situ*-formed  $\text{FeO}_x$  subnanoclusters, thereby avoiding catalyst deactivation and product oxidation. Thus, metal-incorporated POMs hold immense potential for developing robust  $\text{CO}_2\text{RR}$  catalysts capable of synthesizing specific products with high selectivity.

Notably, the counteranions of POMs not only balance their anionic charges but also substantially influence their solubility and physicochemical properties.<sup>50,51</sup> Typically, W-, Mo-, and V-based POMs exhibit reduced solubility in water when larger counteranions such as  $\text{Cs}^+$  and  $\text{Ba}^{2+}$  are incorporated. Leveraging this characteristic, Blasco-Ahicart *et al.* used  $\text{Cs}^+$  and  $\text{Ba}^{2+}$  salts of nonacobalt-incorporated POMs as heterogeneous electrocatalysts for the oxygen evolution reaction in a 1 M  $\text{H}_2\text{SO}_4$  aqueous solution.<sup>52</sup> Thus, we envisaged that selecting appropriate counteranions of POMs holds significant promise for developing robust and selective catalysts for the  $\text{CO}_2\text{RR}$ .

Building upon these insights, this study is the first to investigate the  $\text{CO}_2\text{RR}$  performance of Pd-incorporated POMs and the effect of their counteranions. Specifically, a  $\text{TBA}^+$  salt of a dipalladium-incorporated POM ( $\text{Pd}_2$ ,  $[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Pd}_2(\text{OAc})_2]^{4-}$ , Fig. 1a)<sup>44</sup> immobilized on a carbon support ( $\text{TBAPd}_2/\text{C}$ ) was first synthesized. Subsequently, to explore the influence of different counteranions, various analogs— $\text{CsPd}_2/\text{C}$ ,  $\text{SrPd}_2/\text{C}$ , and  $\text{BaPd}_2/\text{C}$ —were prepared by exchanging  $\text{TBA}^+$  with alkali metal or alkaline earth metal cations ( $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , or  $\text{Ba}^{2+}$ ) in an organic solvent (Fig. 1b). These catalysts were then deposited on

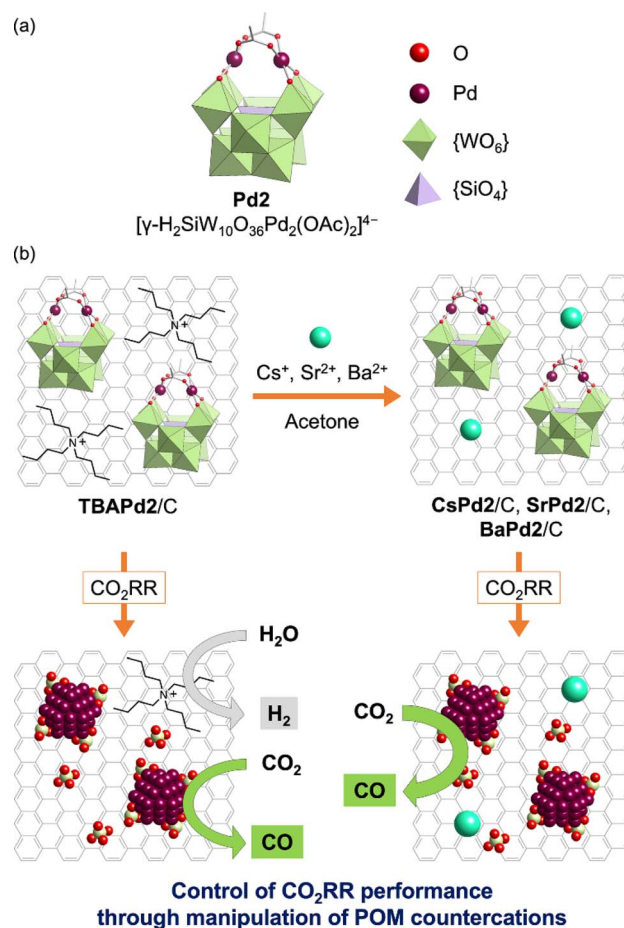


Fig. 1 Preparation of POM-based electrocatalysts and their application in electrochemical  $\text{CO}_2\text{RR}$ . (a) Structure of  $\text{Pd}_2$  ( $[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Pd}_2(\text{OAc})_2]^{4-}$ ). (b) Schematic depicting the preparation procedure of  $\text{CsPd}_2/\text{C}$ ,  $\text{SrPd}_2/\text{C}$ , and  $\text{BaPd}_2/\text{C}$  through manipulation of counteranions of  $\text{TBAPd}_2/\text{C}$  and their applications in electrochemical  $\text{CO}_2\text{RR}$ .

a gas-diffusion carbon electrode, and  $\text{CO}_2\text{RR}$  was conducted using a gas-diffusion flow electrolysis cell containing a 1 M potassium bicarbonate ( $\text{KHCO}_3$ ) aqueous solution. Our results revealed that  $\text{BaPd}_2/\text{C}$  exhibited the highest selectivity toward  $\text{CO}$  production (*ca.* 90%) and maintained its catalytic performance over 12 h. Conversely,  $\text{TBAPd}_2/\text{C}$  produced  $\text{CO}$  and hydrogen ( $\text{H}_2$ ) with moderate selectivity (*ca.* 40% for  $\text{CO}$  and *ca.* 60% for  $\text{H}_2$ ) (Fig. 1b). Subsequent analyses of the electrodes after participating in the  $\text{CO}_2\text{RR}$  revealed the transformation of both  $\text{BaPd}_2/\text{C}$  and  $\text{TBAPd}_2/\text{C}$  into Pd NPs and  $\text{WO}_x$  nanospecies. Furthermore, Pd acetate ( $\text{Pd}(\text{OAc})_2$ ), a precursor of  $\text{Pd}_2$ , showed a significant decline in  $\text{CO}$  selectivity during the  $\text{CO}_2\text{RR}$ . These results reveal the significant influence of POMs and their counteranions on the performance of POM-based electrocatalysts for the  $\text{CO}_2\text{RR}$ .

## Results and discussion

### Preparation and characterization of catalysts

Initially,  $\text{TBAPd}_2$  (Fig. 1a)<sup>44</sup> was immobilized on a carbon support by mixing an acetone solution of  $\text{TBAPd}_2$  with an ethyl



acetate suspension of the carbon support, yielding **TBAPd2/C** (Fig. 1b).<sup>53</sup> Subsequently, cation exchange was performed by immersing **TBAPd2/C** in an acetone solution containing trifluoromethanesulfonate salts of Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> to obtain **CsPd2/C**, **SrPd2/C**, and **BaPd2/C**, respectively (Fig. 1b, see ESI† for the detailed procedure).<sup>54</sup> This approach of conducting cation exchange on a carbon support was preferred over direct immobilization of Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> salts of **Pd2** (*i.e.*, **CsPd2**, **SrPd2**, and **BaPd2**) owing to the low solubility of the resulting POMs in water and organic solvents,<sup>50</sup> which complicates their direct immobilization.

Following synthesis, the prepared catalysts were characterized through X-ray absorption fine structure (XAFS) measurements. Notably, the Pd K-edge and W L<sub>3</sub>-edge extended X-ray absorption fine structure (EXAFS) oscillation patterns, as well as the Fourier-transformed EXAFS spectra, of **TBAPd2/C** closely resembled those of **TBAPd2** (Fig. 2), suggesting that the anion structure of **TBAPd2** remained intact upon immobilization on the carbon support. Subsequently, the EXAFS spectra of the cation-exchanged samples were similarly examined. As depicted in Fig. 2a, c, S1a and Table S1,† although the Fourier-transformed Pd K-edge EXAFS spectrum of **BaPd2/C** presented a lower intensity of scattering from the Pd–O bond compared to that of **TBAPd2/C**, the Pd K-edge EXAFS oscillation pattern of **BaPd2/C** closely resembled that of **TBAPd2/C**. Similarly, the W L<sub>3</sub>-edge EXAFS oscillation pattern of **BaPd2/C** closely matched that of **TBAPd2/C** (Fig. 2b). However, compared to the Fourier-

transformed W L<sub>3</sub>-edge EXAFS spectrum of **TBAPd2/C**, that of **BaPd2/C** displayed increased scattering intensity from the terminal W=O bond (peak around 1.3 Å)<sup>55</sup> and decreased scattering intensity from the W–O(W) bond (bonds between tungsten atoms and the bridging oxygen atom, with a peak around 1.7 Å)<sup>55</sup> (Fig. 2d, S1b and Table S1†). These findings suggest that although the coordination environment of Pd and W partially changed during the cation exchange process, the fundamental structure of **Pd2** was intrinsically maintained.

Based on these XAFS findings, we further investigated the structure of **Pd2** during cation exchange by subjecting **TBAPd2/C** and **BaPd2/C** to infrared (IR) measurements. However, IR peaks originating from the POMs were difficult to discern owing to interference from the carbon support. To resolve this, we subsequently analyzed the IR spectra of **TBAPd2** and **BaPd2** without their carbon supports (Fig. S2†). Specifically, **BaPd2** was synthesized through the cation exchange of **TBAPd2** with Ba<sup>2+</sup>. Interestingly, the IR spectrum of **BaPd2** displayed no peak corresponding to TBA<sup>+</sup> in the range of 2800–3000 cm<sup>−1</sup>, indicating successful cation exchange. Furthermore, the IR spectrum of **BaPd2** in the range of 300–1000 cm<sup>−1</sup> closely resembled that of **TBAPd2**. Given that this region is characteristic of Keggin-type POMs,<sup>56</sup> the cation exchange was deemed to not adversely affect the anion structure of **Pd2**.

Our next investigation focused on the elemental analysis of the prepared catalysts. As indicated in Table S2,† the ratio of Pd to W remained nearly constant at 2:10 across all samples, consistent with the composition of **TBAPd2**, containing two Pd atoms and ten W atoms. Hence, this finding further corroborates the results of the EXAFS analysis, indicating that the structure of **Pd2** is largely preserved during immobilization on the carbon support and cation exchange. Furthermore, our elemental analysis revealed that the numbers of Cs, Sr, and Ba species in **CsPd2/C**, **SrPd2/C**, and **BaPd2/C** were approximately four, two, and two, respectively. Given that **Pd2** is a tetravalent anion ([γ-H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>Pd<sub>2</sub>(OAc)<sub>2</sub>]<sup>4−</sup>) and Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> are monovalent, divalent, and divalent, respectively, these results suggest that most of the TBA<sup>+</sup> was exchanged with the corresponding alkali metal and alkaline earth metal cations.

### CO<sub>2</sub>RR study

After characterizing the prepared catalysts, we evaluated their catalytic performance in the electrochemical CO<sub>2</sub>RR using a gas-diffusion flow electrolysis cell (Fig. S3†).<sup>57,58</sup> The working electrodes for the CO<sub>2</sub>RR were fabricated by depositing **TBAPd2/C**, **CsPd2/C**, **SrPd2/C**, and **BaPd2/C** onto a gas-diffusion carbon electrode (Sigracet 39 BB, see ESI† for the detailed method). These electrodes were then put in the gas-diffusion flow electrolysis cell, and their catalytic performance was assessed *via* constant potential electrolysis at approximately −0.8 V<sub>RHE</sub> for 1 h, using a 1 M KHCO<sub>3</sub> aqueous solution as the electrolyte. As illustrated in Fig. 3a and S4 and Table S3,† **TBAPd2/C** exhibited a faradaic efficiency for CO production (FE<sub>CO</sub>) of 40.5 ± 7.7% and a total current density of 27.4 ± 1.1 mA cm<sup>−2</sup>. Conversely, **CsPd2/C**, **SrPd2/C**, and **BaPd2/C** displayed FE<sub>CO</sub> values of 72.9 ± 0.1%, 78.9 ± 2.5%, and 92.9 ± 4.8%, respectively. Furthermore,

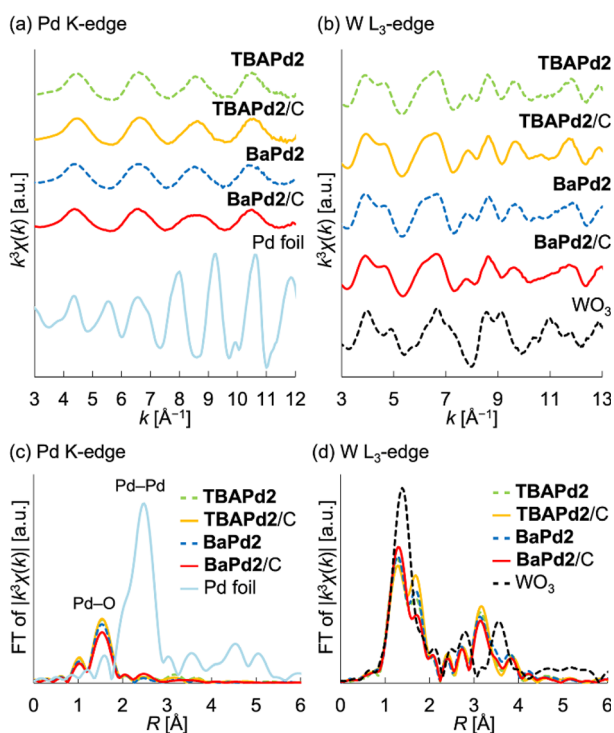
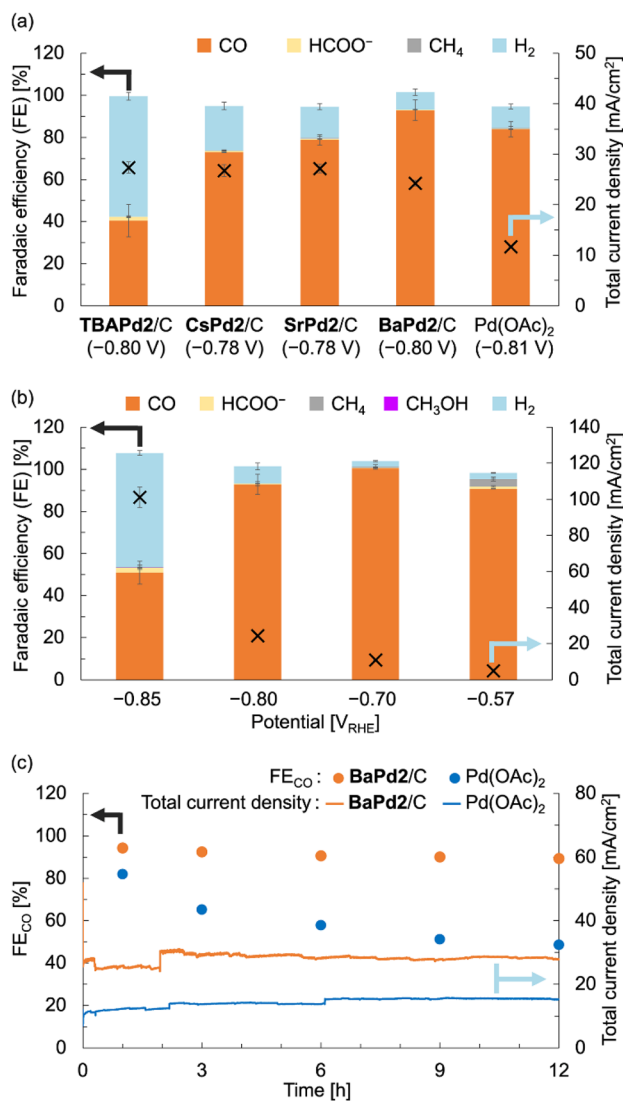


Fig. 2 XAFS characterizations of **TBAPd2/C** and **BaPd2/C**. (a)  $k^3$ -weighted Pd K-edge EXAFS oscillations ( $k = 3$ – $12 \text{ \AA}^{-1}$ ). (b)  $k^3$ -weighted W L<sub>3</sub>-edge EXAFS oscillations ( $k = 3$ – $13 \text{ \AA}^{-1}$ ). (c) Fourier-transformed Pd K-edge EXAFS spectra. (d) Fourier-transformed W L<sub>3</sub>-edge EXAFS spectra.





**Fig. 3** CO<sub>2</sub>RR performance of BaPd<sub>2</sub>/C-modified electrode and other electrodes in a 1 M KHCO<sub>3</sub> aqueous solution. (a) FEs for all CO<sub>2</sub>RR products (left axis) and total current densities (right axis) of TBAPd<sub>2</sub>/C-, CsPd<sub>2</sub>/C-, SrPd<sub>2</sub>/C-, BaPd<sub>2</sub>/C-, and Pd(OAc)<sub>2</sub>-modified electrodes determined through constant potential electrolysis at  $-0.8 V_{RHE}$  for 1 h. (b) FEs for all CO<sub>2</sub>RR products (left axis) and total current density (right axis) of BaPd<sub>2</sub>/C-modified electrode determined through constant potential electrolysis at different potentials for 1 h. (c) FE<sub>CO</sub> (left axis) and total current density (right axis) of BaPd<sub>2</sub>/C-modified electrode ( $-0.75 V_{RHE}$ , orange) and Pd(OAc)<sub>2</sub>-modified electrode ( $-0.73 V_{RHE}$ , light blue) for 12 h. Error bars represent standard deviations calculated from two independent measurements. Symbols X in (a and b) denote the total current density (right vertical axes). All potentials were IR-corrected (see ESI†).

the total current densities for CsPd<sub>2</sub>/C, SrPd<sub>2</sub>/C, and BaPd<sub>2</sub>/C were  $26.8 \pm 1.2$ ,  $27.2 \pm 0.8$ , and  $24.3 \pm 0.6 \text{ mA cm}^{-2}$ , respectively. These findings indicate significant enhancements in CO<sub>2</sub>RR performance following cation exchange from TBA<sup>+</sup> to Cs<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>, with BaPd<sub>2</sub>/C demonstrating the highest efficiency. Collectively, these results underscore the critical significance of counterion identity in catalytic performance, as well as the superior efficiency of BaPd<sub>2</sub>/C for the CO<sub>2</sub>RR.

Encouraged by these outcomes, we subsequently compared the catalytic performance of BaPd<sub>2</sub>/C with that of Pd(OAc)<sub>2</sub>, a precursor of Pd<sub>2</sub>, deposited on a gas-diffusion carbon electrode in a similar manner to the other catalysts, at the same Pd content (Fig. 3a). The results revealed that Pd(OAc)<sub>2</sub> exhibited lower FE<sub>CO</sub> ( $83.9 \pm 3.6\%$ ) and lower total current density ( $11.66 \pm 0.04 \text{ mA cm}^{-2}$ ) compared to BaPd<sub>2</sub>/C (FE<sub>CO</sub>  $92.9 \pm 4.8\%$ ,  $24.3 \pm 0.6 \text{ mA cm}^{-2}$ ). Although various reports have addressed CO<sub>2</sub>RR using POM-containing electrodes in aqueous electrolytes, there have been no reports on CO<sub>2</sub>RR using Pd-incorporated POMs or the effect of the counterions of POMs on CO<sub>2</sub>RR (Table S8†).

Subsequently, CO<sub>2</sub>RR experiments were performed utilizing the BaPd<sub>2</sub>/C-modified electrode at various applied potentials to elucidate the potential dependence of its catalytic performance. Although the CO<sub>2</sub>RR experiments at  $-0.70$  and  $-0.57 V_{RHE}$  exhibited reduced total current densities compared to the reaction at  $-0.80 V_{RHE}$ , CO was exclusively produced at each potential (Fig. 3b and Table S4†). However, reducing the potential to  $-0.85 V_{RHE}$  resulted in a decrease in FE<sub>CO</sub> and an increase in a faradaic efficiency for H<sub>2</sub> production (FE<sub>H<sub>2</sub></sub>) to nearly 50%. We also confirmed that CO and HCOO<sup>-</sup> were not produced in reactions using an electrode without Pd<sub>2</sub> deposition or in reactions conducted in an Ar atmosphere (Table S5†).

To assess the long-term stability of the catalyst, a CO<sub>2</sub>RR experiment employing BaPd<sub>2</sub>/C as the catalyst was performed over 12 h at an applied potential of  $-0.75 V_{RHE}$  (Fig. 3c and Table S6†). Note that due to the instability of Sigracet 39 BB in prolonged CO<sub>2</sub>RR, AvCarb P75T was used as a carbon electrode to prepare a BaPd<sub>2</sub>/C-modified electrode in this experiment. As depicted in Fig. 3c, although the total current density of the catalyst fluctuated during the reaction, its selectivity toward CO production was maintained consistently throughout the experiment. In contrast, a 12 h CO<sub>2</sub>RR experiment using Pd(OAc)<sub>2</sub> as the catalyst exhibited a significant decline in FE<sub>CO</sub> during the reaction, accompanied by an increase in FE<sub>H<sub>2</sub></sub> (Fig. 3c and Table S7†). The total current density in this case was stable around  $14 \text{ mA cm}^{-2}$  throughout the reaction, approximately half that of BaPd<sub>2</sub>/C. These results highlight the significant influence of POMs for the CO<sub>2</sub>RR performance.

### Characterization of a BaPd<sub>2</sub>/C-modified electrode after the CO<sub>2</sub>RR

Based on the results of the CO<sub>2</sub>RR experiments, we performed XAFS measurements to probe the structure and electronic state of a BaPd<sub>2</sub>/C-modified electrode obtained after a 1 h CO<sub>2</sub>RR at  $-0.80 V_{RHE}$ . To investigate the electronic state of the Pd species, we measured the Pd K-edge X-ray absorption near-edge structure (XANES) spectra of the electrode before and after the CO<sub>2</sub>RR (Fig. 4a). Notably, the XANES spectrum of the electrode before the reaction was intermediate to the corresponding spectra of a Pd foil and BaPd<sub>2</sub>/C. Conversely, the XANES spectrum of the electrode after the reaction closely resembled that of the Pd foil. These findings indicate that Pd<sup>2+</sup> underwent partial reduction during electrode fabrication and complete reduction to Pd<sup>0</sup> during the CO<sub>2</sub>RR. Subsequently, to glean insights into



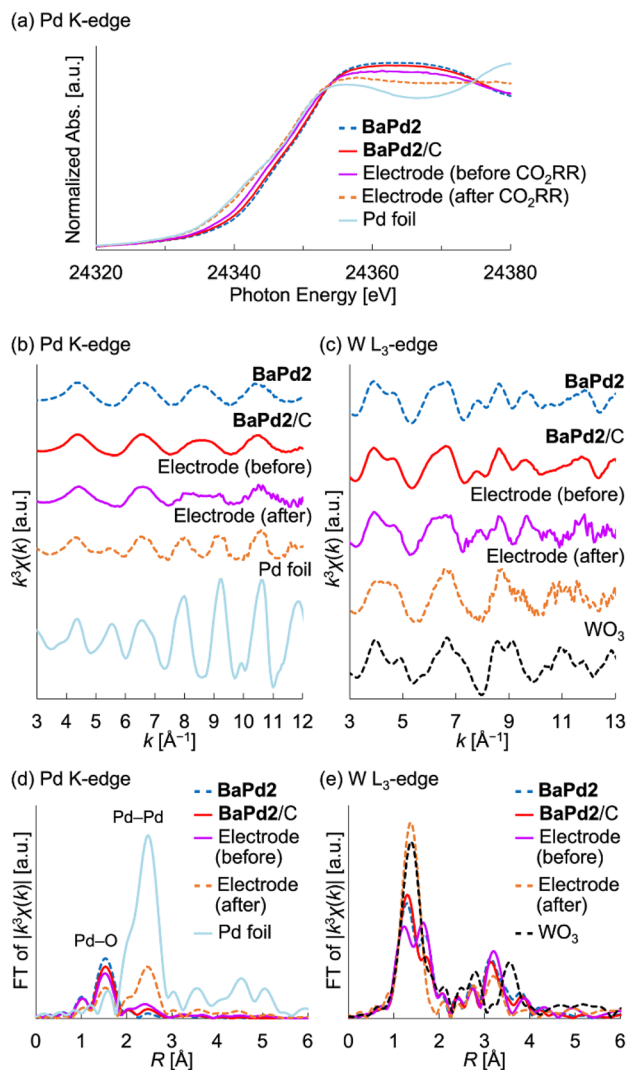


Fig. 4 XAFS characterization of the **BaPd2/C**-modified electrode obtained after a 1 h  $\text{CO}_2\text{RR}$ . (a) Pd K-edge XANES spectra. (b)  $k^3$ -weighted Pd K-edge EXAFS oscillation pattern ( $k = 3\text{--}12 \text{ \AA}^{-1}$ ). (c)  $k^3$ -weighted W  $L_3$ -edge EXAFS oscillation pattern ( $k = 3\text{--}13 \text{ \AA}^{-1}$ ). (d) Fourier-transformed Pd K-edge EXAFS spectra. (e) Fourier-transformed W  $L_3$ -edge EXAFS spectra.

the structure of the POM before and after the reaction, we performed Pd K-edge and W  $L_3$ -edge EXAFS analysis (Fig. 4b–e). Notably, the Pd K-edge EXAFS oscillation pattern of the electrode after the  $\text{CO}_2\text{RR}$  resembled that of the Pd foil but not that of **BaPd2/C** (Fig. 4b). Furthermore, the Fourier-transformed Pd K-edge EXAFS spectra revealed that the electrode after the  $\text{CO}_2\text{RR}$  exhibited reduced scattering intensity from the Pd–O bond and increased scattering intensity from the Pd–Pd bond compared to that before the reaction (Fig. 4d). These results suggest the structural transformation of **BaPd2** to Pd NPs during the reaction. Conversely, the W  $L_3$ -edge EXAFS analysis of the electrode after the reaction displayed a similar yet partially distinct oscillation pattern compared to that of  $\text{WO}_3$  (Fig. 4c). Furthermore, compared to the Fourier-transformed W  $L_3$ -edge EXAFS spectra of  $\text{WO}_3$ , that of the electrode after the

$\text{CO}_2\text{RR}$  displayed differences around the second coordination sphere (Fig. 4e).

For comparison, we also conducted XAFS measurements on a  $\text{Pd}(\text{OAc})_2$ -modified electrode subjected to a 1 h  $\text{CO}_2\text{RR}$  (Fig. S5 and S6†). Notably, the Pd K-edge XANES spectrum of the electrode before the reaction was intermediate to those of the Pd foil and  $\text{Pd}(\text{OAc})_2$ , whereas after the  $\text{CO}_2\text{RR}$ , it closely resembled that of the Pd foil (Fig. S5†). Similarly, the Pd K-edge EXAFS oscillation pattern of the electrode after the  $\text{CO}_2\text{RR}$  resembled that of the Pd foil but not that of  $\text{Pd}(\text{OAc})_2$  (Fig. S5†). Furthermore, the Fourier-transformed Pd K-edge EXAFS spectrum of the  $\text{Pd}(\text{OAc})_2$ -modified electrode after the  $\text{CO}_2\text{RR}$  exhibited a similar intensity of scattering from the Pd–O bond but a greater intensity of scattering from the Pd–Pd bond compared to the **BaPd2/C**-modified electrode after the reaction (Fig. S6†). These results suggest that the Pd NPs transformed from  $\text{Pd}(\text{OAc})_2$  were larger than those formed from **BaPd2/C** after the  $\text{CO}_2\text{RR}$ .

Based on these findings, we subjected the **BaPd2/C**-modified electrode obtained after the  $\text{CO}_2\text{RR}$  to electron microscopy observations. Notably, transmission electron microscopy (TEM) images of the **BaPd2/C** after the  $\text{CO}_2\text{RR}$  revealed the formation of NPs with an average particle size of  $4.0 \pm 1.3 \text{ nm}$  on the carbon support (Fig. 5a and b). Conversely, larger NPs with a broader size distribution (an average particle size of  $6.0 \pm 3.1 \text{ nm}$ ) were formed on the  $\text{Pd}(\text{OAc})_2$ -modified electrode after the  $\text{CO}_2\text{RR}$  (Fig. S7†), consistent with the XAFS results. Subsequently, high-angle annular dark-field scanning TEM (HAADF-STEM) images (Fig. 5c) and STEM-energy-dispersive spectroscopy (EDS) mappings (Fig. 5d–g) of the **BaPd2/C** after the reaction revealed that most Pd NPs were surrounded by W atoms, with some W species present in locations where Pd NPs were absent. This observation also confirms the retention of Ba on the electrode after the  $\text{CO}_2\text{RR}$ . Collectively, these results indicate that **BaPd2** transformed into  $\text{WO}_x$  nanospecies and Pd NPs surrounded by  $\text{WO}_x$  nanospecies during the reaction. Adopting a similar approach, our research group previously developed various metal NPs stabilized by lacunary POMs.<sup>59–61</sup> Furthermore, previous reports suggest that  $\text{WO}_x$  nanoclusters derived from diiron-incorporated POMs hinder the aggregation of *in situ*-formed  $\text{FeO}_x$  subnanoclusters.<sup>49</sup> Consequently, it is plausible that  $\text{WO}_x$  nanospecies prevented the aggregation of Pd NPs in our  $\text{CO}_2\text{RR}$  system.

### Effect of countercations on the $\text{CO}_2\text{RR}$

To examine the impact of countercations on  $\text{CO}_2\text{RR}$  performance, we characterized the **TBAPd2/C**-modified electrode subjected to a 1 h  $\text{CO}_2\text{RR}$  at  $-0.80 \text{ V}_{\text{RHE}}$ , which exhibited poor  $\text{CO}_2\text{RR}$  performance compared to the **BaPd2/C**-modified electrode (Fig. 3a and Table S3†). Notably, the Pd K-edge and W  $L_3$ -edge EXAFS oscillation and Fourier-transformed EXAFS spectra of the **TBAPd2/C**-modified electrode after the  $\text{CO}_2\text{RR}$  closely resembled those of the **BaPd2/C**-modified electrode after the reaction (Fig. S6 and S8†). Furthermore, the TEM image of the **TBAPd2/C** after the  $\text{CO}_2\text{RR}$  revealed the formation of NPs with an average particle size of  $2.9 \pm 1.1 \text{ nm}$  on the carbon support



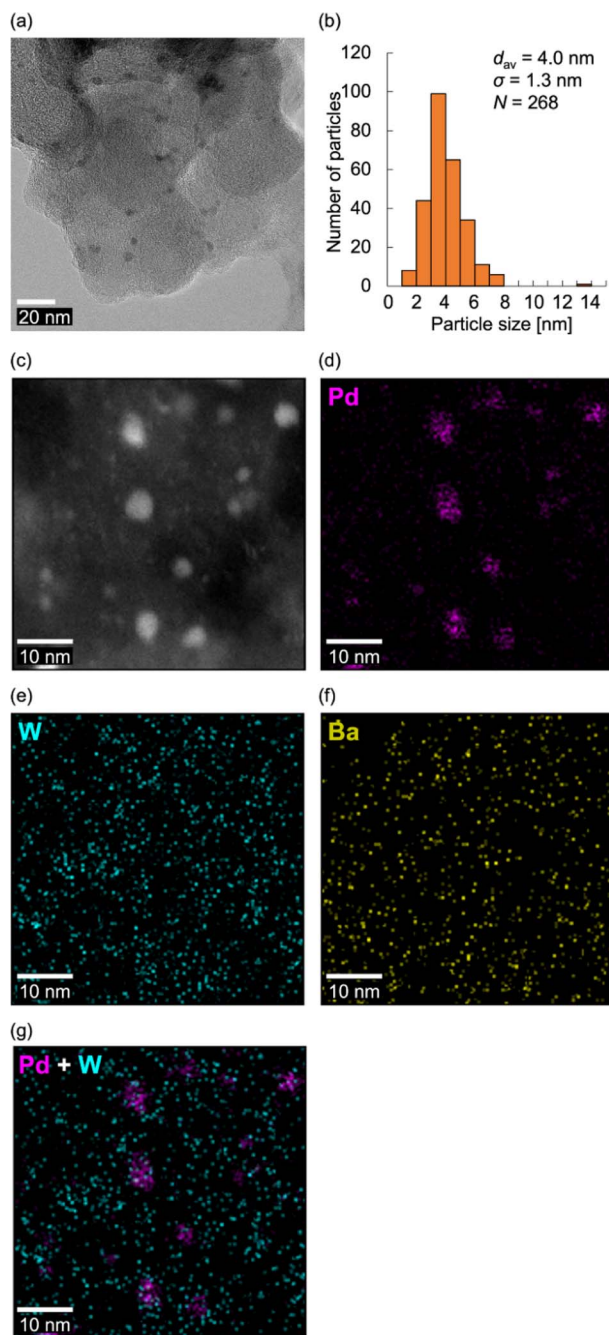


Fig. 5 TEM and HAADF-STEM images of the **BaPd<sub>2</sub>/C**-modified electrode obtained after a 1 h CO<sub>2</sub>RR. (a) TEM image and (b) the corresponding size-distribution histogram. (c) HAADF-STEM image and (d–g) the corresponding STEM-EDS mappings (Pd, pink; W, turquoise; Ba, yellow).

(Fig. S9a and S9b†). Similarly, the HAADF-STEM image (Fig. S9c†) and STEM-EDS mappings (Fig. S9d–9f†) of the **TBAPd<sub>2</sub>/C** after the CO<sub>2</sub>RR were nearly identical to those of the **BaPd<sub>2</sub>/C** after the CO<sub>2</sub>RR (Fig. 5). These results indicate that similar species were formed after the CO<sub>2</sub>RR regardless of the counteranion type.

An explanation for the enhanced CO production could be related to the electronic state of the Pd species. For instance,

electron-rich Pd species modified with *N*-heterocyclic carbene ligands have been reported to demonstrate superior CO<sub>2</sub>RR performance.<sup>62,63</sup> To probe the electronic states of the Pd species, we performed CO stripping voltammetry experiments on the **TBAPd<sub>2</sub>/C**-, **CsPd<sub>2</sub>/C**-, **SrPd<sub>2</sub>/C**-, and **BaPd<sub>2</sub>/C**-modified electrodes after the CO<sub>2</sub>RR (Fig. S10, see ESI† for additional details). Notably, the CO stripping potential of the **TBAPd<sub>2</sub>/C**-modified electrode was more positive than those of the **CsPd<sub>2</sub>/C**-, **SrPd<sub>2</sub>/C**-, and **BaPd<sub>2</sub>/C**-modified electrodes, indicating the presence of more electron-rich Pd NPs in the **TBAPd<sub>2</sub>/C**-modified electrode.<sup>62</sup> Considering that POMs can donate electrons to metal NPs depending on their anion charges, as evidenced by the findings of our previous studies,<sup>59–61</sup> the observed varying electronic states of Pd NPs likely stem from the differential ability of WO<sub>x</sub> nanospecies to donate electrons to Pd NPs depending on the counteranions. However, despite exhibiting a more electron-rich state, Pd NPs derived from the **TBAPd<sub>2</sub>/C**-modified electrode displayed poor CO<sub>2</sub>RR performance (Fig. 3a and Table S3†), indicating that the electronic state of Pd NPs does not critically influence the CO<sub>2</sub>RR performance of our system.

Another plausible explanation for the enhanced CO production could be related to the cationic effect. Generally, in the CO<sub>2</sub>RR, electrolytes containing larger cations often demonstrate higher productivity for various CO<sub>2</sub>RR products such as CO.<sup>9–19</sup> Several theories have been proposed to elucidate the origin of this cationic effect, including (i) modulation of the electric field near the electrode surface, (ii) pH buffering at the electrode interface, and (iii) stabilization of reaction intermediates.<sup>9,64–67</sup> For instance, Jiang *et al.* recently investigated the CO<sub>2</sub>RR performance of Pd NPs formed on a carbon support using electrolytes containing various alkali metal cations. As anticipated, they observed higher FE<sub>CO</sub> values for electrolytes containing larger cations, and they attributed these findings to the intensified electric field near the electrode surface.<sup>19</sup> Although the primary influencing factor in our system remains unidentified at this stage, we propose that the enhanced CO production observed for **CsPd<sub>2</sub>/C**, **SrPd<sub>2</sub>/C**, and **BaPd<sub>2</sub>/C** may be attributed to the abovementioned cationic effect caused by the POM counteranions.

## Conclusions

In conclusion, this study highlighted the significant impact of the counteranions of POM-based electrocatalysts on their catalytic performance in the CO<sub>2</sub>RR. Specifically, **TBAPd<sub>2</sub>/C**, synthesized by immobilizing **TBAPd<sub>2</sub>** on a carbon support, was compared with its analogs **CsPd<sub>2</sub>/C**, **SrPd<sub>2</sub>/C**, and **BaPd<sub>2</sub>/C**, synthesized by exchanging the TBA<sup>+</sup> cations of **TBAPd<sub>2</sub>/C** with alkali metal and alkaline earth metal cations (Cs<sup>+</sup>, Sr<sup>2+</sup>, or Ba<sup>2+</sup>) in acetone. Assessments of their catalytic CO<sub>2</sub>RR performance in a 1 M KHCO<sub>3</sub> aqueous solution using a flow electrolysis cell with gas-diffusion carbon electrodes modified with these catalysts revealed that the **BaPd<sub>2</sub>/C**-modified electrode exhibited selective CO production over 12 h, whereas the **TBAPd<sub>2</sub>/C**-modified electrode exhibited lower CO selectivity owing to inadequate suppression of the HER. Detailed analyses indicated



that both **TBAPd2** and **BaPd2** transformed into Pd NPs and  $\text{WO}_x$  nanospecies during the  $\text{CO}_2\text{RR}$ , highlighting the significant influence of counteranions on the reactivity of the electrocatalyst. Moreover,  $\text{Pd}(\text{OAc})_2$  demonstrated a marked decline in the CO selectivity during the  $\text{CO}_2\text{RR}$ , and the formation of larger Pd NPs with a broader size distribution than **BaPd2** was observed after the  $\text{CO}_2\text{RR}$ . These results highlight the critical role of POMs and their counteranions in modulating the  $\text{CO}_2\text{RR}$  performance of POM-based electrocatalysts. As POMs continue to demonstrate promise in  $\text{CO}_2\text{RR}$  applications, we believe that our findings will contribute to the development of highly effective and durable POM-based electrocatalysts for future  $\text{CO}_2\text{RR}$  applications.

## Data availability

The data supporting this manuscript is available in the ESI† and available on request.

## Author contributions

K. K. performed the synthesis, reaction, and characterizations. T. Y. performed the XAFS analysis. K. S. conceived and directed the project. All authors analyzed and discussed the results and co-wrote the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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