



Unveiling the electrochemical CO oxidation activity on support-free porous PdM (M = Fe, Co, Ni) foam-like nanocrystals over a wide pH range

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ABSTRACT

Binary PdM-based nanocrystals are efficient electrocatalysts for a wide range of renewable and green fuel cell applications; however, their poisoning by CO is a great barrier for commercialization, so it is pivotal to solve this issue. Herein, we fabricated support-free PdM alloys (M = Fe, Co, and Ni) by a prompt one-step aqueous-solution co-reduction with sodium borohydride driven by the coalescence growth mechanism. This forms support-free PdM porous foam-like nanostructures with well-defined compositions from the ICP-OES analysis and clean surface without any hazardous chemicals or multiple reaction steps. The as-prepared PdM foam-like nanostructures were demonstrated for carbon monoxide oxidation (CO_{Oxid}) electrocatalysis at varied electrolyte pH compared with commercial Pd/C catalyst. The foam-like PdFe nanocrystals achieved an excellent electrochemical CO_{Oxid} activity that was at least 2.18-times of PdCo, 4.35-times of PdNi, and 1.56-times of Pd/C in both alkaline (KOH) and acidic (HClO₄) electrolytes, but PdCo was the best in neutral (NaHCO₃) medium. The superior activity of PdM is due to the strain and alloying effect, which promoted the superb CO oxidation durability for 1000 cycles than Pd/C catalyst. This study demonstrated the superiority of support-free bimetallic PdM alloys than Pd/C catalyst in all electrolytes, which may open new gates for understanding CO-poisoning in alcohol-based fuel cells.

Introduction

There is tremendous interest in the development of renewable energy, including fuel cells [1–3], batteries [4], supercapacitors [5], and biofuels [6,7], to reduce carbon-foot print and preserve conventional fossil fuels [8–11]. This has endeared alcohol-based fuel cells (i.e., ethanol, methanol, and glucose) [12,13] to be among the most green and effective energy systems, however, the electrodes are prone to poisoning by carbon monoxide (CO) intermediate species, which is a major setback for their optimal operation [14]. Thus, CO oxidation (CO_{Oxid}) is a crucial indicator, not only in heterogeneous catalysis but also in different industrial, health, and environment remediation applications [15–17].

The CO_{Oxid} can be driven thermally or electrochemically [16–19]. The latter is mostly preferred because of its low energy intensiveness and room-temperature operation [20,21].

Amongst the potent electrocatalysts, palladium (Pd) with outstanding catalytic merits for various applications and showed excellent CO_{Oxid} activity and durability traced to its tendency to improve the activation and dissociation of CO/O₂ and quick desorption of the adsorbed intermediate species at low applied potential, but its earth-rarity and expensiveness are the main challenges for practical utilization [20,22–25]. This hitch could be surmounted by alloying Pd with earth-abundant and cheap transition metals (M = Fe, Co, Cu, Mn, Ni, Zn) with or without supports (like carbon-based or metal-oxide-based),

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which results in lessened Pd loading and promotes the CO_{oxid} activity and durability [26–28]. Also, alloying Pd with M elements boosts the electronic features of Pd via upshifting or downshifting its d-band center to accelerates the H₂O dissociation at low potential to generate oxygen-containing species (i.e., [•]OH) that is advantageous for CO_{oxid} kinetics [29–31]. For example, PdNiO nanostructures grown CeO₂/carbon black (CB) support (PdNiO-CeO₂/CB) delivered an increased CO_{oxid} activity than PdNiO/CeO₂, PdNiO/CB and Pd/C by at least 1.58-, 1.52- and 1.67-folds in HClO₄, KOH and NaHCO₃ media, due to the utilization of oxygen-rich support, which eases adsorption/activation of CO/O₂ and dissociation of O₂ along with the physicochemical features of CB (i.e., high surface area and electrical conductivity), and catalytic merits of PdNiO (i.e., strain, active sites and H₂O splitting to generate OH species) [32]. Also, Pd nanostructures anchored on carbon nanosheets derived from zeolitic imidazole frameworks (Pd/ZIF-67/C) had a superior CO_{oxid} electrocatalysis and durability than Pd/C in acid, alkaline and neutral conditions, attributable to the improved electronic merits of Pd by Co-N_x and the porosity of the ZIF/C [33]. Surface nitride PdCu nanosheets (N-Pd₆₀Cu₄₀ NSs) endowed with coupled electronic and structural effects beneficial for declined CO-intermediate adsorption that led to its improved CO_{oxid} activity compared to N-Pd NSs, and commercial-Pd/C [34]. In spite of the advantages of alloying, the influence of alloying and varied electrolytes media on support-free binary Pd-based electrocatalysts are not emphasized enough [32,35–38].

These few reports serve as a motivation for the fabrication of support-free PdM (i.e., PdFe, PdCo, and PdNi) foam-like nanocrystals via rapid chemical reduction of aqueous solutions of metal precursors by NaBH₄ in ice-bath. This simplistic method is green (i.e., without surfactants or capping agents or organic solvents), instant (i.e., only takes 5 min), and high-yield with controlled compositions of PdM having interconnected pores and clean surfaces. The incorporation of oxophilic M into Pd lattice enables quick H₂O splitting to generate oxygen-containing species (i.e., [•]OH) beneficial for a quick CO_{oxid} kinetics at low potential. The investigation of the physicochemical of the as-obtained PdM foam-like nanocrystals reveals their surface and bulk analysis regarding the shape, compositions, and electronic effect. The performance of the as-obtained PdM foam-like nanocrystals toward CO_{oxid} activity and durability are probed and benchmarked to commercial-Pd/C in alkaline (i.e., KOH), acid (i.e., HClO₄) and neutral (i.e., NaHCO₃) media with the view to know the effect of PdM nanocrystal alloys and electrolyte pH.

Materials and methods

Materials

Iron(II) chloride (FeCl₂, ≥ 99 %), cobalt(II) chloride (CoCl₂, ≥ 99 %), nickel(II) chloride (NiCl₂, ≥ 99 %), potassium tetrachloropalladate(II) (K₂PdCl₄, ≥ 99 %), sodium borohydride (NaBH₄, 99 %), potassium hydroxide (KOH, > 98 %), commercial Pd/C (10 wt%) were acquired from Sigma-Aldrich Chemie GmbH (Munich Germany).

Preparation of support-free PdM foam-like nanocrystals

Porous support-free PdFe foam-like nanocrystals were prepared by fast addition of NaBH₄ (0.1 M, 1.0 mL) to a mixture of aqueous solutions of K₂PdCl₄ (15.0 mM, 10 mL) and FeCl₂ (15.0 mM, 10 mL) in an ice-bath with magnetic stirring for 5 min. The opaque black precipitates of PdFe nanocrystals were obtained, washed with double deionized water (ddH₂O), centrifuged at 7000 rpm, and stored for further use.

This preparation method was also used for porous support-free PdCo and PdNi nanocrystals using (15.0 mM, 10 mL) of CoCl₂ and NiCl₂ precursors instead of FeCl₂, respectively with K₂PdCl₄ (15.0 mM, 10 mL).

Materials characterization

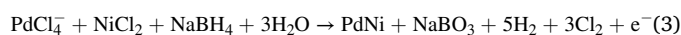
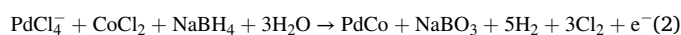
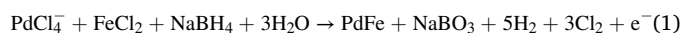
The as-obtained PdM foam-like nanocrystals were analyzed using a scanning electron microscope ((SEM), Hitachi S-4800, Hitachi, Tokyo, Japan) equipped with Energy Dispersive X-Ray Analyzer (EDX) and a transmission electron microscope ((TEM), TecnaiG220, FEI, Hillsboro, OR, USA). The X-ray photoelectron spectroscopy ((XPS) was measured on Ultra DLD XPS Kratos, Manchester, UK). The X-ray diffraction (XRD) was conducted on X'Pert-Pro MPD, PANalytical Co., Almelo, Netherlands). The inductively coupled plasma optical emission spectrometry ((ICP-OES), Agilent 5800) was done on (ICP-OES Agilent 5800, USA).

Electrochemical measurements of CO oxidation

The electrochemical CO_{oxid} performance was carried out on Gamry potentiostat (Reference 3000, Gamry Co., Warminster, PA, USA) utilizing 3-electrode configurations, including Pt wire, Ag/AgCl, and glassy carbon (GC), as counter electrode (CE), reference electrode (RE) and working electrode (WE). Various electrochemical techniques, like cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS), were utilized for the electrochemical CO_{oxid} performance of the support-free PdM nanocrystals. Each PdM nanocrystal (2.0 mg) was added to a mixture of isopropanol/H₂O/Nafion (0.05 wt.%) (3/1/0.5 v/v ratio) and sonicated for 30 min and then drop cast onto the polished GC. The coated GC electrodes were dried in an oven under vacuum at 80 °C for 1 h. The mass loading of Pd in the PdM nanocrystals on the GC was approximately 0.020 ± 0.002 mg_{Pd}/cm², determined by the ICP-OES. The electrochemical active surface area (ECSA) was determined using the formula: ECSA = $\frac{Q}{S \times l}$, where Q is the coulombic charge of hydrogen under-deposition potential (HUDP) peak, S is the coulombic constant for monolayer Pd (0.424 mC/cm²) and l is the Pd mass loading (0.0013–0.0015 mg_{Pd}) on the WE, determined by the ICP-OES analysis.

Results and discussion

Fig. 1a shows the fabrication method for the preparation of PdM foam-like nanocrystals including the chemical reduction of aqueous metal precursors by NaBH₄ in an ice-bath, which is driven by the burst nucleation and coalescence growth mechanism. Mainly, the instantaneous nucleation of Pd²⁺ ions to form Pd nuclei occurred initially, attributed to the high standard reduction potential of Pd²⁺/Pd⁰ (0.915 V) compared to Fe²⁺/Fe⁰ (-0.440 V), Co²⁺/Co⁰ (-0.280 V) and Ni²⁺/Ni⁰ (-0.257 V) and serve as seeds for the second metals to form PdM nuclei. These nuclei are highly unstable thermodynamically, so they prone to coalesce together, leading to oriented attachment growth to form PdM nanocrystals in the form of porous foam-like nanostructures. The in-situ released H₂ gases during the reduction process promote the formation of pores. The balanced chemical interaction of the metal precursors and reducing agent is presented in equations (1)–(3).



The SEM images show the foam-like nanocrystals of the PdFe, PdCo, and PdNi with interconnected pores (Fig. 1b-c, S1a, and S1b), which is advantageous for easy adsorption and diffusion of reactants (CO + O₂) during CO_{oxid} electrocatalysis. The TEM images showed that the foam-like morphology composed of ultra-small spherical-like nanocrystals (Fig. 1d, S1c, and S1d), with a lower mean nanoparticle diameter for PdFe (5.10 nm) relative to PdCo (5.62 nm) and PdNi (6.50 nm) (Fig. S2). The interplanar spacings of 2.236, 1.935, 1.371, and 1.170 Å for PdFe, attributed to with Fourier transform {111}, {200}, {220} and {311}

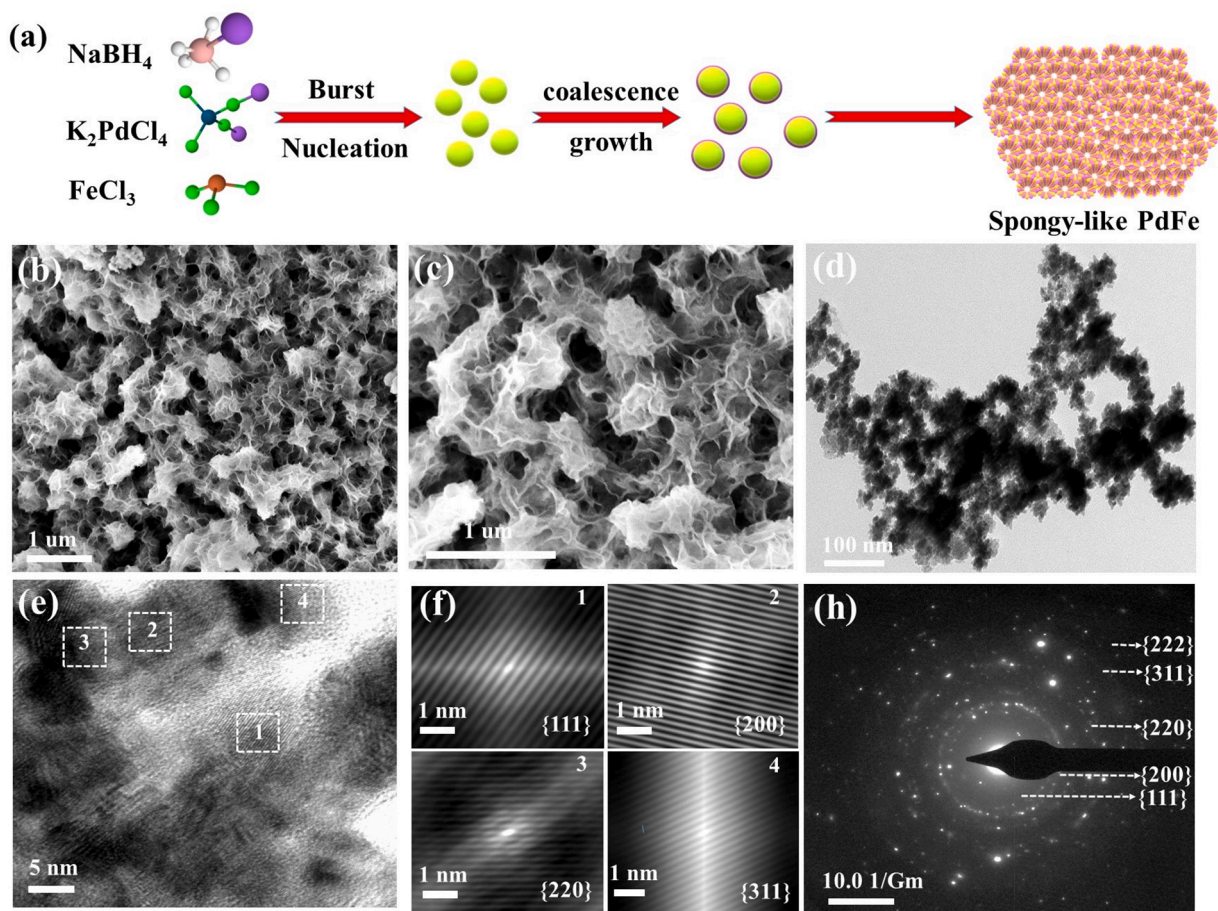


Fig. 1. (a) Fabrication process, (b) SEM, (c) enlarged SEM, (d) TEM, (e) HRTEM, (f) Fourier transform-HRTEM of marked areas (1–4), and (g) SAED of PdFe nanocrystals.

facets, respectively of face-centered cubic (*fcc*) of Pd nanocrystals (Fig. 1e and 1f), whereas 2.235 and 2.236 Å PdCo, and PdNi (Fig. S1e and S1f) for only {1 1 1} facet. This proves that the perfect incorporation of M (Fe, Co, and Ni) into the Pd lattice forming PdM alloy in line with elsewhere reports [35,36].

All the PdM nanocrystals reveal the selected area electron diffraction (SAED) diffraction pattern of {111}, {200}, {220}, {311}, and {222} facets of *fcc* of Pd (Fig. 1g, S1g, and S1h), as usually recorded for Pd-based nanostructures [39,40]. The HAADF-STEM and elemental mapping analysis of the PdM nanocrystals reveals the formation of foam-like morphology with uniform distribution of Pd/Fe/O in PdFe, Pd/Co/O in PdCo, and Pd/Ni/O in PdNi nanostructures (Fig. 2). The EDX analysis shows the existence of Pd/Fe (71.05/28.52/0.43 At.%), Pd/Co (55.10/43.40/1.5 At.%) and Pd/Ni (55.85/42.25/1.90 At.%) (Fig. S1i). Similarly, the actual bulk metal contents in PdFe (Pd/Fe are 83.46/16.54 At.%), PdCo (Pd/Co are 54.09/45.91 At.%) and PdNi (Pd/Ni are 63.05/36.95 At.%), revealed by ICP-OES analysis (Table S1). The unequal surface/bulk atomic compositions of the PdM are traced to the varied standard reduction potentials of the various metals, thereby, metal with a higher standard reduction potential got reduced and integrated rapidly into the Pd lattice to form the binary metal nanostructures [35,36]. The XRD patterns of the PdFe, PdCo, PdNi, and Pd/C nanocrystals showed the main diffraction pattern attributed to {1 1 1}, {200}, {220}, {311} and {222} facets of *fcc* of Pd. Meanwhile, PdFe and PdCo have an additional {110} facet of PdO (Fig. 3a). The presence of PdO on PdFe and PdCo may be due to the tendency of Pd to oxidize in the air with higher oxides of Fe and Co compared to Ni as well be discussed below in the XPS analysis. The PdM nanocrystals have most exposed {1 1 1} facet of Pd, but PdFe showed PdO {110} as the most exposed one. The

absence of distinct diffraction patterns of pure Fe, Co, and Ni and their oxides in the PdM nanostructures reveals the formation of pure nanocrystal alloys. The same diffraction patterns are observed for the commercial Pd/C; however, the 2θ slightly shifts to higher values in the PdM nanocrystals, owing to alloying effect, which leads to increased Pd-Pd interatomic distance and consequent Pd lattice contraction (Fig. 3b) [41]. The lattice contraction of PdM nanostructures is revealed by the lower lattice constant (a) of 2.9320 Å, 3.8660 Å and 3.8720 Å for PdFe, PdNi and PdCo compared to Pd/C (3.8940 Å), due to the incorporation of M into the lattice of Pd in the PdM nanocrystals with low Pd-Pd interatomic distance. The lattice strains (ϵ) of PdFe (0.165), PdCo (0.148), and PdNi (0.174) were determined by the Williamson-Hall plots (Fig. 3c). This confirms the lower synergy in PdNi and PdFe relative to PdCo, due to their dissimilar atomic size and electronic structure.

The full-width at half maximum (FWHM) of {1 1 1} peak for PdFe is higher, resulting in lower crystallite sizes (τ) of PdFe (5.76 nm) compared to PdCo (7.54 nm) and PdNi (8.15 nm) (Fig. 3b), extrapolated from the Scherrer equation using approximation spherical crystallites (shape factor $K = 0.89$) [32]. Also, the degree of alloying of PdFe (53.37%), PdCo (60.95%), and PdNi (60.57%) were calculated using Vegard's law, which reveals lower alloying degree in PdFe, but high strain amongst the PdM nanocrystals.

The XPS spectra of the core level of Pd 3d/Fe 2p, Pd 3d/Co 2p, and Pd 3d/Ni 2p, with surface atomic compositions of Fe, Co, and Ni as 90.43, 56.13 and 30.95% in PdFe, PdCo, and PdNi, respectively, which are dissimilar from the surface/bulk elemental compositions by EDX and ICP-OES (Table S1). The Pd3d of PdFe shifts to higher binding energies relative to PdCo and PdNi, is an indication of downshifted d-band center of the Pd to the Fermi level in PdFe (Fig. 4a). This elucidates the

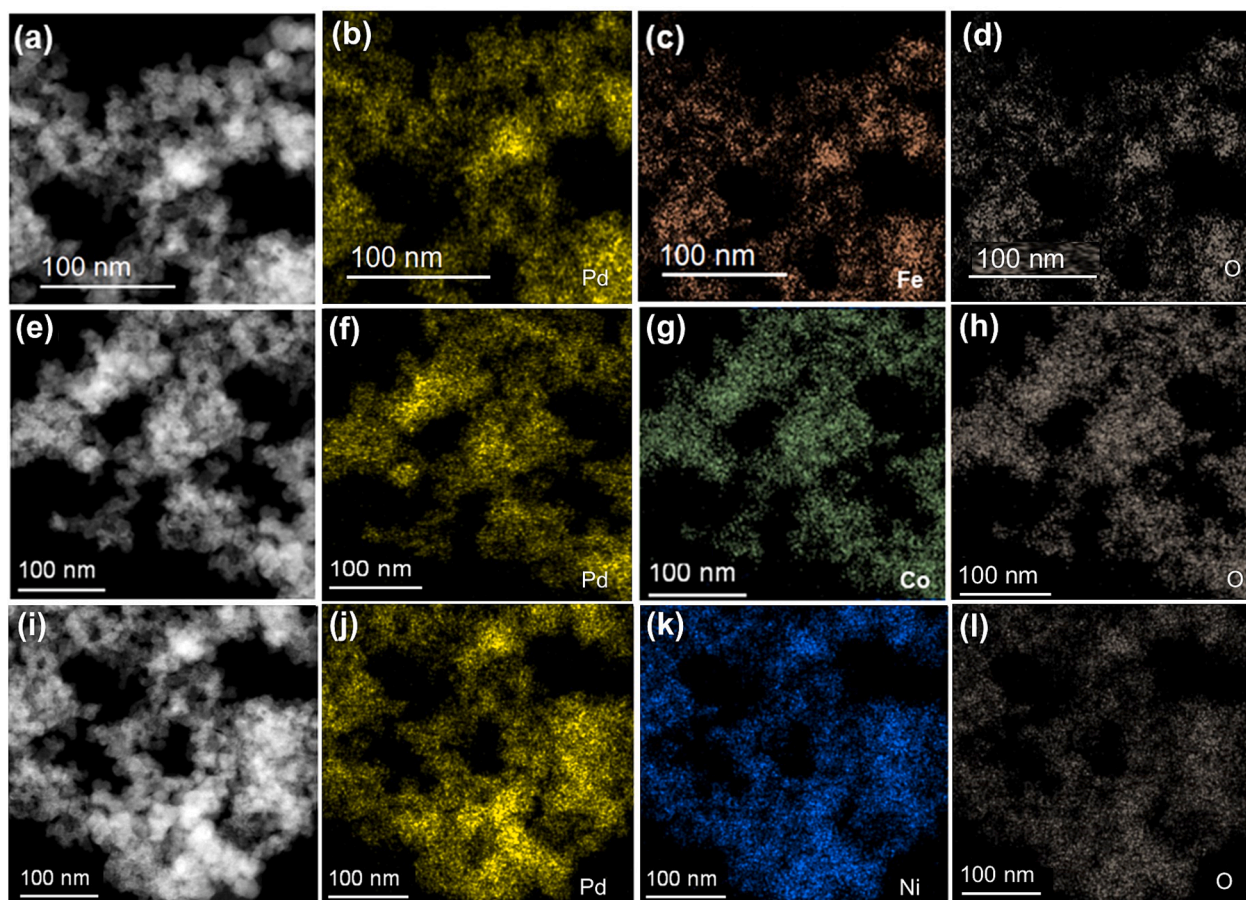


Fig. 2. HAADF-STEM and their elemental mapping analysis of (a-d) PdFe, (e-g) PdCo and (h-l) PdNi nanocrystals.

decreasing d-band center of Pd in PdFe (-1.71 eV) compared to PdCo (-2.23 eV) and PdNi (-1.95 eV) (Table S2), which is advantageous for easy adsorption of reactants ($\text{CO} + \text{O}_2$) and desorption of intermediate species during the electrochemical CO_{Oxid} [40,42]. The Pd 3d spectra of the PdM deconvoluted into $\text{Pd}^0 3d_{5/2}$ and $\text{Pd}^0 3d_{3/2}$, as the metallic phase, in addition to $\text{Pd}^{2+} 3d_{5/2}$ and $\text{Pd}^{2+} 3d_{3/2}$ as the minor oxide phase (Fig. 4b-d). However, the $\text{Pd}^0/\text{Pd}^{2+}$ in PdFe (1.85) is relatively lower than PdCo (2.32) and PdNi (1.98). The deconvolution of Fe2p spectra into $\text{Fe}^0 2p_{3/2}$ and $\text{Fe}^0 2p_{1/2}$, are attributed to the main metallic Fe^0 phase and Fe^{2+} as minor phases, respectively (Fig. 4e) [43]. The presence of a more metallic phase (Fe^0) than the oxide phase (Fe^{2+}) is traced to the optimal ice-chemical reduction by NaBH_4 under magnetic stirring. The Co2p spectra deconvolution into $\text{Co}^0 2p_{3/2}$ and $\text{Co}^0 2p_{1/2}$ corresponded to the metallic Co^0 and Co^{2+} ions as major and minor phases, respectively (Fig. 4f) [44]. Also, the convolution of Ni2p spectra into $\text{Ni}^0 2p_{3/2}$ and $\text{Ni}^0 2p_{1/2}$ is due to the main metallic Ni^0 phase and minor Ni^{2+} phase (Fig. 4g) [40,42]. The existence of the M-O phase in all the PdM is due to the quick oxidation of the M (Pd, Fe, Co, and Ni) in the air, which is highly favorable for promoting CO_{Oxid} [45,46].

The CO_{Oxid} performance and stability of PdM nanocrystals were probed and compared to commercial Pd/C in an alkaline medium. The CV curves in N_2 -purged 0.1 M KOH of the PdFe, PdCo, PdNi, and Pd/C nanocrystals display well-defined voltammograms of HUDP and PdM redox (Fig. S3a). The ECSA of PdFe ($11.80 \text{ m}^2/\text{g}$) is higher than those of PdCo ($2.25 \text{ m}^2/\text{g}$), PdNi ($2.01 \text{ m}^2/\text{g}$), and Pd/C ($6.74 \text{ m}^2/\text{g}$), due to the large peak area of PdFe-O reduction. However, the areas of PdM-O reduction peak of PdM are larger than that of Pd/C nanocrystals, indicating the ease of reduction, high surface state, and rich surface properties of support-free PdM nanocrystals. The CV curves reveal CO_{Oxid} voltammograms of the support-free PdM nanocrystals and Pd/C, with an

obvious sharp peak in the positive potential range (Fig. 5a). The PdFe has an onset potential ($E_{\text{Onset}} = -0.169 \text{ V}$), which was lower than PdCo (-0.157 V) and PdNi (-0.150 V), but higher than Pd/C (-0.217 V), inferring that high CO_{Oxid} kinetic of the PdFe amongst the free-standing PdM nanocrystals. Moreover, the CO_{Oxid} current density (I_{Oxid}) of PdFe ($5.22 \text{ mA}/\text{cm}^2$) is superior to PdCo ($2.15 \text{ mA}/\text{cm}^2$), PdNi ($0.80 \text{ mA}/\text{cm}^2$), and Pd/C ($1.48 \text{ mA}/\text{cm}^2$) by 2.43-, 6.53- and 3.53-folds, respectively, ascribable to the optimized strain and downshifted d-band center of Pd in PdFe. This was further explained by the amount of CO-adsorption in 0.1 M KOH, evidenced by the increased CO_{Oxid} charge integrated for the PdFe ($522.4 \text{ } \mu\text{C}$) compared to PdCo ($365.0 \text{ } \mu\text{C}$), PdNi ($108.2 \text{ } \mu\text{C}$) and Pd/C ($99.5 \text{ } \mu\text{C}$). Notably, the CO_{Oxid} on PdFe in 0.1 M KOH proceeded in a two-step manner via the initial formation of intermediate species at -0.29 V and finally CO_2 formation at -0.10 V . Hence, the mass activity of CO_{Oxid} in 0.1 M KOH of the PdFe ($18.44 \text{ A}/\text{g}$) is superior to those of PdCo ($7.59 \text{ A}/\text{g}$), PdNi ($2.83 \text{ A}/\text{g}$) and Pd/C ($17.43 \text{ A}/\text{g}$) (Table 1). This shows that the optimized strain and downshifted d-band center of PdFe are advantageously utilized for excellent CO_{Oxid} electrocatalysis in alkaline condition. As further seen in the LSV curves, which revealed the lower E_{Onset} and higher I_{Oxid} of PdFe than PdCo, PdNi (Fig. 5b). This proves that there is higher oxidative removal of CO-species on PdFe, amongst others, resulted in increased CO_{Oxid} kinetics on its active sites. Notably, the CO_{Oxid} activity of PdFe is higher than previously reported of Pd-based electrocatalysts and others (Table S3) [36,38,47–50].

The scan rate studies of CO_{Oxid} in 0.1 M KOH on the PdM and Pd/C were demonstrated with CV curves at different scan rates (v), which show a steady rise of I_{Oxid} as the scan rate (v) increases (Fig. 5c-f). Hence, the plots of I_{Oxid} against $v^{1/2}$ gave straight lines (Fig. 5c-f inset), which is an indication of the diffusion-controlled process of the CO-intermediates

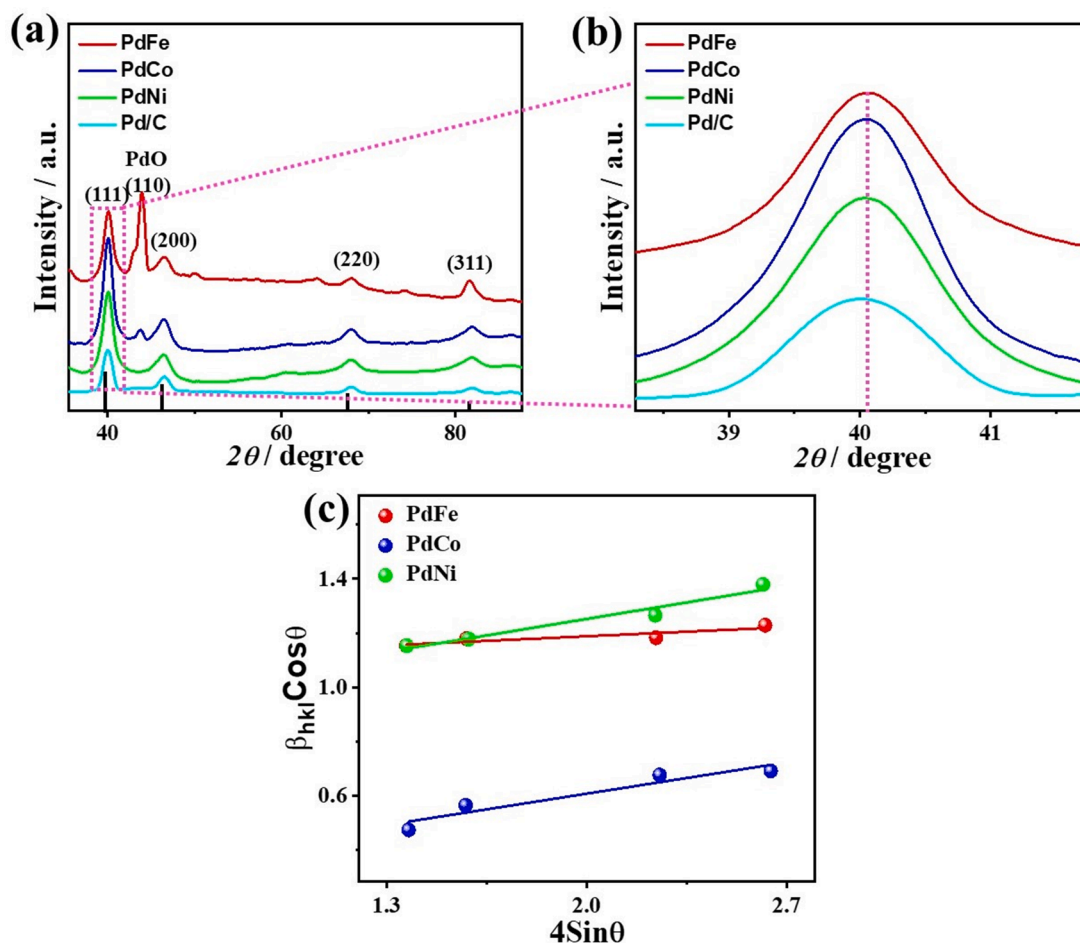


Fig. 3. (a) XRD, (b) magnified peak of {111} facet of Pd, and (c) Williamson-Hall plots of the as-obtained PdFe, PdCo, and PdNi nanocrystals.

on PdM and Pd/C during CO_{Oxid} electrocatalysis. This is proved by the higher slope of PdFe (1.13) relative to PdCo (0.48), PdNi (0.11), and Pd/C (0.29) with regression coefficient ($R^2 = 0.9827-0.9968$), attributable to the optimized strain of the constituents of PdFe and its downshifted d-band center.

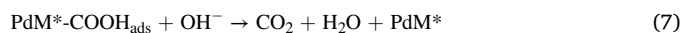
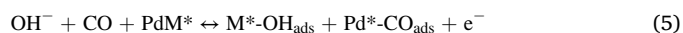
The CO_{Oxid} stability of PdFe in 0.1 M KOH was greater than PdCo, PdNi, and Pd/C, evidenced by the CA (Fig. 6a). Also, 1000 cycles of CV curves measured after CA show that the voltammograms were maintained with PdFe having 84.84% of its initial I_{Oxid} relative to PdCo (80.30%), PdNi (83.54%), and Pd/C (72.59%) (Fig. 6b-e). The higher CO_{Oxid} stability of PdFe in the alkaline condition is due to the optimized strain effect and modulated d-band center that allowed easy adsorption of reactants along with desorption of intermediate species and products. Also, 86.23% of ECSA is retained on the PdFe compared to PdCo (80.83%), PdNi (84.15%) and Pd/C (73.60%) (Fig. S4a). The morphology of the PdM remains the same after the stability test, evidenced by retained structure in the TEM images after the stability test (Fig. S5).

The EIS analysis shed light on the electrode-electrolyte interfacial interaction during CO_{Oxid} electrocatalysis. The Nyquist plots of the PdM nanostructures and Pd/C show a pseudo-semicircle with diameters in the following order of PdFe < PdCo < Pd/C < PdNi (Fig. 6f). This was fitting with the Voigt electrical equivalent circuit (EEC, Fig. 6g) to extract the EIS data, summarized in Table S4. Lower solution resistance (R_s)/charge transfer resistance (R_{ct}) were recorded on PdFe (86.30 Ω /4.60 k Ω), relative to PdCo (129.30 Ω /5.84 k Ω), PdNi (147.40 Ω /7.10 k Ω) and Pd/C (84.70 Ω /6.78 k Ω), signifying increased ionic conductivity and higher CO_{Oxid} kinetics on the PdFe, owing to the optimized strain between Pd and Fe. This was corroborated by the power law

constant phase elements (CPE) (i.e., $Z_{CPE} = \frac{1}{Q_0(j\omega)^n}$) having ideality factor (n) [36]. However, The PdFe has CPE impedance (166.60 $\mu S.s^{(1-n)}$), which is higher than PdCo (96.99 $\mu S.s^{(1-n)}$), PdNi (30.34 $\mu S.s^{(1-n)}$) and Pd/C (72.25 $\mu S.s^{(1-n)}$). This implies moderate adsorption of intermediate species on the PdFe, leading to high charge mobility. The closeness of the n (0.88–0.89) of the PdM than Pd/C (0.84) elucidates the tendency of the PdM toward ideal capacitive behavior.

This observation is explicated by the Bode plot, which reveals a lower overall impedance for PdFe at the low frequency compared to PdCo, PdNi, and Pd/C (Fig. 6h), designating a higher CO_{Oxid} kinetics on PdFe nanostructures, amongst others. Also, the lower phase angles of the PdFe (61°) than PdCo (64.5°), Pd/C (65.1°) and PdNi (76°), is an indication of higher diffusion capability of CO-intermediate species on the PdFe nanostructures.

The mechanism of CO_{Oxid} electrocatalysis in 0.1 M KOH on the PdM nanostructures is proposed to follow the conventional Langmuir-Hinshelwood mechanism, shown in equations (4)–(7) [51]. The oxygenated species (i.e., OH⁻) is generated from water splitting.



The CV curves of the PdM and Pd/C in N₂-saturated 0.1 M HClO₄ show the usual voltammogram for Pd-based electrocatalysts, but PdFe had higher HUDP than PdCo, PdNi, and Pd/C (Fig. S3b), which is an

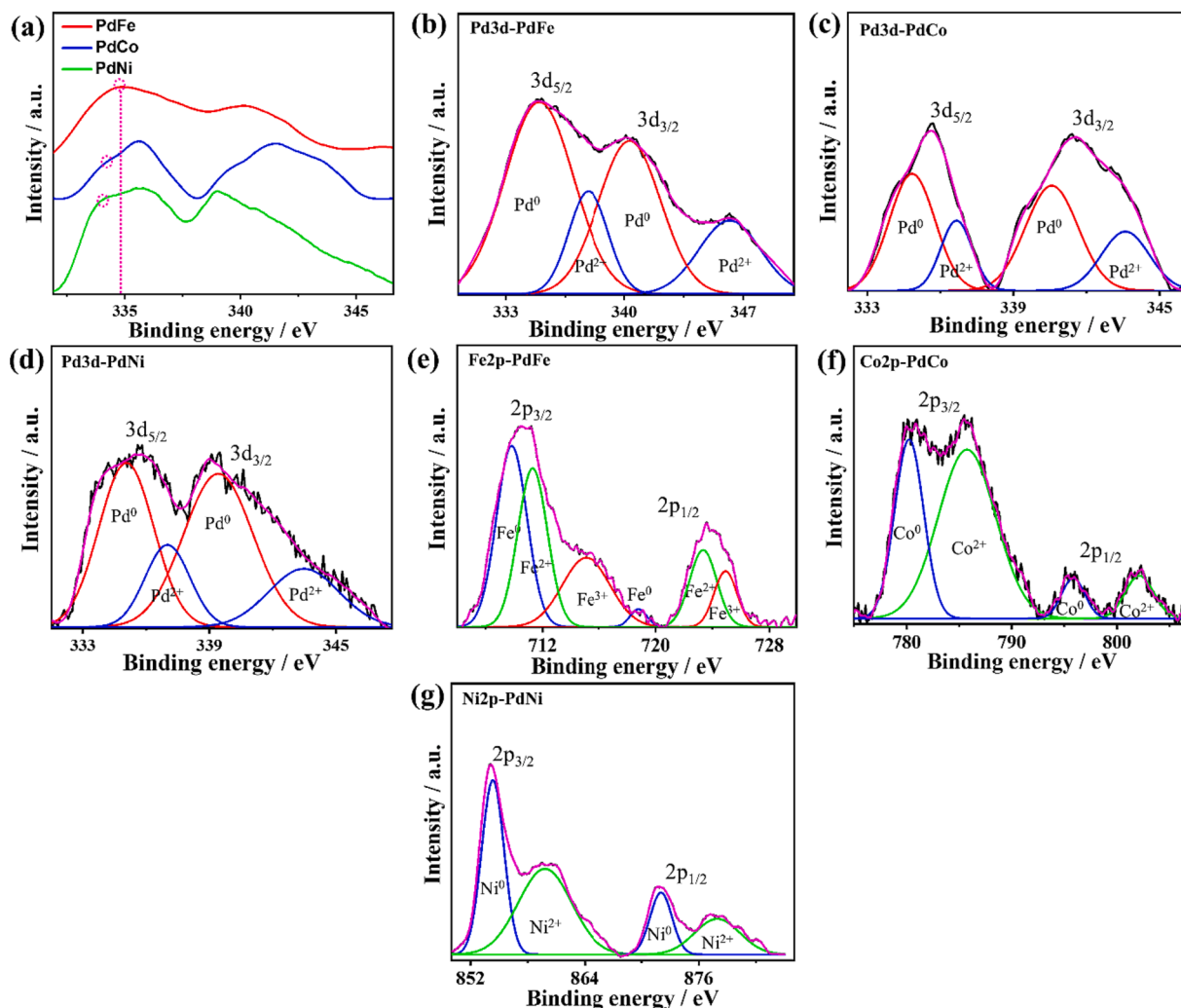


Fig. 4. High-resolution XPS (a) Pd3d, (b) Pd3d of PdFe, (c) Pd3d of PdCo, (d) Pd3d of PdNi, (e) Fe2p, (f) Co2p and (g) Ni2p.

indication of higher ECSA of PdFe. Hence, the higher ECSA of PdFe (10.41 m^2/g) than PdCo (1.65 m^2/g), PdNi (0.71 m^2/g) and Pd/C (2.77 m^2/g). Remarkably, the PdM-O reduction peak of PdFe shifted to low potential, inferring the high formation of oxygenated species and increased active sites on the PdFe amongst the electrocatalysts. The CV curves of the PdM nanocrystals and Pd/C in CO-saturated 0.1 M HClO_4 gave a higher I_{Oxid} for PdFe (1.48 mA/cm^2) than PdCo (0.81 mA/cm^2), PdNi (0.34 mA/cm^2) and Pd/C (0.95 mA/cm^2) by factors of 2.28, 4.35, and 1.56, respectively (Fig. 7a). This was corroborated by the CO_{Oxid} integrated charges of 404.0 μC for PdFe, which is superior to PdCo (269.0 μC), PdNi (188.0 μC) and Pd/C (223.0 μC), due to the improved reactants adsorption on the PdFe nanocrystals. Moreover, the facile formation of $\cdot\text{OH}$ species on the PdFe is proven by the lower potential of the PdM-O reduction peak, which is needed for fast CO_{Oxid} kinetics. The LSV curves in CO-saturated 0.1 M HClO_4 show a similar trend of PdFe > Pd/C > PdCo > PdNi for I_{Oxid} , but PdM nanocrystals have lower E_{Onset} than the Pd/C (Fig. 7b), implying higher CO_{Oxid} kinetics on the PdM nanocrystals. Thus, the mass activity of 5.23, 2.39, 1.21 and 11.18 A/g are measured for PdFe, PdCo, PdNi, and Pd/C, respectively in CO-saturated 0.1 M HClO_4 .

The scan rate studies of the PdM and Pd/C in CO-saturated 0.1 M HClO_4 reveal a linear relationship of I_{Oxid} with $\nu^{1/2}$, indicating diffusion-controlled process of the CO_{Oxid} (Fig. 7c-f). Meanwhile, PdFe has a higher line slope of 0.34, compared to PdCo (0.21), PdNi (0.11), and Pd/C (0.20), revealing that more reactants/intermediate species diffused fast on the PdFe. This is due to the downshifted d-band center and

optimized strain of PdFe.

The CA tests show insignificant I_{Oxid} attenuation on all the electrocatalysts, but the retained I_{Oxid} increased in the order of PdFe > Pd/C > PdCo > PdNi (Fig. 8a). The electrocatalysts are further subjected to 1000 cycle of CV in CO-saturated 0.1 M HClO_4 , after which the PdFe reserved 74.86% of its initial I_{Oxid} relative to PdCo (77.30%), PdNi (86.59%) and Pd/C (65.76%) (Fig. 8b-e). This implies a higher stability of CO_{Oxid} in HClO_4 on the PdM nanocrystals, owing to the lower loss of ECSA (23.90–29.30%) on the PdM nanocrystals after the stability test compared to Pd/C (36.81%) (Fig. S4b).

The Nyquist plots of the electrocatalysts in CO-saturated 0.1 M HClO_4 show pseudo-semicircle with a lower diameter for the PdFe than Pd/C, PdCo and PdNi, implying enhanced electrode–electrolyte interaction on the PdFe nanocrystals (Fig. 8f). This is evidenced by the EIS data extracted from the Voigt EEC that reveals lower R_s/R_{ct} on the PdFe nanocrystals than Pd/C, PdCo and PdNi (Fig. 8g) (Table S5), implying higher ionic conductivity and charge transport on the PdFe nanocrystals. The Z_{CPE} power law showing a higher CPE of the PdFe, compared to PdCo, PdNi, and Pd/C, corroborates this; meanwhile, the low n is an indication of fast charge mobility on the PdFe. This is also shown with the low overall impedance at the frequency region and phase angle of the PdFe nanocrystals compared to Pd/C, PdCo and PdNi in the Bode plots (Fig. 8g), confirming the rapid diffusion of reactants and intermediate species on the PdFe during the CO_{Oxid} electrocatalysis.

The CV curves of the PdM and Pd/C in N_2 -saturated 0.5 M NaHCO_3 reveal the usual voltammograms for Pd-based electrocatalyst, including

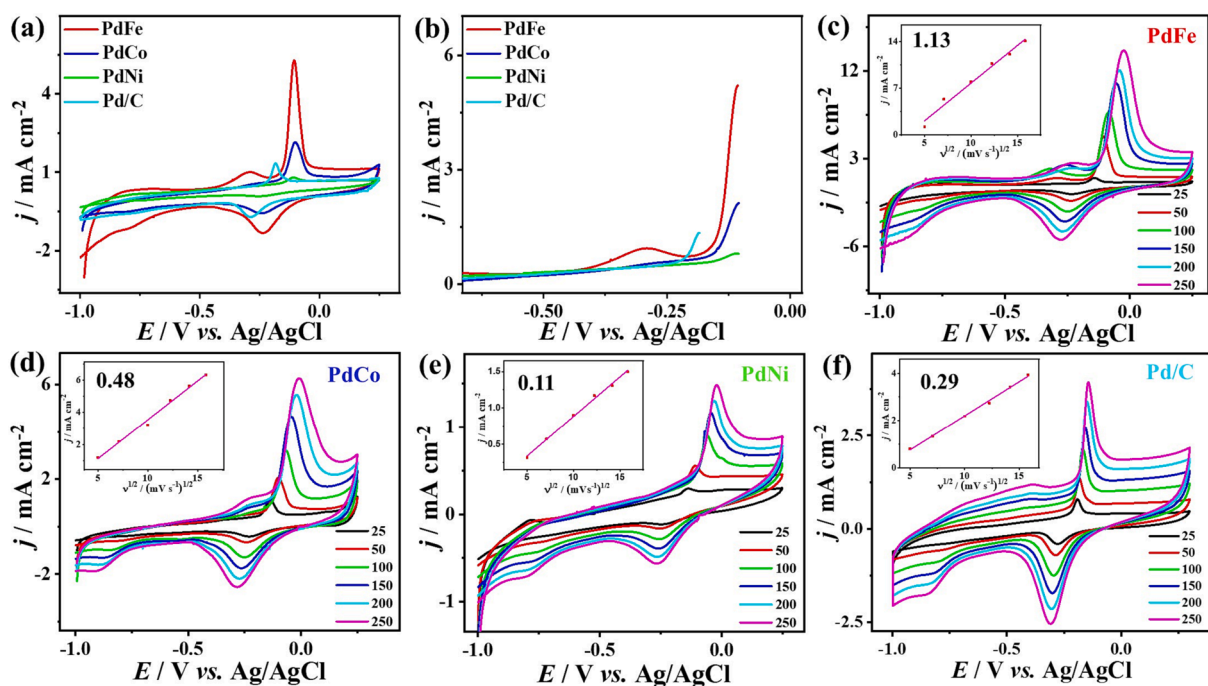


Fig. 5. (a) CV curves, (b) LSV curves at 50 mV/s, and (c-f) scan rate studies of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.1 M KOH.

Table 1

Electrocatalytic CO_{oxid} activity of PdFe, PdCo, PdNi, and Pd/C in the three media.

Catalyst	Onset potential (V)	Oxidation potential (V)	Current density / mA cm ⁻²	Slope (j vs. $v^{1/2}$)	ECSA _{H₂} (m ² /g)	Charge of CO _{ads} (μC)	Mass activity (A/g)
Alkaline (0.1 M KOH)							
PdFe	-0.169	-0.104	5.22	1.13	11.82	522.4	18.44
PdCo	-0.157	-0.104	2.15	0.48	2.25	365.0	7.59
PdNi	-0.150	-0.105	0.80	0.11	2.01	108.2	2.83
Pd/C	-0.217	-0.185	1.48	0.29	6.74	99.5	17.43
Acid (0.1 M HClO ₄)							
PdFe	0.637	0.770	1.48	0.34	10.41	404.0	5.23
PdCo	0.648	0.688	0.81	0.21	6.50	269.0	2.39
PdNi	0.654	0.688	0.34	0.11	1.71	188.0	1.21
Pd/C	0.830	0.878	0.95	0.20	2.78	223.0	11.18
Neutral (0.5 M NaHCO ₃)							
PdFe	0.127	0.266	1.45	0.62	8.45	355.0	5.12
PdCo	0.144	0.274	1.59	0.34	8.79	369.1	5.61
PdNi	0.196	0.350	0.22	0.07	2.00	84.0	0.78
Pd/C	0.341	0.451	0.52	0.129	5.11	64.4	6.12

an increased HUDP and PdM-O reduction area for PdFe and PdCo, relative to PdNi and Pd/C, owing to more abundant active sites of PdFe and PdCo in the neutral condition (Fig. S3c). Hence, the PdFe, PdCo, PdNi, and Pd/C have ECSA of 8.45, 8.79, 2.00, and 5.11 m²/g, respectively. However, the significant shift of the PdM-O to lower potential and high area of PdCo and PdFe relative to PdNi and Pd/C justify the ease of oxygenated species formation on both PdCo and PdFe in the neutral condition. The CV curves of PdM nanocrystals and Pd/C in CO-saturated 0.5 M NaHCO₃ gave an oxidation peak with higher I_{Oxid} for PdCo (1.59 mA/cm²), compared to PdFe (1.45 mA/cm²), PdNi (0.22 mA/cm²) and Pd/C (0.52 mA/cm²) (Fig. S6a). Also, the CO_{oxid} charge integration is considerably higher for PdCo (369.1 μC) than PdFe (355.0 μC), PdNi (54.0 μC) and Pd/C (64.4 μC). This reveals that the reactants (CO + OH) are more adsorb on the PdCo than PdFe, PdNi, and Pd/C, implying increased CO_{oxid} activity. This is substantiated by the LSV curve showing higher I_{Oxid} at all applied potential on the PdCo, relative to PdFe, PdNi, and Pd/C, due to the higher degree of alloying in the PdCo and strong synergism (Fig. S6b).

The scan rate studies of CO_{oxid} on the PdM nanocrystals and Pd/C in the neutral condition, where the I_{Oxid} increase linearly with the v , and higher slope for I_{Oxid} vs. $v^{1/2}$ for PdFe (0.62) compared to PdCo (0.34), PdNi (0.07) and Pd/C (0.13) (Fig. S6c-f). This is attributed to the diffusion-controlled process of CO_{oxid} with more intermediate species' diffusion on the PdFe, emanating from the optimized strain. The CA tests show improved CO_{oxid} stability in the neutral condition in the following trend of PdFe > PdCo > Pd/C and PdNi (Fig. S7a). After which 1000 cycles of CV curves reveal that PdCo retained 94.33% of its I_{Oxid} compared to PdFe (76.01%), PdNi (82.25%) and Pd/C (68.10%) (Fig. S7b-e). Moreover, retained ECSA of 94.42, 74.65, 56.38, and 70.30% correspond to the PdCo, PdFe, PdNi, and Pd/C, respectively (Fig. S4c). The Nyquist plots of the PdM and Pd/C for neutral CO_{oxid} show pseudo-semicircle lines for all, but a lower diameter for PdCo, implying fast charge transport and improved electrode-electrolyte interaction (Fig. S7f). Table S6 summarizes the EIS data extracted using the Voigt EEC model (Fig. S7g), revealing lower R_s/R_{ct} for PdCo compared to PdFe, Pd/C and PdNi, coupled with high CPE, but lower n ,

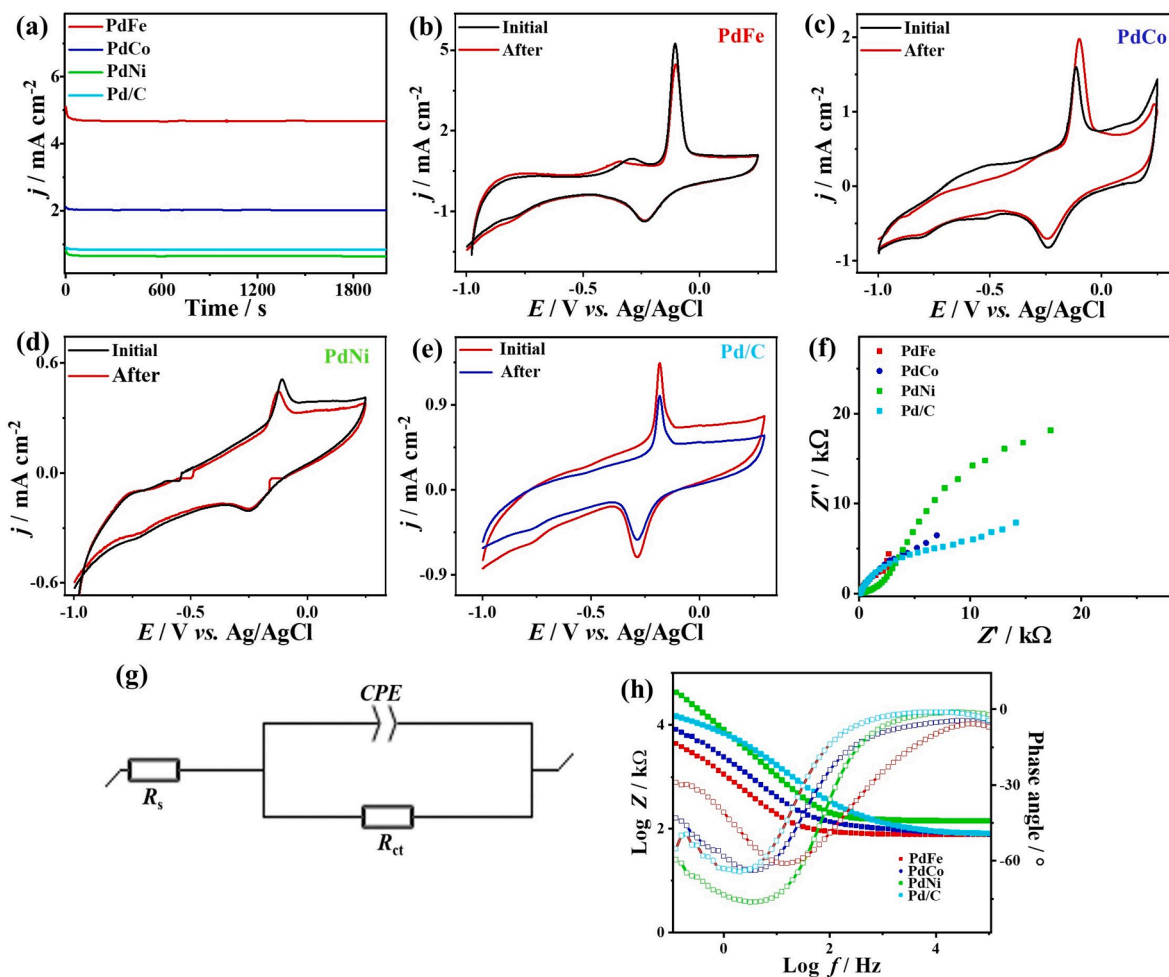


Fig. 6. (a) CA curves, (b-e) CV curves at initial and 1000 cycles, (f) Nyquist plots, (g) Voigt electrochemical equivalent circuits (EEC), and (h) Bode plots of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.1 M KOH.

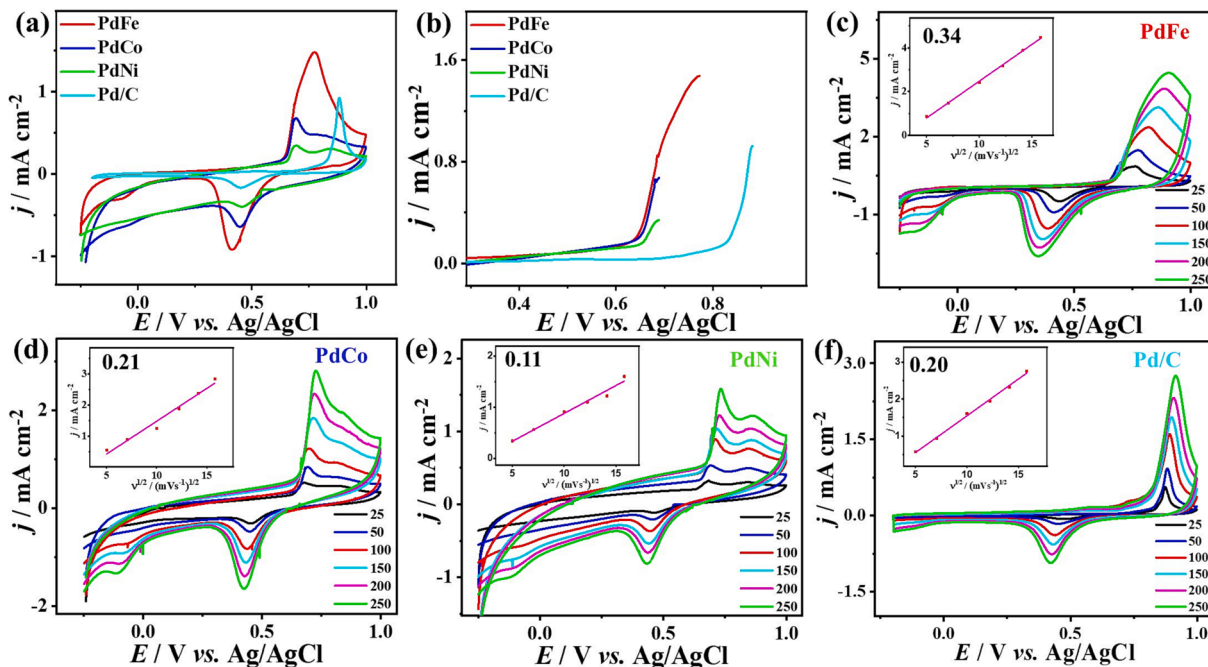


Fig. 7. (a) CV curves, (b) LSV curves at 50 mV/s, and (c-f) scan rate studies of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.1 M HClO₄.

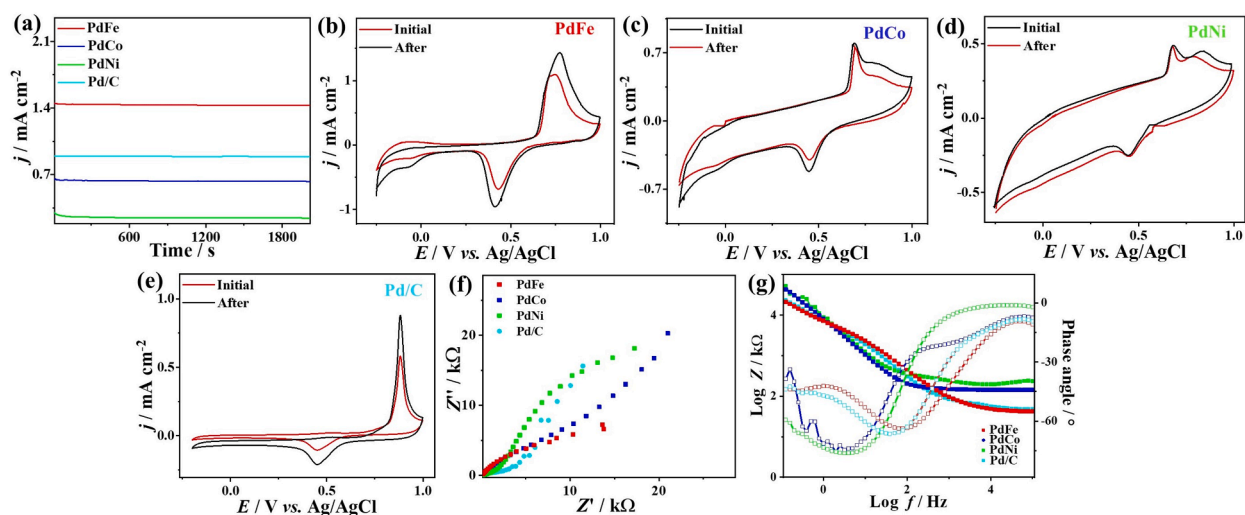


Fig. 8. (a) CA curves, (b-e) CV curves at initial and 1000 cycles, (f) Nyquist plots, and (g) Bode plots of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.1 M HClO₄.

resulted in increased ionic conductivity and charge mobility on the PdFe. This result aligns with the Bode plots, which show low impedance and phase angle at the low-frequency range on the PdCo relative to PdFe, Pd/C and PdNi (Fig. S7g).

A comparative electrocatalytic measurements of PdFe on carbon paper and glassy carbon substrate in 0.1 M KOH, where the CV curves of PdFe/carbon paper is higher than PdFe/glassy carbon (Fig. 9a). Also, the CO_{oxid} is higher on the PdFe/carbon paper than PdFe/glassy carbon with respect to E_{Onset} , E_{Oxid} , I_{Oxid} , and R_{ct} (Fig. 9b-d). This implies that carbon paper is a better substrate for the electrochemical measurements because of its improved conductivity, proved by the lower R_{ct} . Thus, it is imperative to explore carbon paper as substrate in future studies.

The findings in the work reveal the significant effect of alloying, modulated d-band center, and electrolyte pH on the CO_{oxid}

electrocatalysis of PdFe, PdCo, PdNi, and Pd/C. This could be traced to the augmented physicochemical merits for easy adsorption/diffusion of reactants/intermediate species and desorption of product of CO_{oxid} electrocatalysis.

Conclusions

In summary, this work presents a rapid aqueous-solution reduction approach for the fabrication of support-free foam-like PdM (i.e., PdFe, PdCo, and PdNi) nanocrystals with impressive CO_{oxid} electrocatalysis and stability at varied electrolyte pH. This is based on ice-reduction of metal precursors by sodium borohydride (NaBH₄) in an aqueous solution following the nucleation and coalescence growth process that results in foam-like morphology of support-free PdM nanocrystals. The

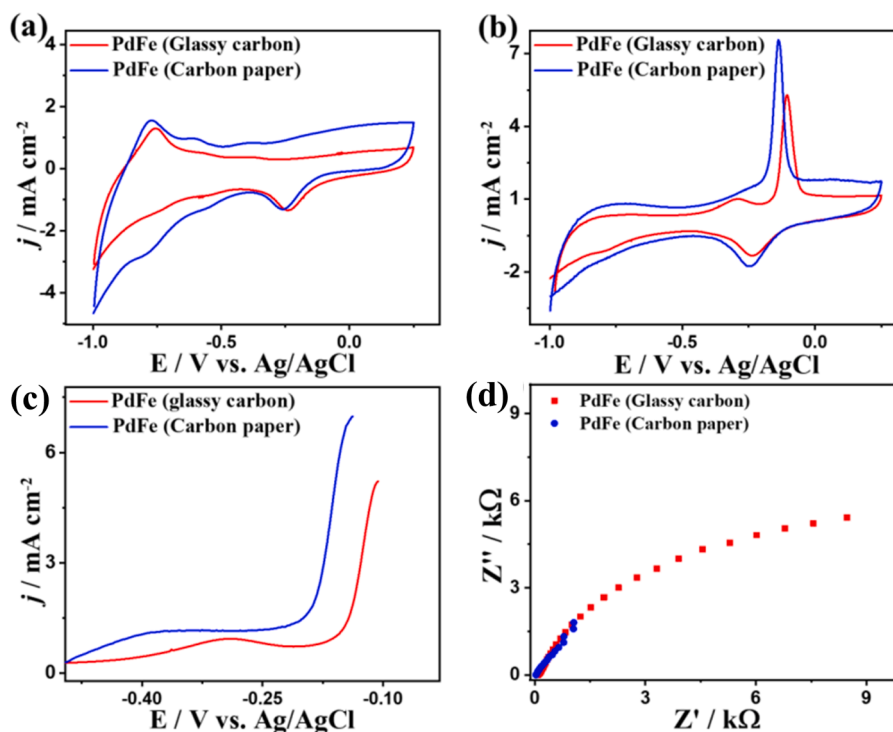


Fig. 9. (a) CV curves in 0.1 M KOH, (b) CV curves in CO-saturated 0.1 M KOH, (c) LSV and (d) Nyquist plots of the PdFe/glassy carbon and PdFe/carbon paper.

PdFe exhibits superior CO_{oxid} electrocatalysis to PdCo by at least 2.18-folds, PdNi by at least 4.35-folds, and Pd/C by at least 1.56-fold in KOH and HClO₄ electrolytes, owing to the downshifted d-band center and optimized strain of PdFe, in addition to its excellent stability after CA and 1000 cycles of CV. However, PdCo has the best CO_{oxid} activity in only NaHCO₃ electrolyte, traceable to its high degree of alloying. The CO_{oxid} is high at high electrolyte pH (i.e., KOH) for all electrocatalysts compared to acid and neutral conditions. The superb alkaline CO_{oxid} activity and stability of PdFe are ascribable to its unique downshifted d-band center and optimized strain that enabled fast charge mobility and abundant active surface area, beneficial for facile reactants (CO/OH)/intermediate species' adsorption and subsequent CO₂ desorption. This study points to the advantages of strain optimization and augmented d-band center of binary PdM-based nanocrystals for outstanding alkaline carbon monoxide oxidation activity and stability.

CRedit authorship contribution statement

Belal Salah: Methodology, Investigation, Visualization. **Adewale K. Ipadeola:** Methodology, Validation, Writing – original draft. **Aslam Khan:** Investigation, Data Curation. **Qingqing Lu:** Formal analysis, Funding acquisition. **Yassmin Ibrahim:** Methodology. **Ebrima L Darboe:** Data curation. **Aboubakr M. Abdullah:** Funding acquisition, Project administration. **Kamel Eid:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecmx.2023.100449>.

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