

The Effect of CeO_2 on the Electrocatalytic Oxidation Performance of Nanoporous Pd-Ag Catalyst for Methanol

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Abstract

Al-Pd-Ag-Ce precursor alloys with different Ce contents are prepared by arc melting and melt quenching methods, and the nanoporous Pd-Ag/CeO₂ catalysts are obtained by a simple dealloying treatment to investigate the electrocatalytic oxidation performance for methanol. The results show that CeO₂ exists in the form of nanorods and is uniformly distributed within the nanoporous Pd-Ag alloy matrix. When the Ce content is 0.3 at% in Al-Pd-Ag-Ce precursor alloys and the dealloying time is 12 h, the obtained nanoporous Pd-Ag/CeO₂ catalyst exhibits the best electrocatalytic performance. Compared with the commercial Pt/C and commercial Pd/C catalysts, its activity is about 8.9 times and 13.8 times, respectively, and stability is about 13.8 times and 39.1 times, respectively. These performance improvements are due to the synergistic effects at the interface between Pd and Ag, as well as between Pd and CeO₂, the electronic effect of Ce on Pd, and the presence of oxygen vacancies on the surface of CeO₂.

1. Introduction

With the continuous growth of global energy demand and increasing awareness of environmental protection, developing efficient and clean energy conversion and storage technologies has become a key direction in current technological research. Direct Methanol Fuel Cells (DMFC), a device that directly converts the chemical energy of methanol fuels into electrical energy, are considered an emerging clean energy technology due to their high energy density, low pollution, and ease of storage. Recently, it has garnered considerable attention^[1–2].

Currently, Pt, as a precious metal, exhibits specific catalytic activity as an anode catalyst. Still, its cost is high, and it is prone to poisoning and deactivation^[3–4], which limits the widespread application of DMFC. Pd has similar properties to Pt, which has the advantages of abundant reserves and low cost as a substitute for Pt. Research has found that Pd is similar to metal co-catalysts such as Ag, Fe, Au, Cu, and Co^[5–10]. The bimetallic alloy catalyst formed can effectively improve the electronic configuration, particle size, dispersion, and surface distribution of precious metal atoms in the catalyst while reducing costs and improving its catalytic performance. The Pd-Ag^[11] and Pd-Ni^[12] catalysts have been proven to have better catalytic effects than Pd. Some oxides, such as CoO, FeO, and MnO₂, are added as co-catalysts to electrocatalytic oxidation, playing a significant catalytic role^[13–15].

Ding Yi et al.^[16] found that nanoporous precious metals have advantages such as good conductivity, high utilization rate of precious metals, and broad exposure to active areas, especially when used as catalysts, they can exhibit strong durability. Zhang et al.^[17] synthesized bimetallic Pt-Pd mesoporous nanospheres with enhanced electrocatalytic activity for methanol oxidation using a one-pot method guided by soft templates. Cao et al.^[18] synthesized bimetallic Pd-Sn nanoparticle assemblies using a one-step oil bath method. These studies significantly improved catalytic performance by introducing co-catalysts.

This article uses arc melting and melt quenching methods to prepare Al-Pd-Ag-Ce precursor alloys with different cerium contents. After simple dealloying treatment, Pd-Ag/CeO₂ catalysts are obtained. Study the effect of different CeO₂ contents on the activity and stability of the nanoporous Pd-Ag catalyst in alkaline solution. To verify the performance of the Pd-Ag/CeO₂ catalyst, in addition to comparing it with the nanoporous Pd-Ag catalyst prepared by dealloying under the same conditions, it is also compared with commercial Pd/C and Pt/C catalysts.

2. Experiment

2.1 Preparation of the nanoporous Pd-Ag/CeO₂ catalysts

Preparation of the nanoporous Pd-Ag and Pd-Ag/CeO₂ catalysts: Al_{84-x}Pd₈Ag₈Ce_x (x = 0, 0.1, 0.3, 0.5, 0.7) alloy ingots are prepared according to a specific atomic percentage using the arc melting method. Argon is introduced as a protective gas during the process, and then the alloy ingots are placed in a quartz tube for current induction heating to a molten state. Using a single-roller quenching device, with a rotational speed of 2500 r/min, the molten metal is rapidly cooled to form a precursor alloy ribbons with a width of 3 mm and a thickness of approximately 30 μm. Subsequently, the precursor alloy ribbons are subjected to free dealloying corrosion in a 20 wt% NaOH solution for 30 minutes. When there are no apparent bubbles in the beaker, it is placed in a 90 °C water bath for 48 h (This involves dealloying reactions, formation and refinement of porous structures, as well as precipitation and distribution of CeO₂) for further corrosion. After that, the catalysts are repeatedly washed with deionized water and dried at room temperature to obtain the nanoporous Pd-Ag and Pd-Ag/CeO₂ catalysts. The catalysts obtained Al_{84-x}Pd₈Ag₈Ce_x (x = 0, 0.1, 0.3, 0.5, 0.7) precursor alloy are named PdAg, PdAgCe_{0.1}, PdAgCe_{0.3}, PdAgCe_{0.5}, and PdAgCe_{0.7}, respectively. The catalysts obtained from Al_{83.7}Pd₈Ag₈Ce_{0.3} precursor alloy with dealloying times of 6 h, 12 h, 24 h, and 36 h are named PdAgCe_{0.3-6h}, PdAgCe_{0.3-12h}, PdAgCe_{0.3-24h}, and PdAgCe_{0.3-36h}, respectively. The preparation process flowchart for the catalysts is shown in Fig. 1(a) .

2.2 Characterization

The phase composition of the Pd-Ag/CeO₂ catalysts is analyzed in depth using a Bruker D8 Advanced X-ray diffractometer (XRD) produced by Bruker GmbH in Germany. The microstructure characteristics of the catalysts are observed in detail using JEOL Ltd's JSM-7000F field emission scanning electron microscope (SEM) and JEM-2100 high-resolution transmission electron microscope (HRTEM). The valence states of Pd, Ce, and Ag elements in the catalysts are accurately detected by a Shimadzu/Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS).

2.3 Electrochemical performance testing

Conducted at room temperature (25 °C) on a standard CHI 660E three-electrode electrochemical workstation. This standard three-electrode system consists of a glassy carbon electrode with a diameter

of 3 mm as the working electrode, a Pt mesh electrode with an area of 1 cm² as the counter electrode, and an Hg/Hg₂Cl₂ electrode as the reference electrode. Mix 2 mg of finely ground catalyst powder, 0.4 mg of acetylene black, 200 μ L of Nafion solution, and 200 μ L of isopropanol thoroughly in a centrifuge tube. Subsequently, ultrasonic treatment is performed for 60 minutes to ensure uniform dispersion of each component. Afterward, take 2 μ L of the obtained suspension and drop it evenly onto the surface of the polished glassy carbon working electrode, allowing it to dry naturally. This way, the catalyst mass loaded on the working electrode is about 10 μ g. The voltammetric characteristics of the catalyst are measured in a 1 M KOH solution. The electrochemical activity test is conducted in a mixed electrolyte containing 1 M methanol and 1 M KOH. All electrochemical tests are performed at room temperature in an ultra-pure N₂ protective atmosphere to ensure the accuracy and reliability of the test results. The schematic diagram of DMFC is shown in Fig. 1(b).

3. Results and discussion

The SEM and TEM images of the nanoporous Pd and porous Ag catalysts are shown in Fig. 2. As shown in Figs. 2(a)-(d), the nanoporous Pd catalyst exhibits a three-dimensional nanoporous structure with the ligaments/pore size approximately being 5 nm, and the ribbons after dealloying corrosion have uniform thickness^[11]. The crystal grain planes exposed on the surface of the ligaments have a spacing of approximately 0.224 nm, which corresponds to the (111) crystal plane of Pd. As shown in Figs. 2(e)-(h), it can be seen that the porous Ag catalyst exhibits a three-dimensional porous structure composed of large particles of Ag, the particle size is approximately 50–200 nm. Figure 2(i) illustrates the evolution process by which the precursor alloy undergoes dealloying to transform into nanoporous structure. Figure 2(j) shows the EDS spectra of the nanoporous Pd and porous Ag catalysts, revealing the characteristic peaks of Pd and Ag, respectively. Figure 2(k) shows the XRD patterns of the nanoporous Pd and porous Ag catalysts. It can be seen that the characteristic diffraction peaks of the nanoporous Pd catalyst at 40.1, 46.7, 68.1, and 81.8 correspond to the (111), (200), (220), and (311) planes of the labeled PDF card Pd (JCPDS NO. 46-1043), respectively. At the same time, the peaks of the porous Ag catalyst are located at 38.1, 44.3, 64.4, 77.5, and 81.5, corresponding to the (111), (200), (220), (311), and (222) planes labeled with Ag on the PDF card (JCPDS NO. 04-0783). Figure 2(l) shows the XPS spectra of the nanoporous Pd catalyst, which exhibits the presence of C, O, and Pd elements on its surface. Figure 2(m) shows the Pd 3d XPS spectra of the nanoporous Pd catalyst, Pd 3d_{5/2} and 3d_{3/2} peaks located at 334.7 and 340.0 eV, respectively. Two forms of Pd element are observed, with the strong double peaks (334.7 and 340.0 eV) mainly in the form of metallic Pd⁰ and the weak double peaks (335.6 and 341.0 eV) in the form of PdO, due to the inevitable oxidation reaction of a small amount of Pd during the dealloying process^[19].

Figure 3(a) shows the cyclic voltammetry (CV) curve of the nanoporous Pd catalyst in 0.5 M KOH solutions, and corresponding electrochemical activity specific surface area (EASA) can be estimated to be 21.6 mA·mg⁻¹ based on the reduction peak area of PdO. Figure 3(b) shows the CV and corresponding peak current density (*j_p*) of the nanoporous Pd catalyst in 0.5 M KOH + 0.5 M CH₃OH solutions. It can be

seen that the j_p value of the nanoporous Pd catalyst is $249.6 \text{ mA}\cdot\text{mg}^{-1}$ ^[11]. Figure 3(c) shows $i-t$ curve of the nanoporous Pd catalyst. It can be seen that after 3000 s testing, the j value of the nanoporous Pd catalyst reaches a dynamic balancing state, and at 3000 seconds, its j is $78.92 \text{ mA}\cdot\text{mg}^{-1}$. The illustration shown in Fig. 3(c) illustrates the process of methanol oxidation catalyzed by the nanoporous Pd catalyst. It can be clearly seen from Fig. 3(d) and 3(d₁) that with the increase of scanning rate, j_p is gradually increasing, E_p is moving toward the direction of positive voltage, and there is a linear relationship between j_p and E_p in the forward scan. In addition, the linear relationship exists not only between j_p and the square root of the scan rate ($v^{1/2}$), but also between E_p and $\ln(v)$, as shown in Fig. 3(d₂) and 3(d₃), indicating that MOR in the nanoporous Pd catalyst is an irreversible kinetic process controlled by diffusion^[20]. The CV curves of the porous Ag catalyst are measured in 0.5 M KOH and 0.5 M KOH + 0.5 M CH₃OH solution, as shown in Fig. 3(e). It can be clearly seen that the porous Ag catalyst doesn't have MOR performance, and the formation peak and reduction peak of the Ag₂O appear when the E is greater than 0.1 V.

The SEM and TEM images of the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts are shown in Fig. 4. Figure 4(a) is the SEM image of the nanoporous Pd-Ag catalyst, it can be seen that a dual continuous nanoporous structure is present in the catalyst. Figure 4(b) shows the SEM image of the PdAgCe_{0.3} catalyst, from the figure, it can be seen that the catalyst still has a nanoporous structure. Some nanorods appear on the ligaments of the catalyst, which is due to the natural oxidation of Ce in the precursor alloy to form CeO₂ during the dealloying process, and CeO₂ preferentially crystallizes in specific directions forming a nanorod structure^[21–23]. The diffusion of oxygen will not be limited to the vicinity of the PdAg alloy and CeO₂ interface, it extends through the entire CeO₂ lattice, providing abundant active oxygen for the active sites and enhancing catalytic activity^[24]. Figure 4(c) shows the SEM image of the PdAgCe_{0.7} catalyst, as more Ce elements are added to the precursor alloy, more nanorods appear on the catalyst's nanoporous structure surface, the approximate range of the nanorods is 14.12–19.24 nm. Figure 4(d) shows the EDS images of the nanoporous Pd-Ag and PdAgCe_{0.7} catalysts, where the EDS spectral lines of the nanoporous Pd-Ag catalyst display the characteristic peaks of Ag and Pd. After adding Ce to the precursor alloy, the EDS of the PdAgCe_{0.7} catalyst detected Pd, Ag, and Ce elements, this proves that the Ce element has indeed successfully been present in the catalyst.

Figure 4(e) shows the TEM image of the nanoporous Pd-Ag catalyst, showing its unique nanoporous structure characterized by uniform and distinct pore distribution. As shown in Fig. 4(f), the HRTEM image reveals that the pore size is approximately 5 nm. At the same time, the ligaments are composed of the Pd-Ag alloy nanoparticles and their size is approximately 8 nm. The interplanar spacing of the Pd-Ag alloy nanoparticles is about 0.227 nm, which corresponds precisely to the (111) crystal plane^[25]. Figure 4(g) presents the TEM image of the PdAgCe_{0.3} catalyst, it further indicates that the addition of the Ce element does not significantly alter the nanoporous structure of the catalyst, which retains its nanoporous characteristics. Figure 5(h) shows the HRTEM image of the PdAgCe_{0.3} catalyst, further

observation reveals that the interplanar spacing of Pd-Ag alloy nanoparticles in the PdAgCe_{0.3} catalyst is approximately 0.240 nm, corresponding to the (111) crystal plane. Figure 4(i) shows the preparation diagram of the nanoporous Pd-Ag/CeO₂ Catalyst. Using the nanoporous Pd catalyst as raw material, a porous network structure (green cube diagram) is constructed for the first time through structural regulation, significantly increasing the specific surface area and exposing more active centers. Subsequently, Ag is introduced as a cocatalyst, and the electronic structure of Pd is optimized by alloying modification to improve its intrinsic catalytic activity. The uniform nanoporous Pd-Ag alloy (blue cube diagram) is prepared. Finally, the catalyst CeO₂ is added and loaded on the nanoporous Pd-Ag framework in the form of nanorods (yellow rods). The multi-step modification strategy not only retains the high open pore structure and high mass transfer efficiency, but also realizes the collaborative catalysis of PdAg alloy and CeO₂, which effectively improves the catalytic performance and stability of related electrocatalytic reactions.

Figure 5(a) shows the XRD diffraction patterns of the typical nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe_{0.7}) catalysts. It can be seen that the diffraction peaks of the nanoporous Pd-Ag catalyst are located at 39.10°, 45.40°, 66.20°, and 79.60°, respectively, corresponding to the (111), (200), (220), and (311) crystal planes of the Pd-Ag alloy. The diffraction peak position of the nanoporous Pd-Ag catalyst is located between the diffraction peaks of Pd and Ag, which indicates that Pd and Ag in the Al-Pd-Ag precursor alloy form a solid solution alloy after dealloying. Compared with the diffraction peaks of the nanoporous Pd-Ag catalyst, the diffraction peaks position of the PdAgCe_{0.7} catalyst shows no significant changes, and no prominent diffraction peaks related to the Ce element are detected. These phenomena may be due to the content of Ce in the catalyst being too low, which results in the diffraction signal not reaching the sensitivity threshold of the detection instrument^[26].

Perform XPS measurements to characterize the elemental states in the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts, and the test results are shown in Fig. 5(b). It can be observed that Pd and Ag signals are detected in the nanoporous Pd-Ag catalyst. In the PdAgCe_{0.3} catalyst, except for Pd and Ag, there are also signals related to Ce, which confirms the presence of Ce. According to the XPS spectrum and binding energy of the Ce element in Fig. 5(c), the position of the Ce⁴⁺ peak appears at 882.68 eV and 888.58 eV, and the position of the Ce³⁺ peak appears at 885.88 eV, so Ce in the PdAgCe_{0.3} catalyst exists in two forms of Ce³⁺ and Ce⁴⁺^[27]. Generally, Ce in ceria is mainly stable in the form of Ce⁴⁺, but Ce³⁺ appears in this catalyst, which is obviously different from the conventional state. This valence state distribution indicates that during catalyst preparation or reaction processes, some Ce⁴⁺ is reduced to Ce³⁺. And this change in valence state does not occur in isolation, it is inevitably closely related to the microstructure and performance of the catalyst. This reduction process is closely related to the formation of oxygen vacancies. When oxygen atoms in the crystal lattice detach, leaving vacancies, adjacent Ce⁴⁺ ions capture electrons to convert to Ce³⁺ ions, thereby maintaining charge balance. This dynamic redox cycle ultimately contributes to the stable existence of CeO₂ with an oxygen vacancy defect structure^[28].

Figure 5(d) shows the Pd 3d XPS characteristic spectral lines of the PdAg and PdAgCe_{0.3} catalyst. The PdAg catalyst contains Pd 3d_{5/2} and Pd 3d_{3/2}, which can be divided into two pairs of peaks^[29], of which the stronger bimodal (335.45 eV and 340.53 eV) is due to the main form of metal Pd⁰, while the other weaker bimodal (336.34 eV and 341.89 eV) belongs to PdO, which is due to the inevitable oxidation of a small amount of Pd in the process of dealloying^[30]. Figure 5(e) is an enlarged view of Fig. 5(d). It is obvious from the Fig. 5(e) that the Pd 3d_{5/2} peak of PdAgCe_{0.3} catalyst shifts slightly to the left compared with PdAg catalyst. This is because the PdAgCe_{0.3} catalyst contains a large number of oxygen vacancies, which can promote the electron transfer between CeO₂ and PdAg to trigger strong interactions within the PdAgCe_{0.3} catalyst^[31], and this, in turn, alters the peak position of the Pd 3d orbitals, leading to significant electronic effects^[32]. Figure 5(f) shows the Ag 3d XPS characteristic spectral lines of the PdAg and PdAgCe_{0.3} catalyst. The PdAg catalyst contains Ag 3d_{5/2} and Ag 3d_{3/2}. According to the references, corresponding to metallic silver at 367.52 eV and 373.61 eV^[33]. Compared with the PdAg catalyst, after adding Ce to the precursor alloy and forming CeO₂, the peak of the Ag 3d orbital of the PdAgCe_{0.3} catalyst did not show an obvious shift in its binding energy position.

Figure 6(a) presents the CV curves, measured at a scan rate of 50 mV·s⁻¹ in 1 M KOH, for the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts. It is not difficult to find that the CV curve of the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts has the same characteristics, and all present typical Pd feature contours, which indicates that the addition of the Ce element and the formation of CeO₂ have no significant impact on the CV characteristics of Pd. However, as the Ce content gradually increases in the Al-Pd-Ag-Ce precursor alloys, the CV contour of the Pd becomes increasingly apparent, and the peak intensity also increases accordingly. When the Ce content exceeds 0.3 at% in the precursor alloys, the peak contour begins to shrink again, and the peak value decreases accordingly. Generally, the EASA of the catalyst can be estimated by the reduction peak area of PdO^[34-36]. The corresponding EASA values of the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts are shown in Fig. 6(b). With the addition of Ce to the precursor alloys and the increase in the amount of Ce added, the EASA values of the Pd-Ag/CeO₂ catalysts show a trend of first increasing and then decreasing. When the amount of Ce in the precursor alloy is 0.3 at%, the EASA value of the nanoporous Pd-Ag/CeO₂ catalyst is the highest, at 72.60 mA·mg⁻¹, which is about 2.6 times the EASA value of 29.40 mA·mg⁻¹ for the nanoporous Pd-Ag catalyst.

Figure 6(c) and (d) show the CV curves and j_p of the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts measured at a scan rate of 50 mV · s⁻¹ in a 1 M KOH + 1 M CH₃OH solution. It can be observed from Fig. 6(c) that the j_p of the PdAg, PdAgCe_{0.1}, PdAgCe_{0.3}, PdAgCe_{0.5}, and PdAgCe_{0.7} catalysts used for methanol electrocatalytic oxidation are 334.12 mA·mg⁻¹, 457.30 mA·mg⁻¹, 471.90 mA·mg⁻¹, 404.80 mA·mg⁻¹, and 224.90 mA·mg⁻¹, respectively. As the Ce content gradually increases in the Al-Pd-Ag-Ce precursor alloys, the j_p of the catalysts shows a trend of first increasing and then

decreasing. When the Ce reaches 0.3 at% in the precursor alloys, the j_p of the PdAgCe_{0.3} catalyst reaches a maximum value, which has increased by 41.2% compared to the nanoporous Pd-Ag catalyst.

Figure 6(e) and (f) show the $i-t$ testing results of the nanoporous Pd-Ag (PdAg) and Pd-Ag/CeO₂ (PdAgCe) catalysts in a 1 M KOH + 1 M CH₃OH solution. In the initial stage of testing, the current density (j) of all samples sharply decreased. This is because the catalyst encountered poisoning issues during methanol catalysis, which may be due to the production of intermediate products and other free radicals.^[37–40] However, over time, the j gradually stabilizes, which indicates that the samples achieve a dynamic balance between catalytic activity and anti-toxicity in the methanol electrocatalytic oxidation reaction. It is worth noting that throughout the entire testing process, the j of the PdAgCe_{0.3} catalyst consistently outperformed others, thus demonstrating the most outstanding stability and anti-toxicity. After 5000 seconds, the j of the PdAgCe_{0.3} sample remains as high as 172.30 mA·mg⁻¹, which is 2.6 times higher than that of the nanoporous Pd-Ag sample (66.70 mA·mg⁻¹).

Figure 6(g) and (h) respectively show the $i-t$ and CV test results of commercial Pt/C and Pd/C catalysts. As shown in Fig. 6(h), after a 5000 s current test, the j values of the commercial Pt/C and Pd/C catalysts are 27.10 mA·mg⁻¹ and 9.60 mA·mg⁻¹, respectively. However, the j value of the PdAgCe_{0.3} samples is 6.3 times that of the commercial Pt/C and 17.9 times that of the commercial Pd/C. As shown in Fig. 6(g), the j_p of the commercial Pt/C and Pd/C catalysts are 188.07 mA·mg⁻¹ and 120.47 mA·mg⁻¹, respectively. The j_p of the PdAgCe_{0.3} (471.9 mA·mg⁻¹) catalyst is 2.5 times and 3.9 times that of the commercial Pt/C and Pd/C catalysts, respectively. The above results indicate that in terms of both the activity and stability of the electrocatalytic oxidation for methanol, the PdAgCe catalyst is significantly inferior to the commercial Pt/C and Pd/C catalysts.

Figure 7 shows the SEM images of the nanoporous Pd-Ag/CeO₂ (PdAgCe) catalysts with different dealloying times. When the dealloying time is 6 h, a large amount of the rod-shaped CeO₂ appears in the nanoporous Pd-Ag alloy. When the dealloying time is further extended to 12 h, the morphology and structure of the catalyst become more refined. However, when the dealloying time is extended to 48 h, a significant agglomeration phenomenon of the Pd-Ag alloy particles is observed in the catalyst. In Fig. 7(b₁), it can be observed that the PdAgCe_{0.3-12h} catalyst matrix still has a porous structure. After calculation, the interplanar spacing of the nanoporous Pd-Ag nanoparticles is 0.214 nm, corresponding to the (111) crystal plane, as shown in Fig. 7(b₂).

Figure 7(d) shows a series of CV curves of the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalysts with different dealloying times in a 1 M KOH solution at a scanning rate of 50 mV·s⁻¹. It can be seen that the CV curves of the catalysts exhibit a characteristic peak profile of the Pd. As the dealloying time increases, the Pd characteristic peak profile first increases and then decreases, the initial increase is due to the gradual completion of the dealloying reaction, and the decrease is due to the prolonged dealloying time, which leads to partial oxidation of Pd^[41–42]. When the dealloying time is 12 h, the EASA value of the

PdAgCe_{0.3-12h} catalyst reaches a maximum value (127.50 mA·mg⁻¹), which is 1.69 times that of the PdAgCe_{0.3} (75.40 mA·mg⁻¹) catalyst. Therefore, the dealloying time has a significant impact on the electrocatalytic oxidation of methanol performance of the catalysts.

Figure 7(e) and (f) present the CV curves of the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalysts with different dealloying times in a solution containing 1 M KOH and 1 M CH₃OH at a scanning rate of 50 mV · s⁻¹. Figure 8(e) and (f) show that with the increase of the dealloying time, the electrocatalytic activity of the catalysts show a trend of first increasing and then decreasing. Especially when the dealloying time is 12 h, the activity of the catalytic is optimal (1666.12 mA·mg⁻¹). Compared with the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalyst, its activity has increased by 3.5 times, which is 8.9 times and 13.8 times higher than that of the commercial Pt/C catalysts and Pd/C catalysts. Figure 8(g) and (h) show the *i*-*t* testing results of the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalysts with different dealloying times in a 1 M KOH + 1 M CH₃OH solution. It can be seen from Fig. 8(g) that the *j* initially decreases sharply with time, and then gradually stabilizes. And with the increase of the dealloying time, the stability of the catalysts also showed a trend of first increasing and then decreasing. After 5000 seconds, the *j* of the PdAgCe_{0.3-12h} catalyst is at 374.90 mA·mg⁻¹, which is approximately 2.2 times that of the PdAgCe_{0.3} (172.3 mA·mg⁻¹) catalyst, 13.8 times that of the commercial Pt/C catalyst, and 39.1 times that of the Pd/C catalyst. These indicate that the dealloying time has a significant impact on the performance of the catalyst for electrocatalytic oxidation of methanol, when the dealloying time is 12 h, the electrocatalytic oxidation performance of the catalyst for methanol reaches the best.

The nanoporous Pd-Ag/CeO₂ catalysts exhibit excellent electrocatalytic oxidation performance for methanol. The reasons are as follows: firstly, the interface synergistic effect between the Pd and Ag, and the Pd and CeO₂. The Ag and CeO₂ act as cocatalyst and react with the -OH on the Pd surface to form -COOH groups with the generated intermediate CO, which are further oxidized to CO₂, thereby achieving rapid removal of CO and avoiding catalyst poisoning, to improve the stability and anti-poisoning ability of the catalyst^[41]. Secondly, the electronic effect of the Ce on Pd. When the Ce is added to the Al-Pd-Ag precursor alloy, the binding energy of Pd shifts negatively, which will reduce the adsorbability of the active Pd for the poisoned intermediate products, decrease the poisoning and deactivation of the active sites Pd, and enable more Pd to participate in the catalytic process, improving the activity and stability of the catalysts for methanol electrocatalytic oxidation^[43]. Thirdly, the CeO₂ contains a large number of oxygen vacancies, some of the Ce⁴⁺ are reduced to the Ce³⁺ due to oxygen vacancies, where oxygen atoms are separated from the lattice to create vacancies, and adjacent Ce⁴⁺ captures electrons and converts them into Ce³⁺ to achieve charge balance. At the same time, the abundant oxygen vacancies on the surface of the CeO₂, when combined with the nanoporous Pd-Ag catalyst, adsorb and dissociate H₂O, continuously producing highly active -OH species that provide an oxygen source for intermediate oxidation, thereby improving the catalyst's performance in the electrocatalytic oxidation of methanol^[44].

The mechanism diagram for the electrocatalytic oxidation of methanol by the nanoporous Pd-Ag/CeO₂ catalyst is shown in Fig. 8.

4. Conclusion

The nanoporous Pd-Ag/CeO₂ catalysts with different Ce content in Al-Pd-Ag-Ce precursor alloys and different dealloying times are successfully prepared. The performance of the catalysts for electrocatalytic oxidation of methanol is systematically studied. When the Ce content is 0.3 at% in Al-Pd-Ag-Ce precursor alloy and the dealloying time is 12 h, the obtained nanoporous Pd-Ag/CeO₂ catalyst exhibits optimal electrocatalytic performance, compared with the commercial Pt/C and commercial Pd/C catalysts, its activity is approximately 8.9 and 13.8 times, respectively, while its stability is about 13.8 and 39.1 times, respectively. These performance improvements are attributed to the synergistic effects at the interfaces between Pd and Ag, as well as between Pd and CeO₂, the electronic effect of Ce on Pd, and the oxygen vacancies on the surface of CeO₂, which have enhanced the catalyst's performance in electrocatalytic oxidation of methanol.

Declarations

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Author Contribution

Conceptualization, Methodology, Validation, Writing—Original Draft, Investigation, Data Curation, Formal Analysis, Funding acquisition; **Yu WenJie**; Methodology, Investigation, Formal analysis, Visualization; **Wang Jiafen**; Investigation, Data curation, Software; **Duan Jinrong**; Investigation, Resources; **Wu Yunlong**; Validation, Formal analysis; **Yi Chuan**; Supervision, Writing—Review and Editing, Project administration; **He Gege**; Supervision, Funding acquisition, Writing—Review and Editing. **Song Yanyan**; All authors reviewed the manuscript and approved the final version of the manuscript.

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Figures

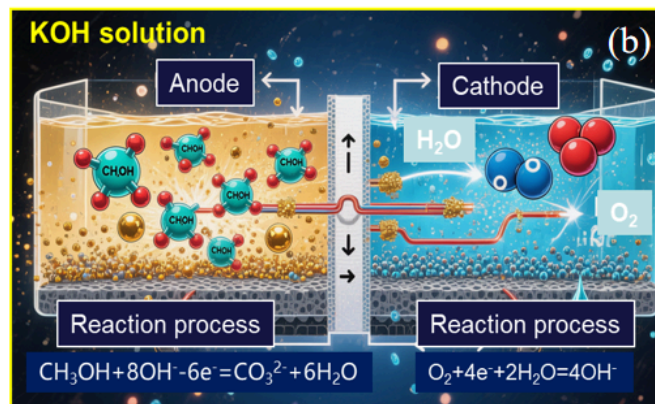
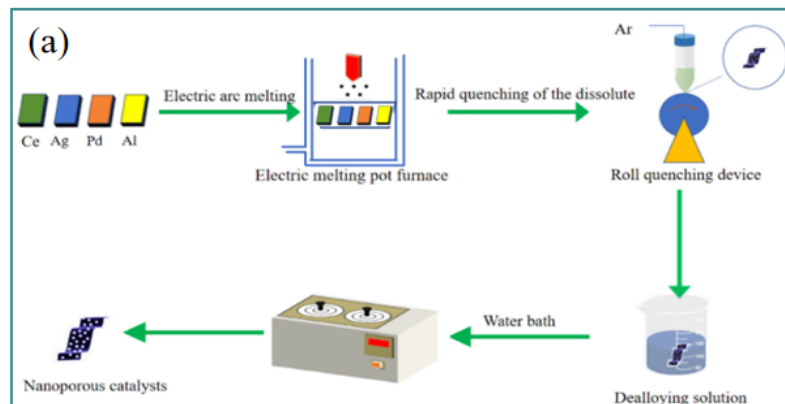


Figure 1

Preparation process of the nanoporous Pd-Ag/CeO₂ catalyst (a) and schematic diagram of DMFC (b).

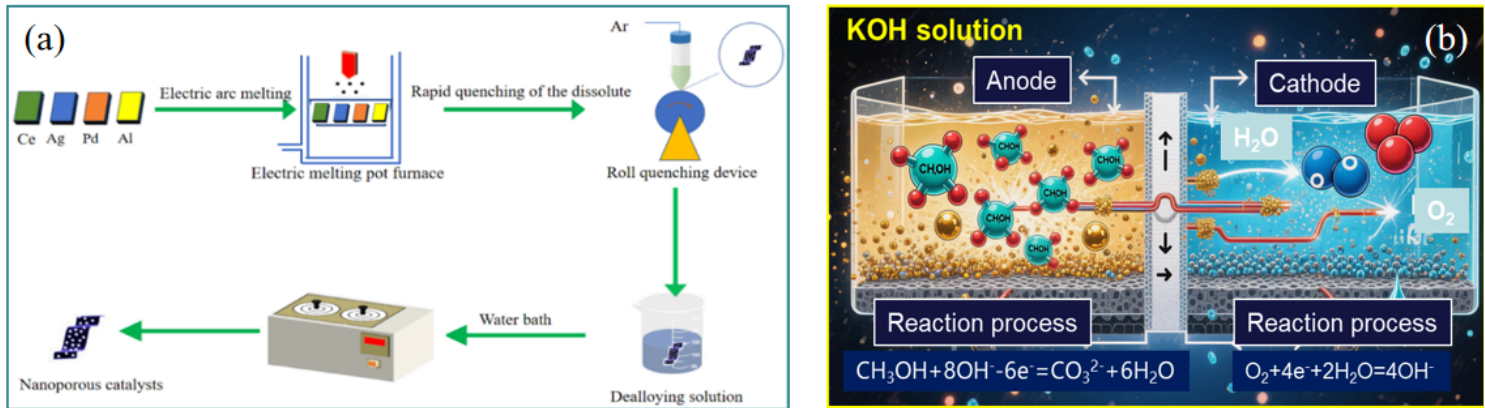


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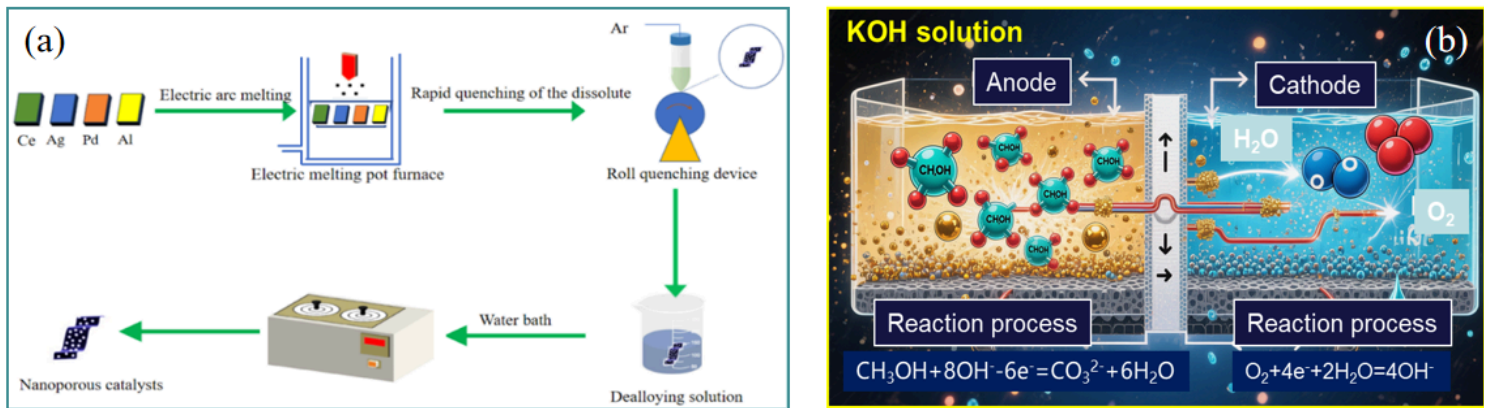


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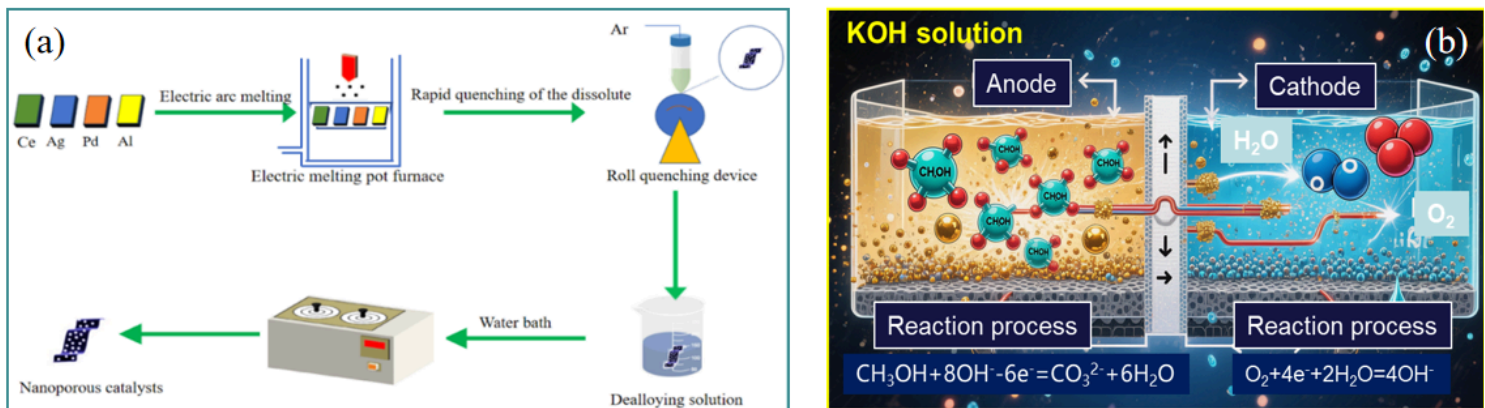


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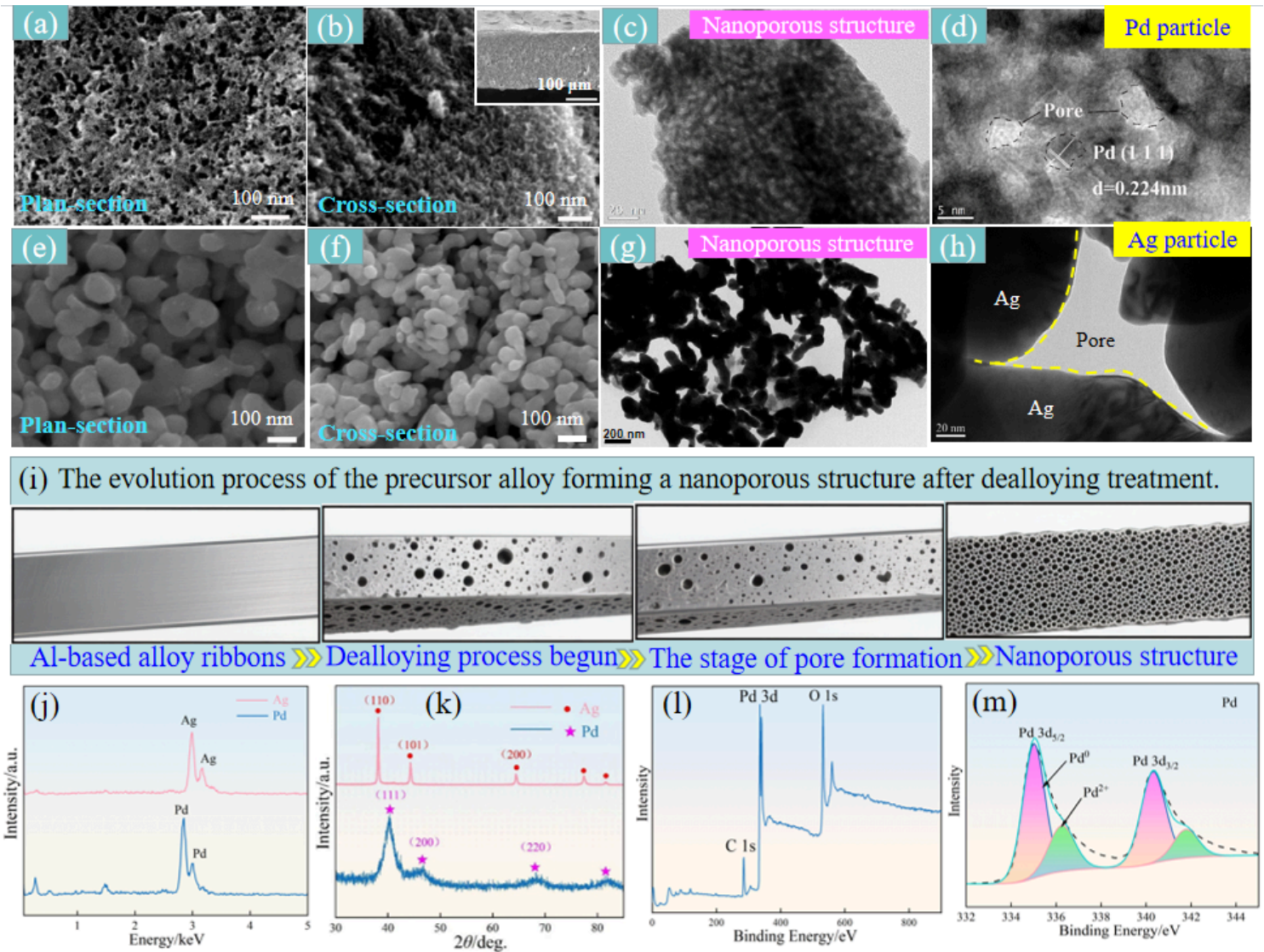


Figure 2

(a-h) show SEM and TEM images of the nanoporous Pd and porous Ag catalyst, (i) show the evolution process of precursor alloy into nanoporous structure through dealloying process, (j-k) show EDS and XRD images of the nanoporous Pd and porous Ag catalyst, and (l-m) show XPS images of the nanoporous Pd catalyst.

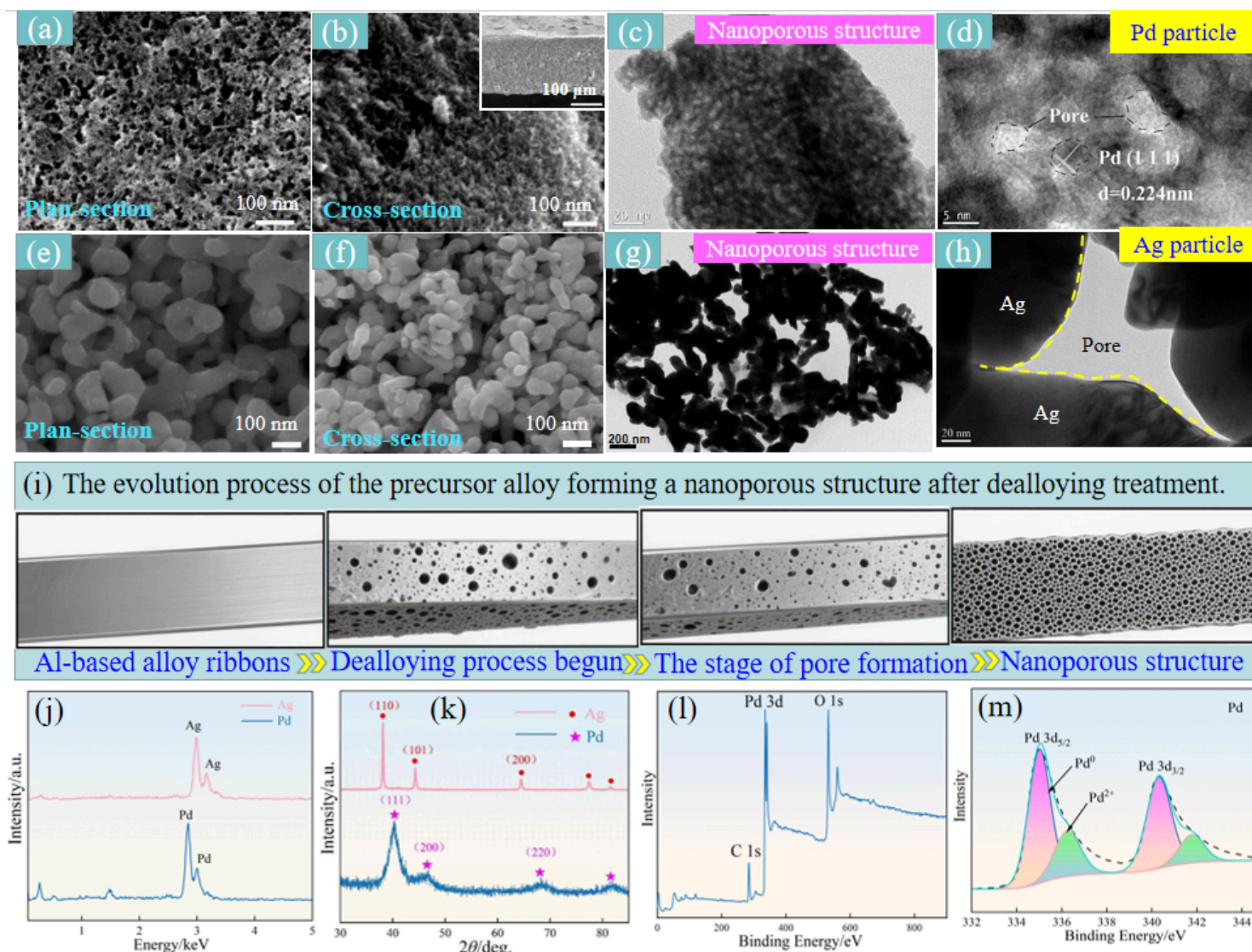


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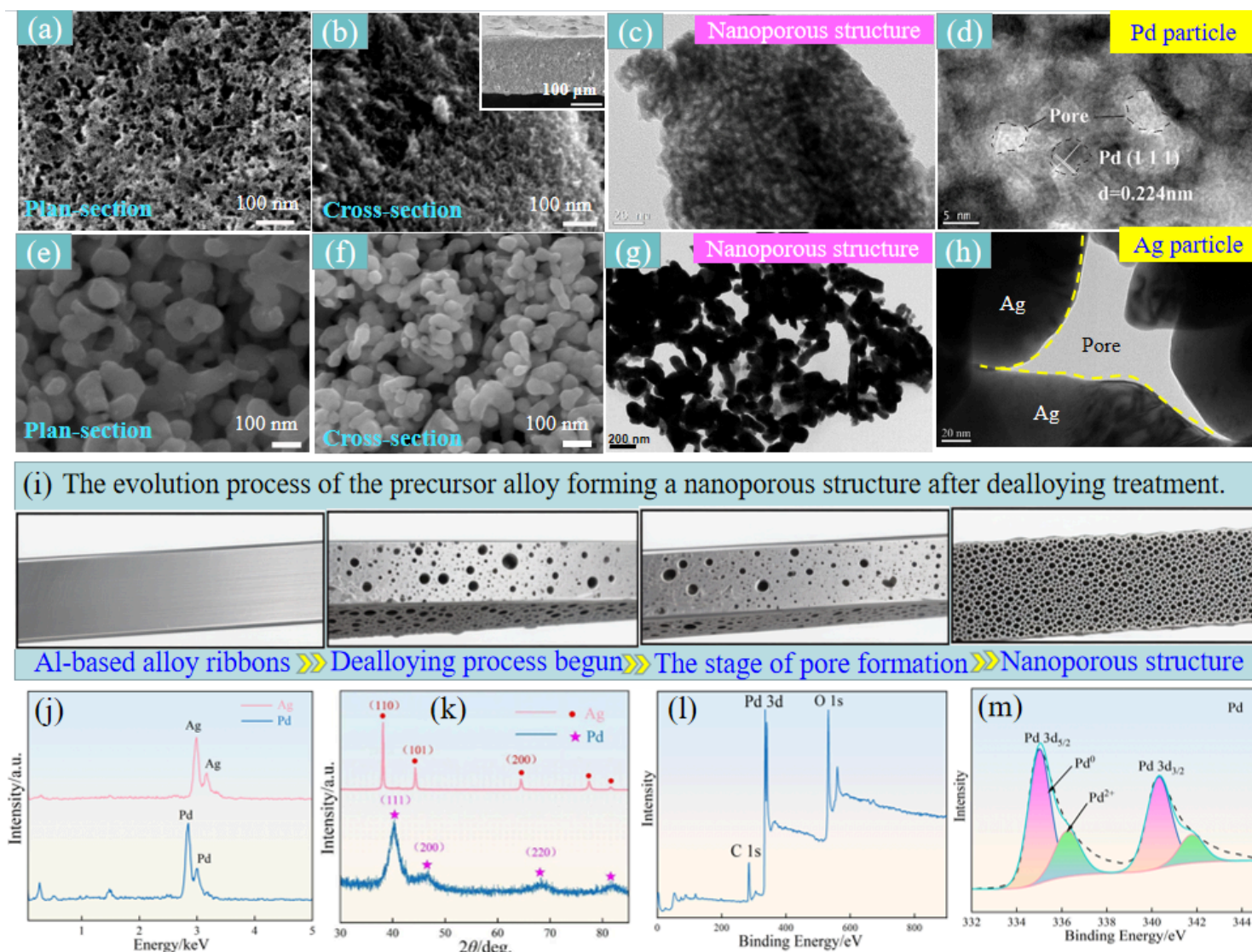


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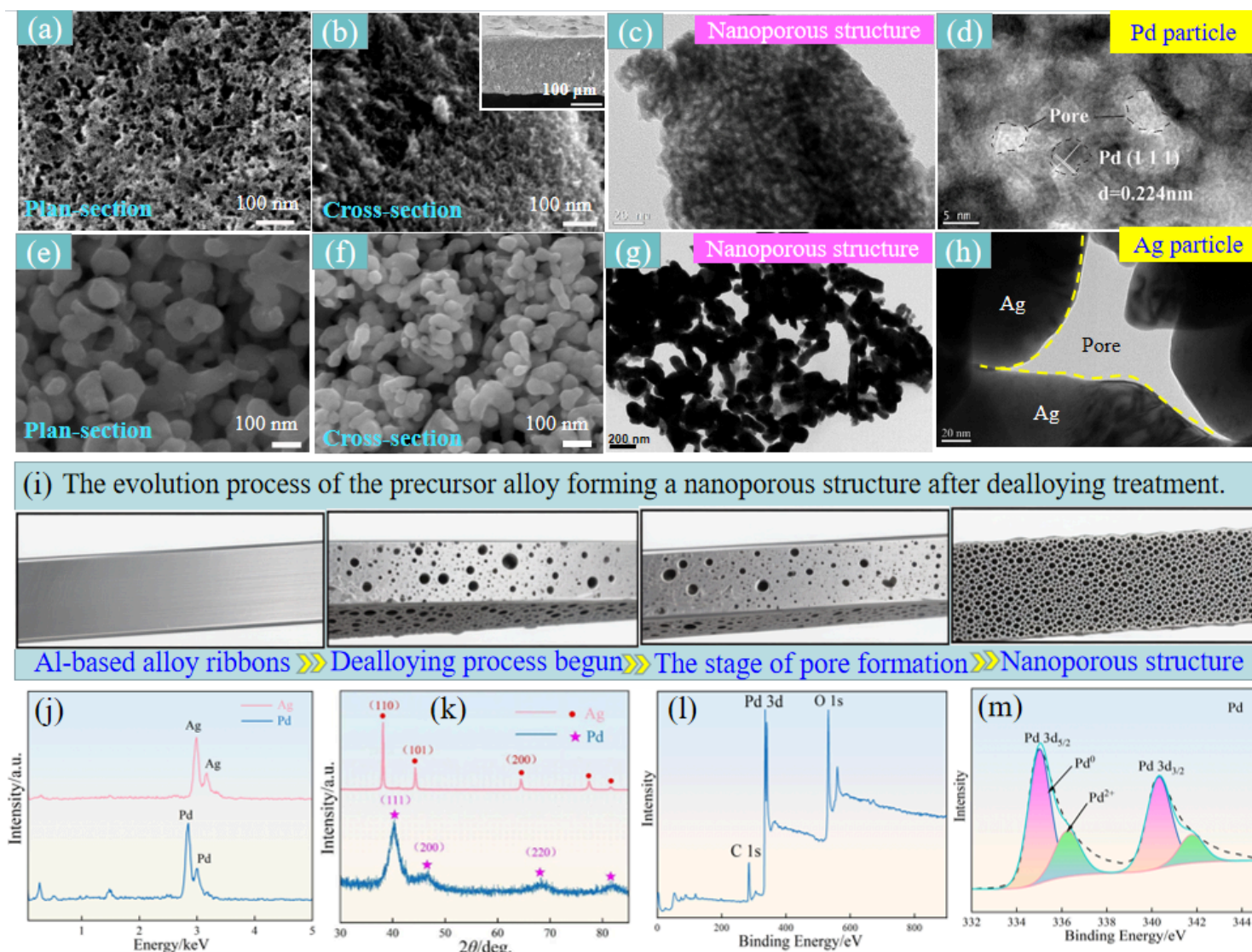


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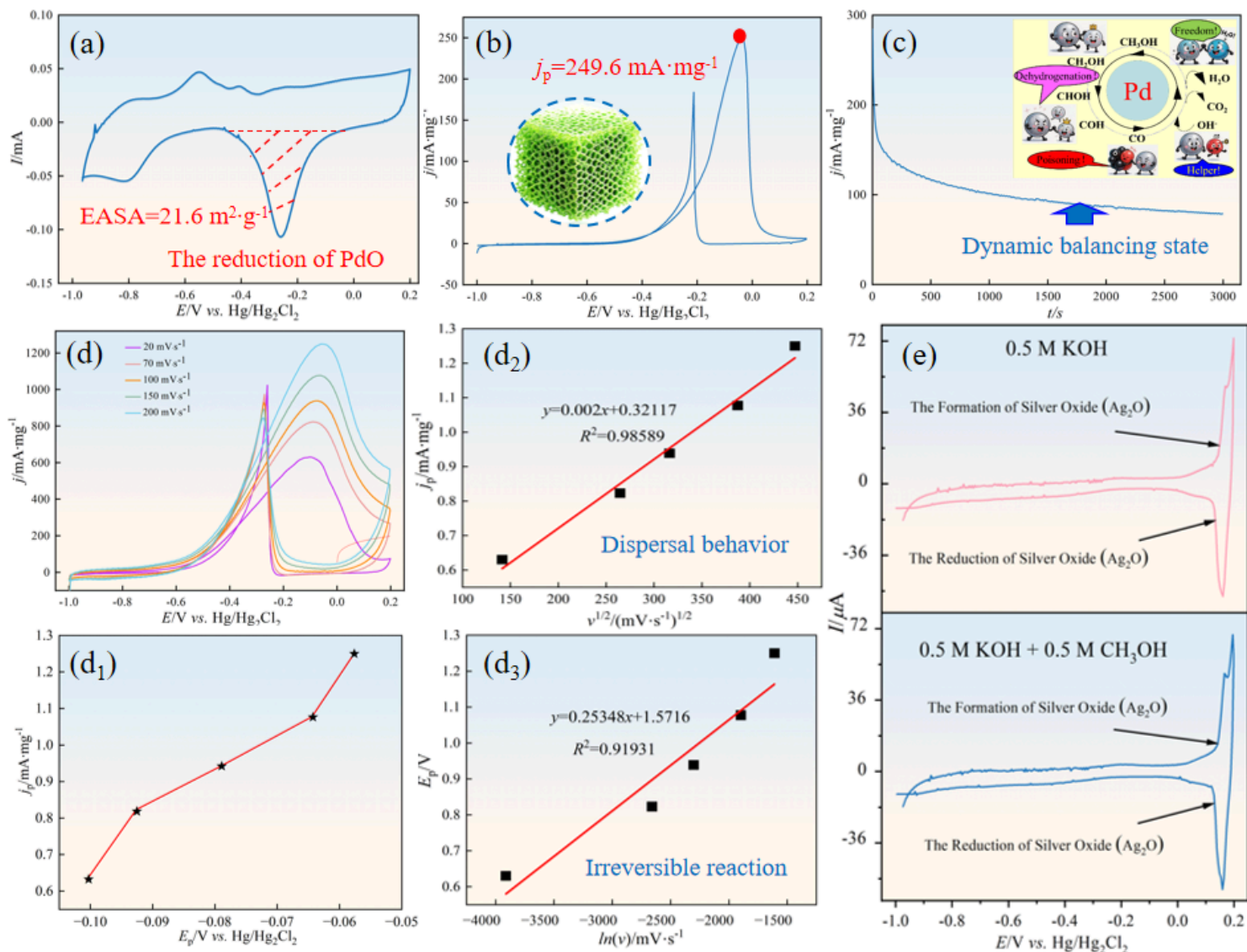


Figure 3

The CV curve and corresponding EASA value of the nanoporous Pd catalyst in 0.5 M KOH solution (a), the CV curve (b), $i-t$ curve (c), CV curve with different scan rates (d), j_p and E_p (d₁), j_p and $v^{1/2}$ (d₂), E_p and $\ln(v)$ (d₃) of the nanoporous Pd catalyst in 0.5 M KOH+0.5 M CH₃OH solution, and the CV curves of the porous Ag catalyst in 0.5 M KOH and 0.5 M KOH+0.5 M CH₃OH solutions (e).

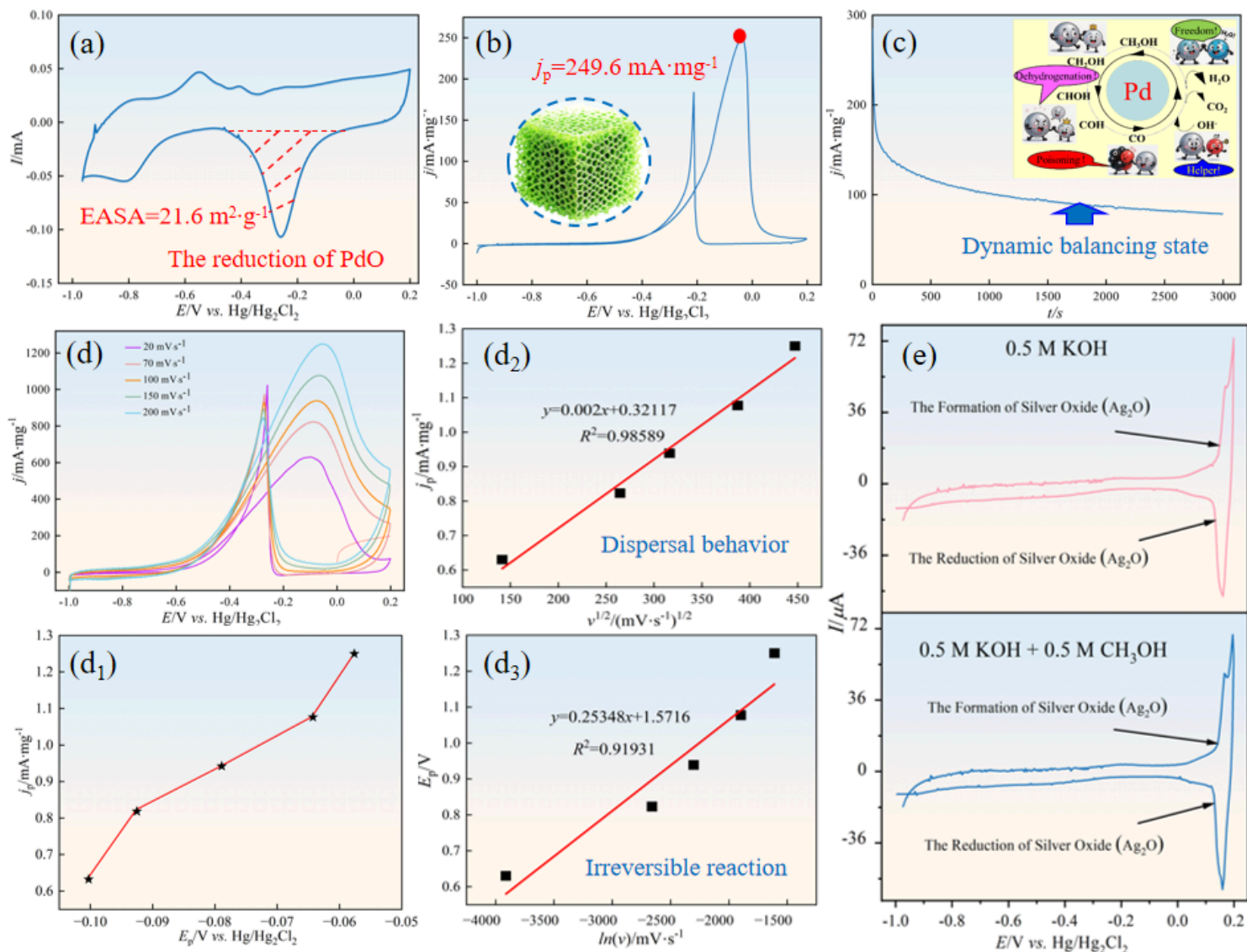


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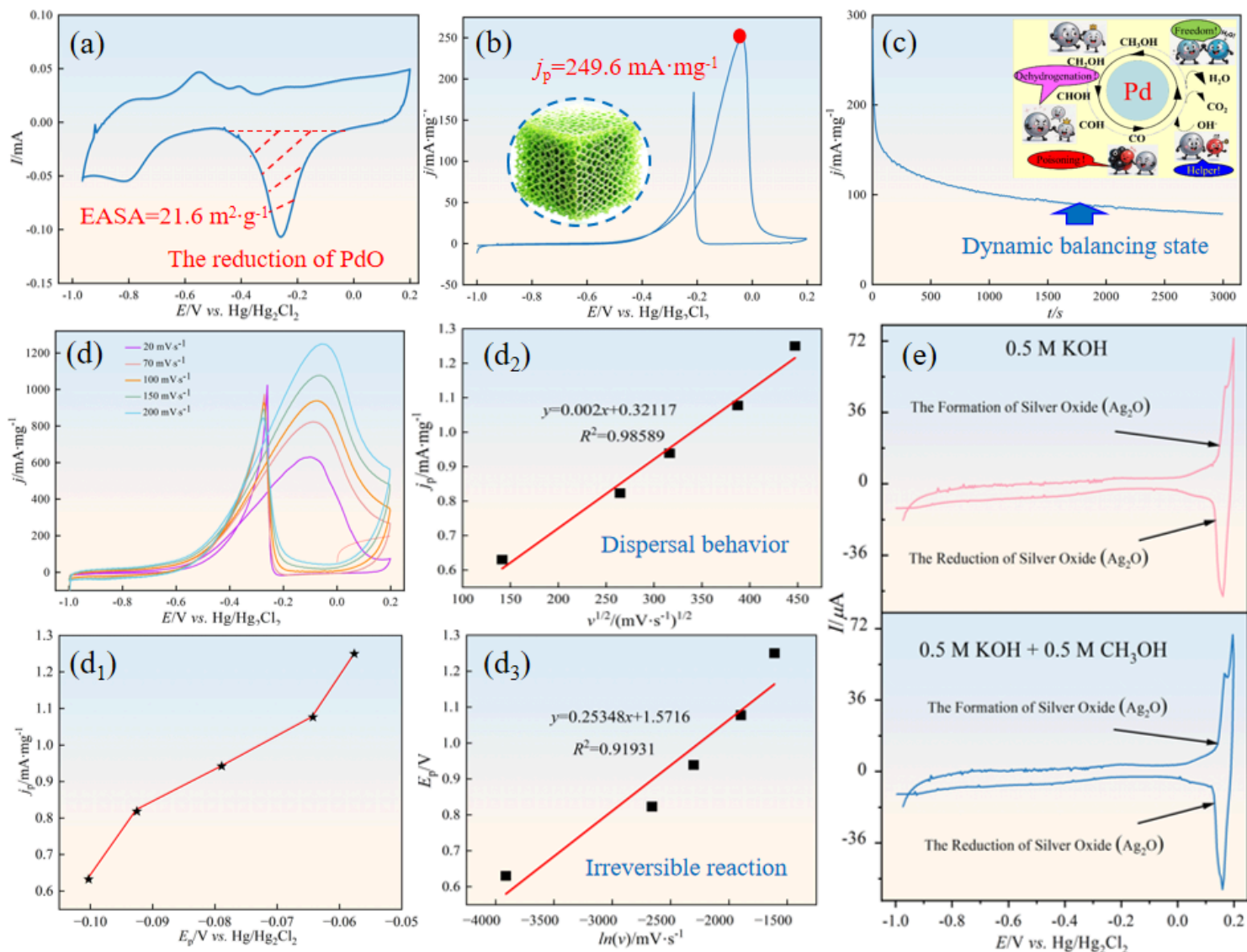


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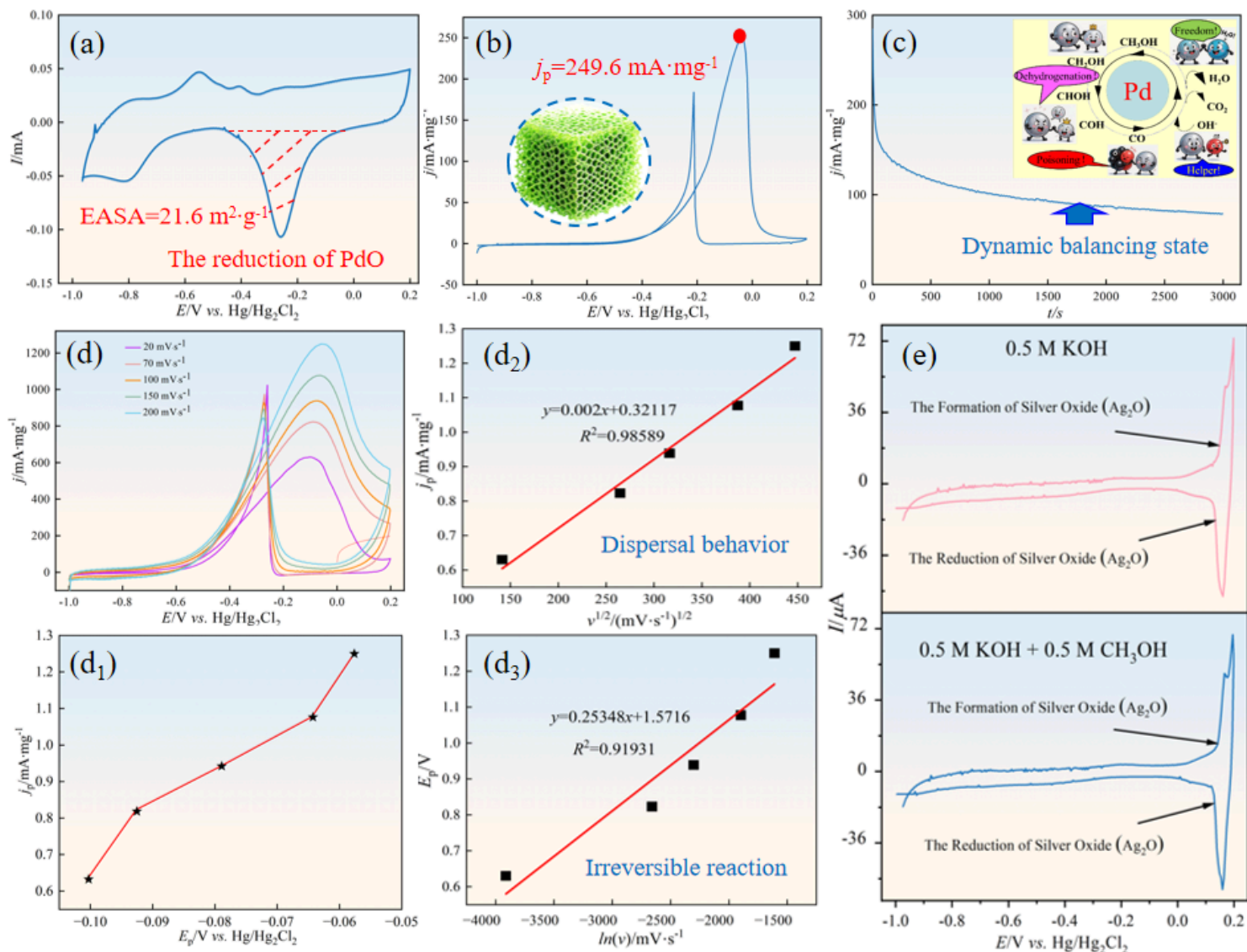


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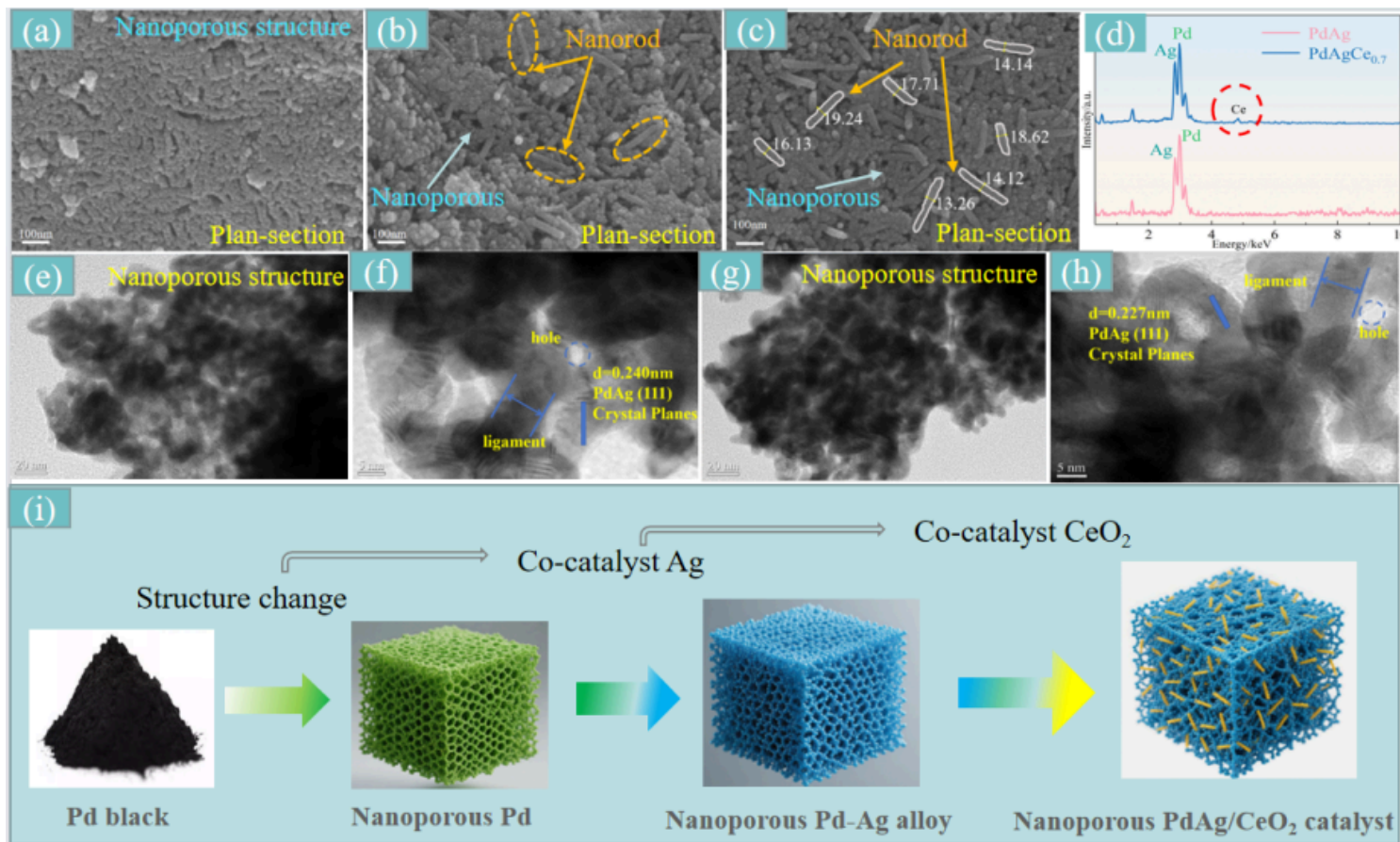


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SEM image of the PdAg (a), PdAgCe_{0.3} (b) and PdAgCe_{0.7} catalyst (c), EDS spectra of the PdAg and PdAgCe_{0.7} catalysts (d), TEM and HRTEM of the PdAg catalyst (e, f) and PdAgCe_{0.3} catalyst (g, h), (i) preparation process diagram of the nanoporous Pd-Ag/CeO₂ catalyst.

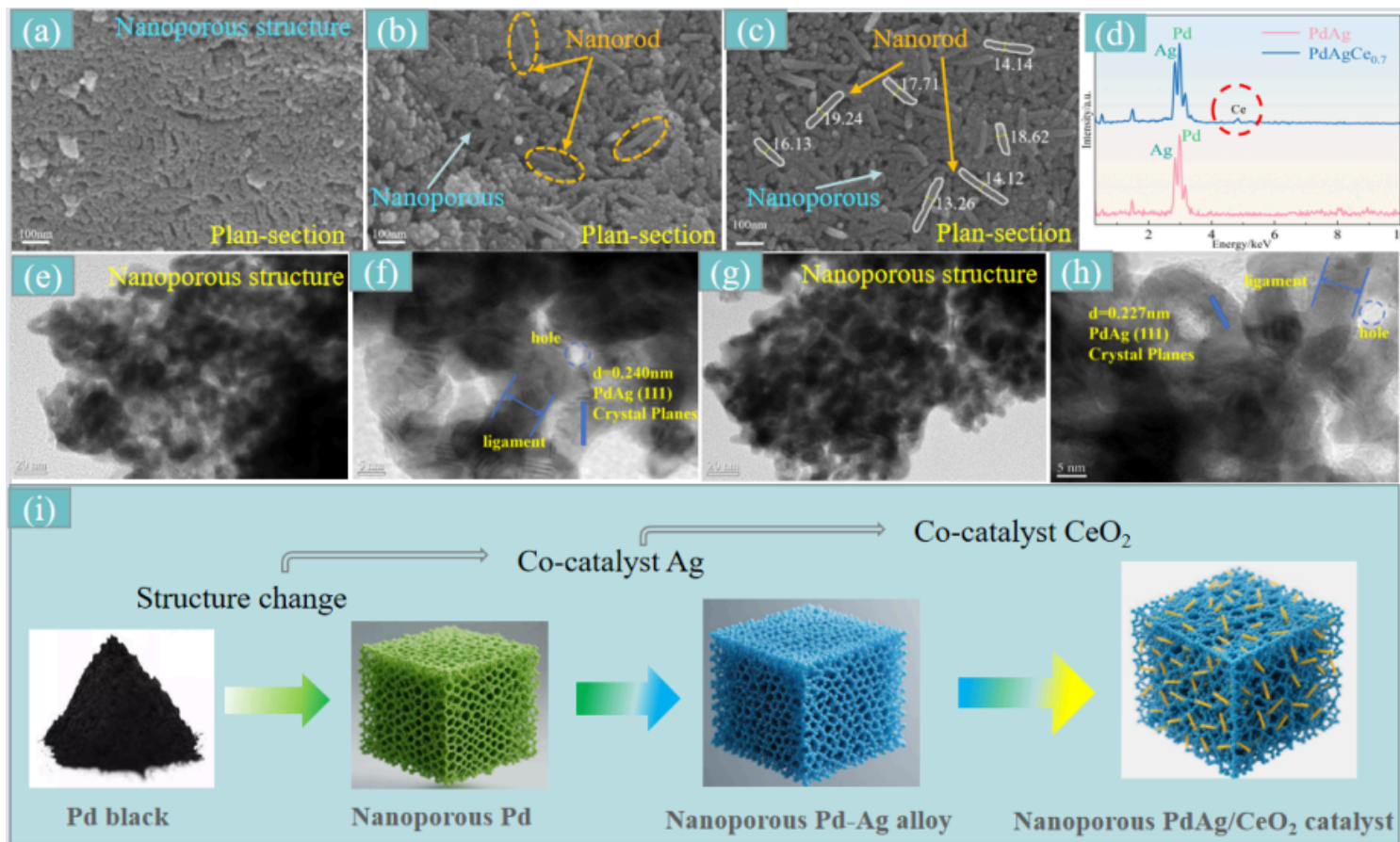


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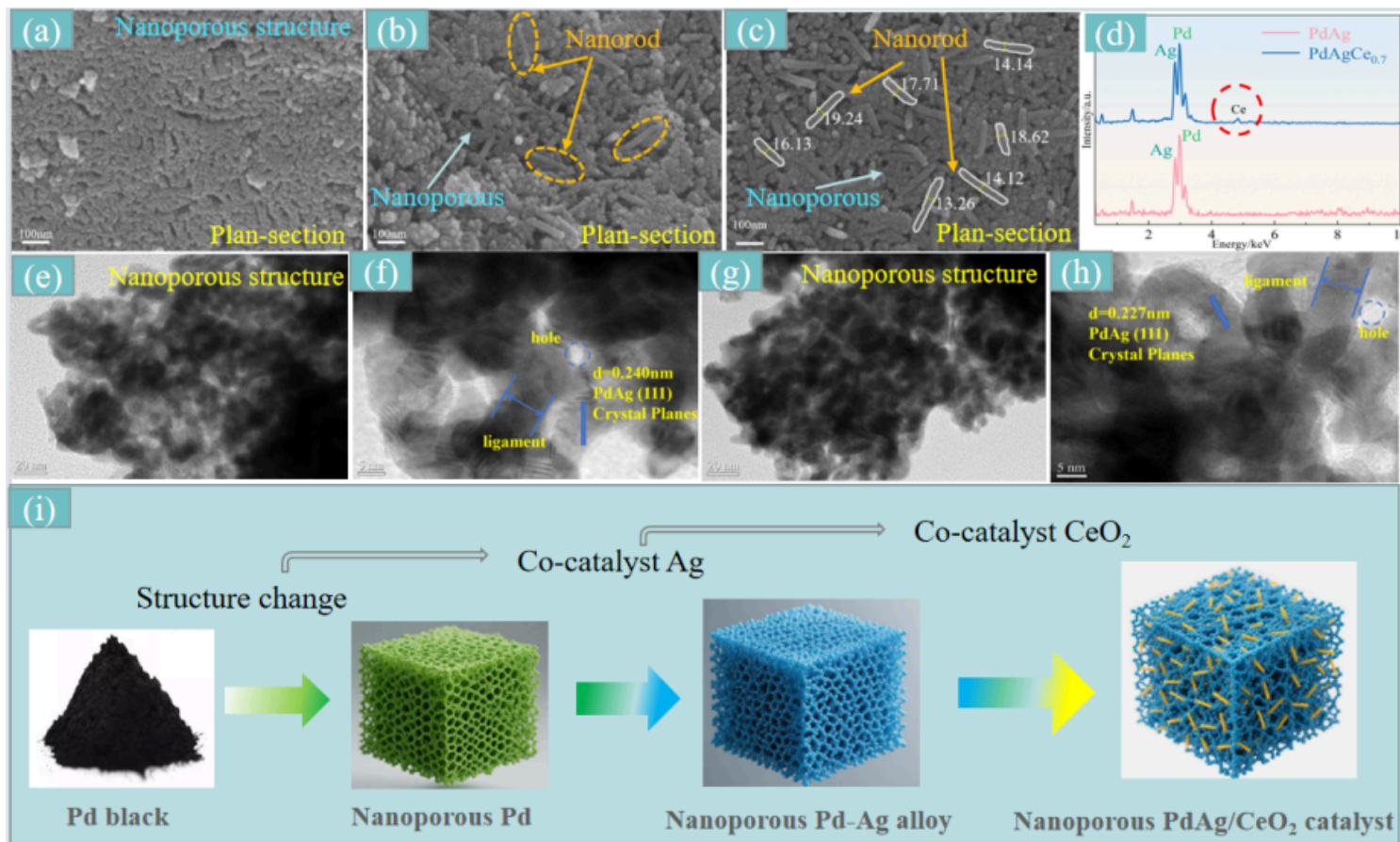


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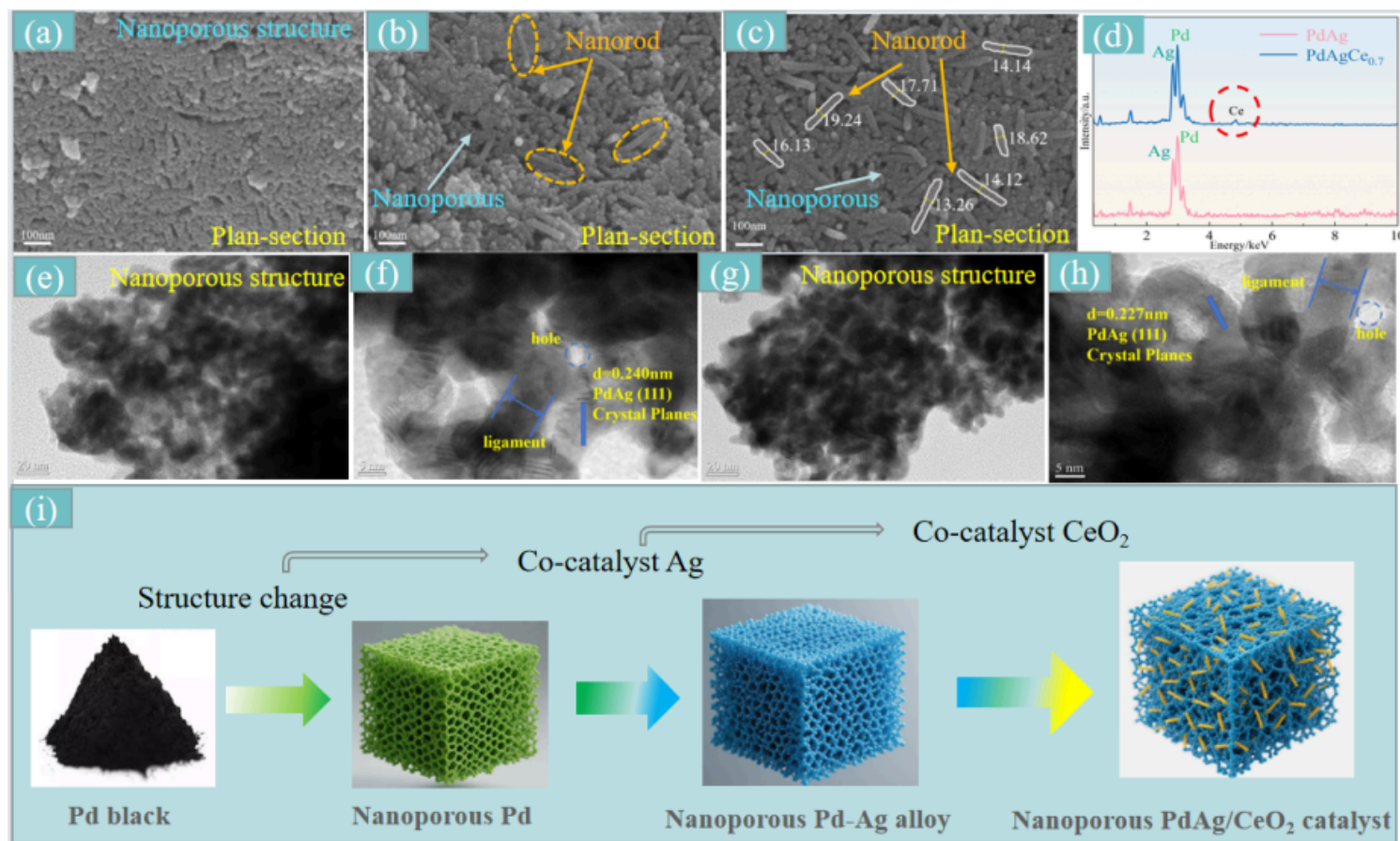


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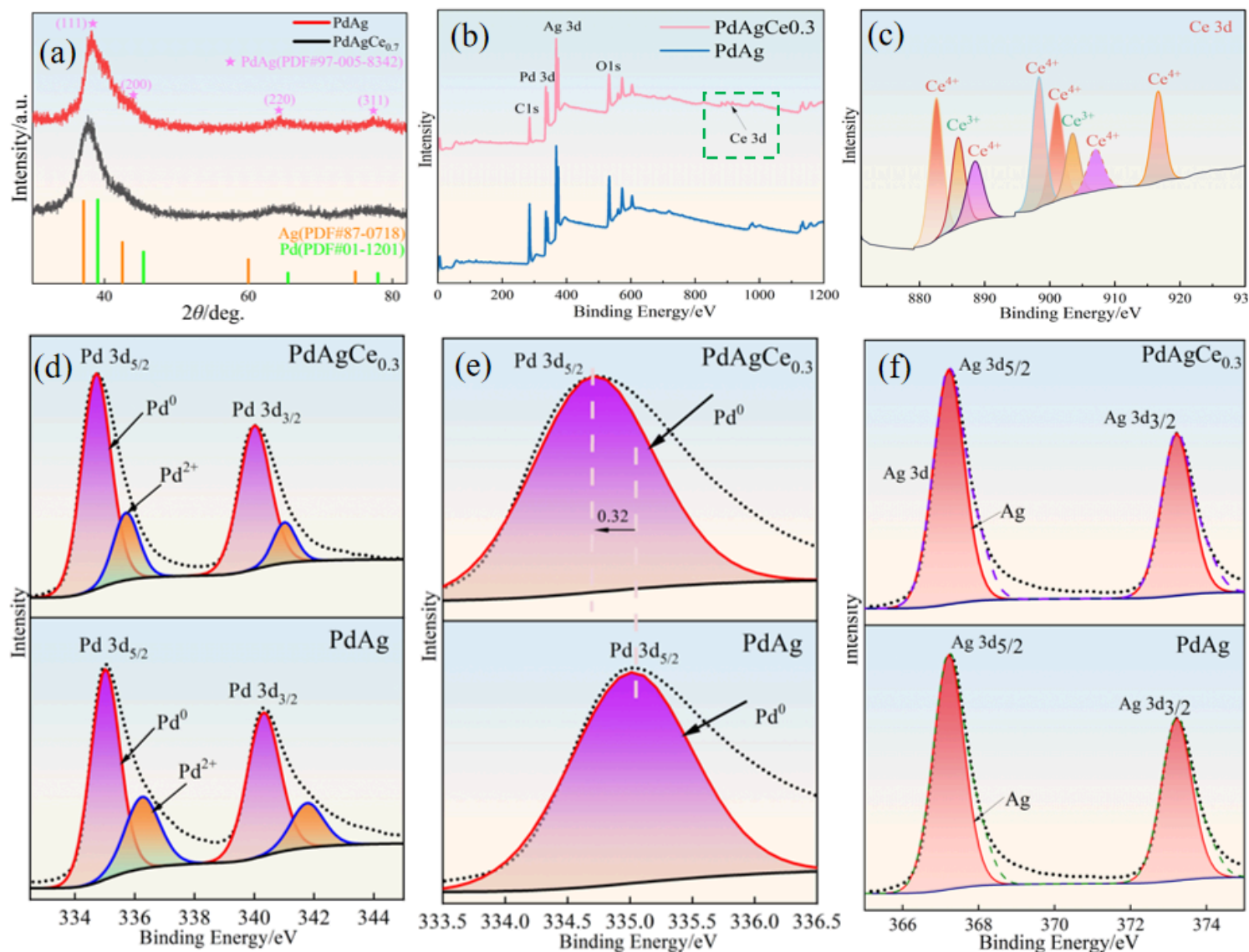


Figure 5

XRD patterns of the PdAg and PdAgCe_{0.3} catalysts (a), XPS spectral line of the nanoporous Pd-Ag and typical Pd-Ag/CeO₂(PdAgCe_{0.3}) samples (b), characteristic peak of Ce 3d (c), Pd 3d (d), and Ag 3d (f).

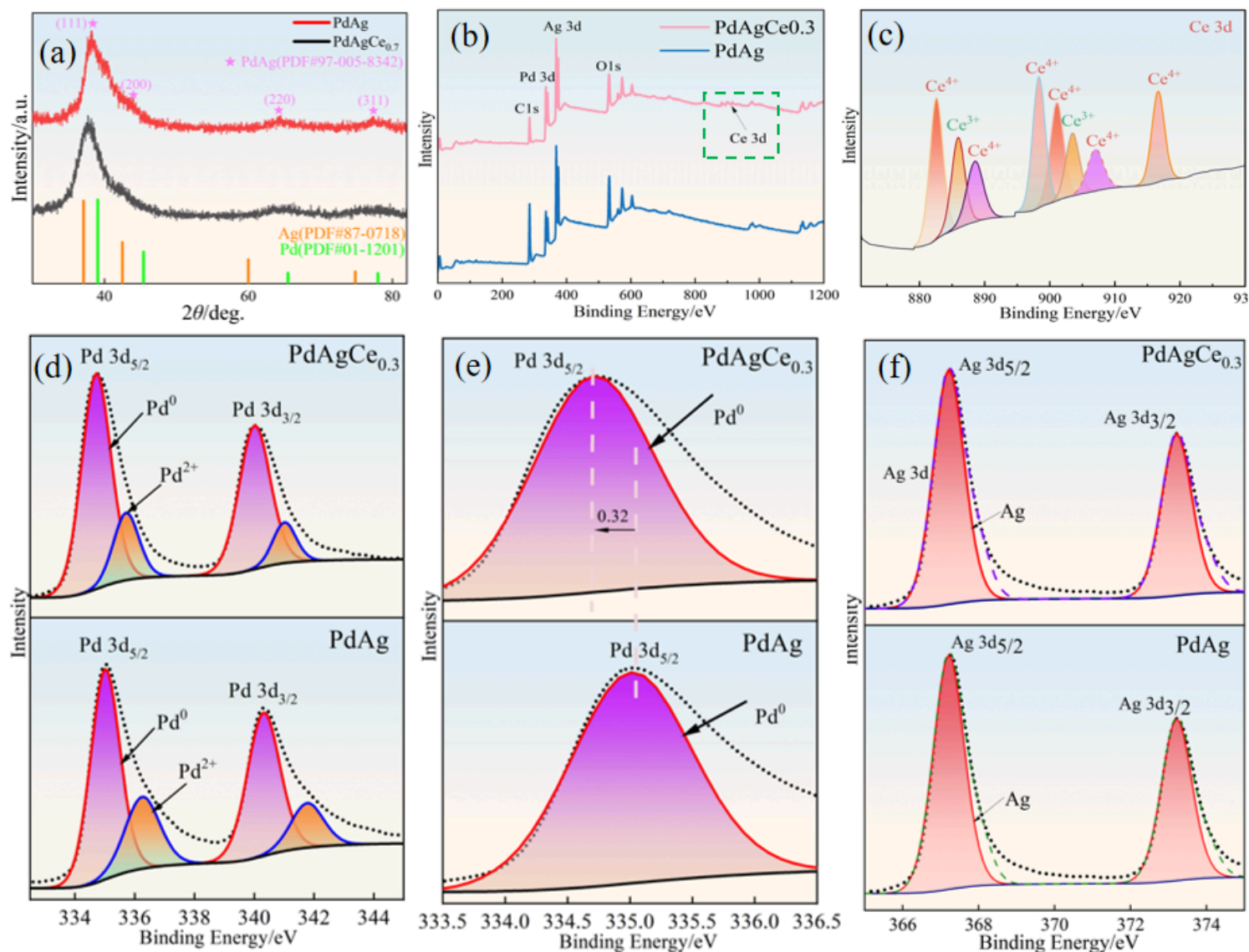


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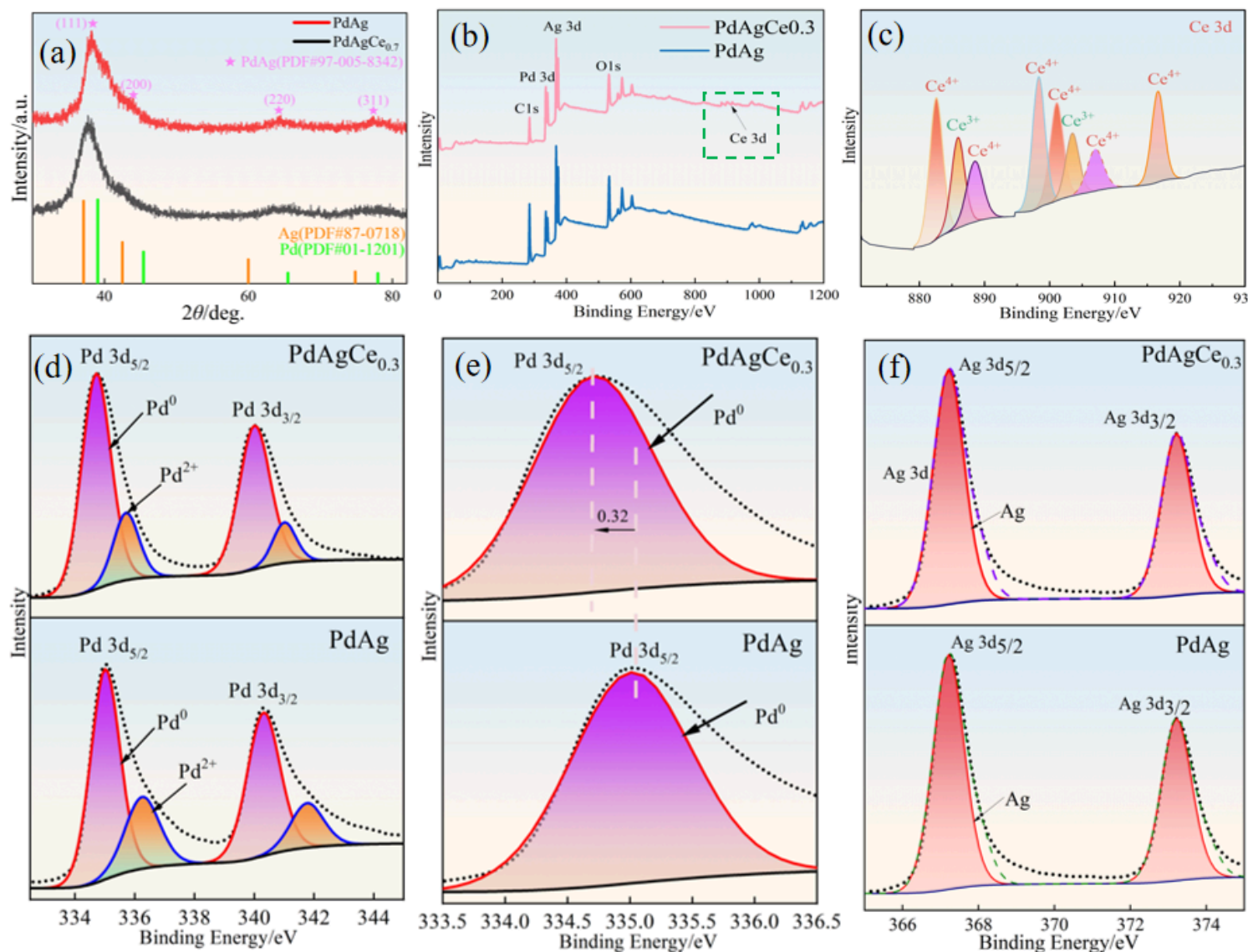


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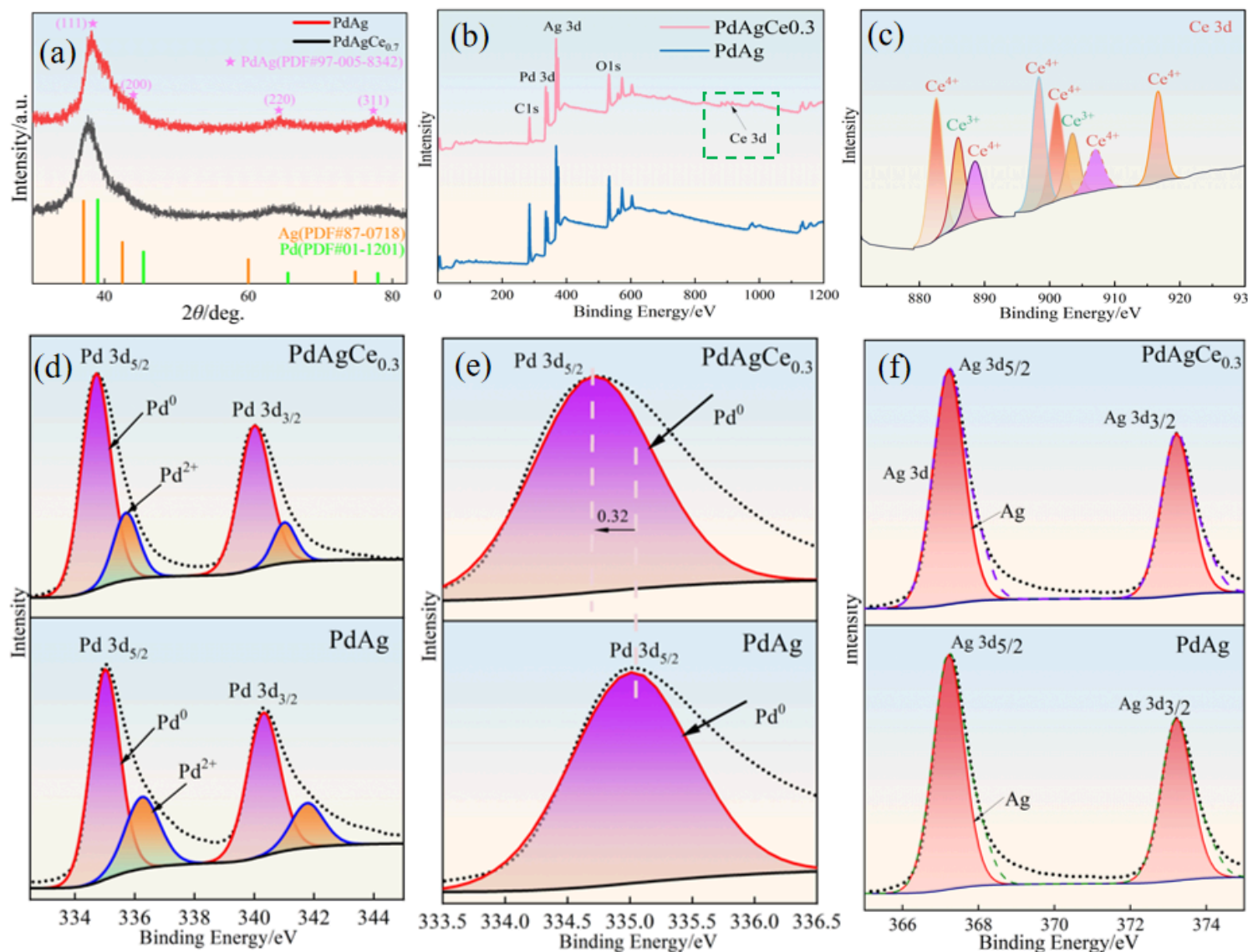


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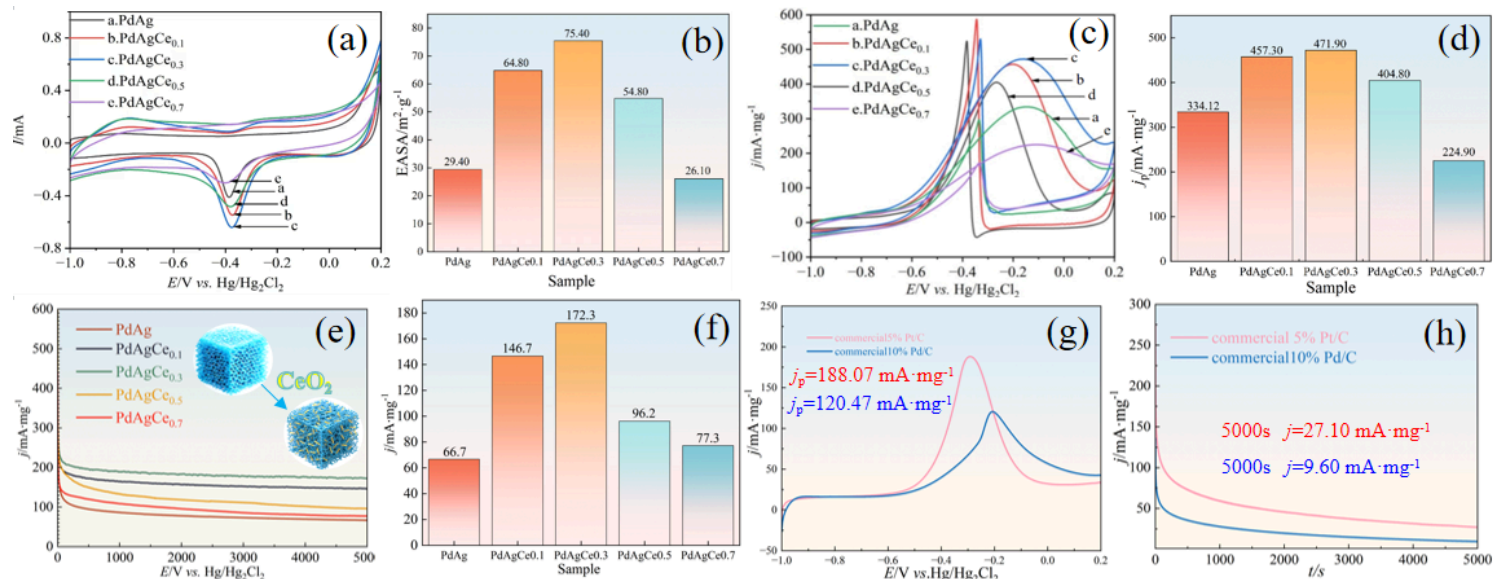


Figure 6

CV curves (a) and corresponding EASA (b) of the nanoporous Pd-Ag and Pd-Ag/CeO₂ catalysts at a scan rate of 50 mV·s⁻¹ in a 1 M KOH solution, CV curves (c) and corresponding j_p data results (d) of the nanoporous Pd-Ag and Pd-Ag/CeO₂ catalysts at a scan rate of 50 mV·s⁻¹ in a 1 M KOH + 1 M CH₃OH solution, the $i-t$ curves (e) and after 5000 seconds the j data result (f) of the nanoporous Pd-Ag catalyst and Pd-Ag/CeO₂ catalyst in 1 M KOH + 1 M CH₃OH solution, the $i-t$ curves (g) and CV curves (h) of the commercial Pd/C and Pt/C catalysts.

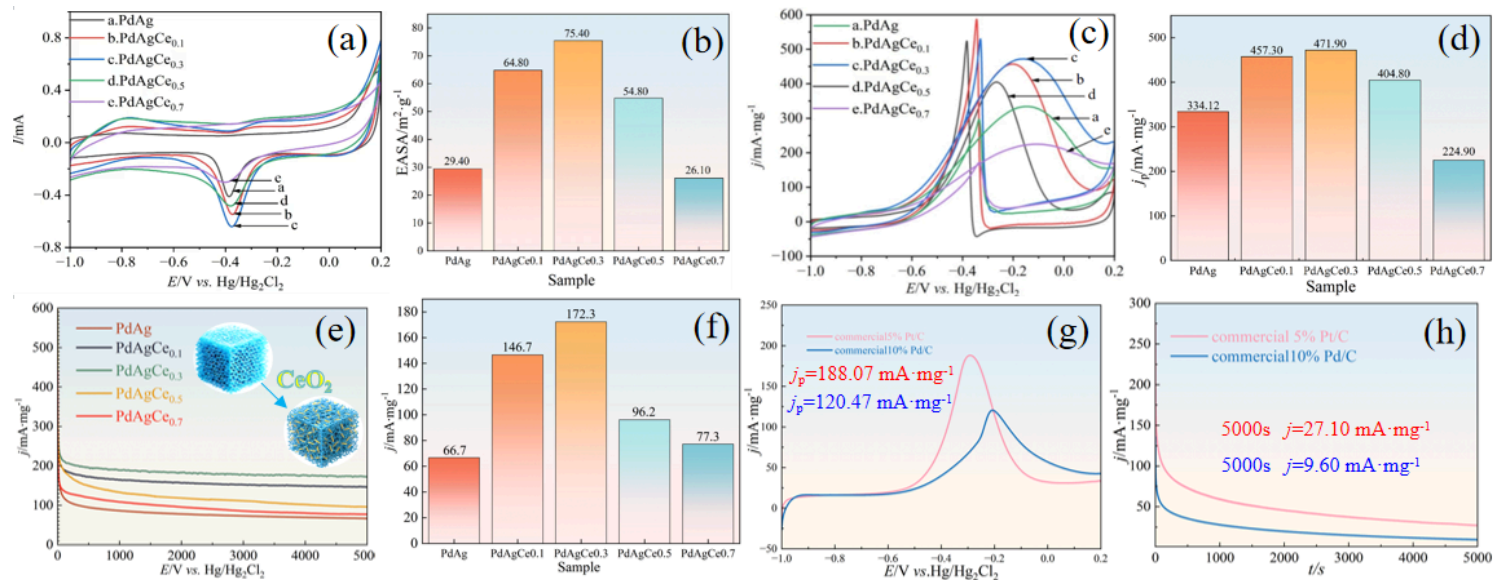


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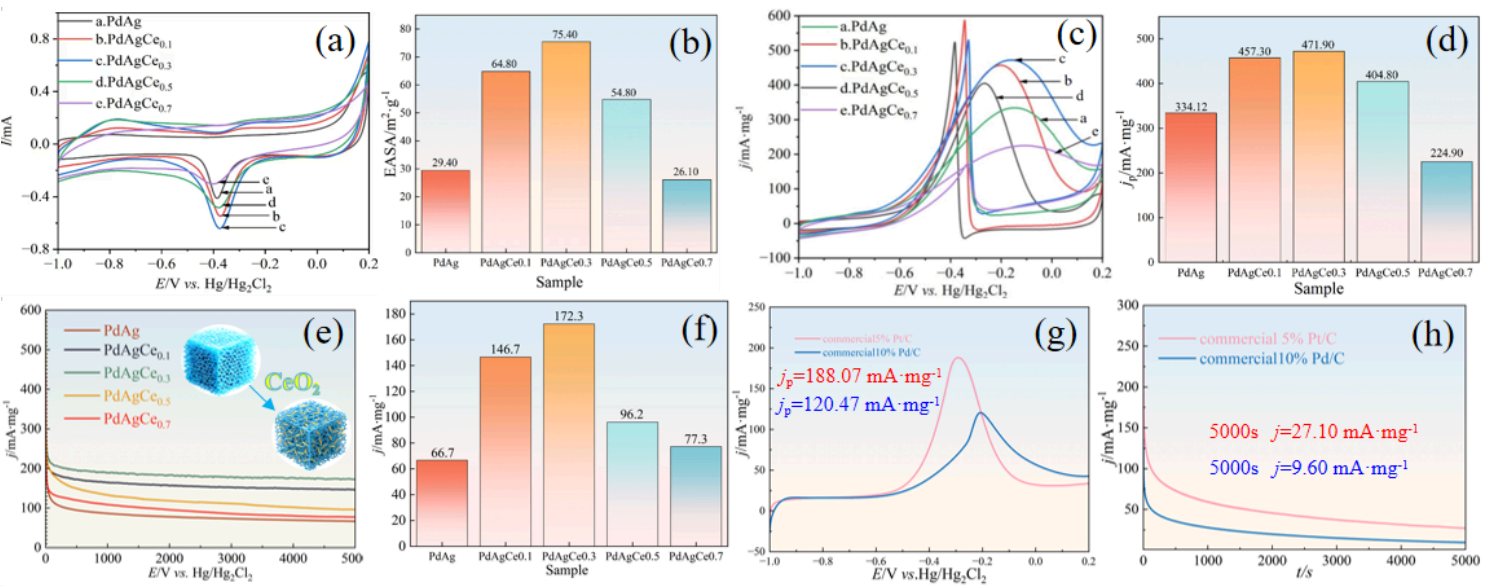


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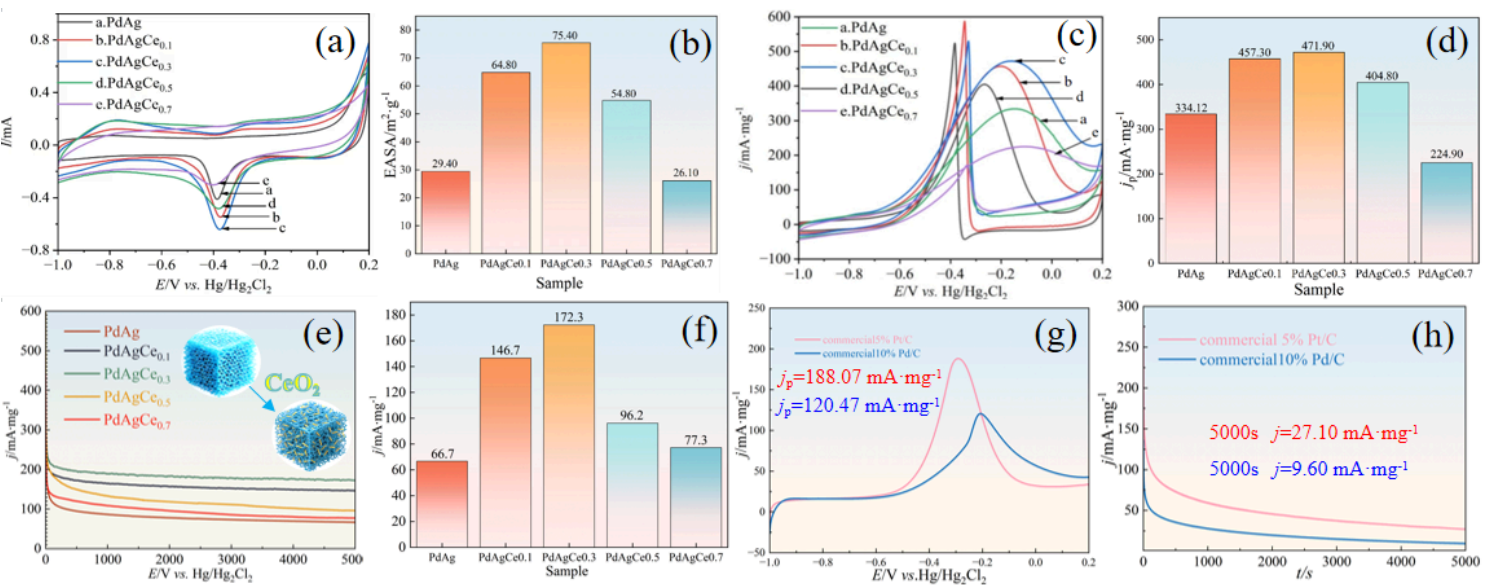


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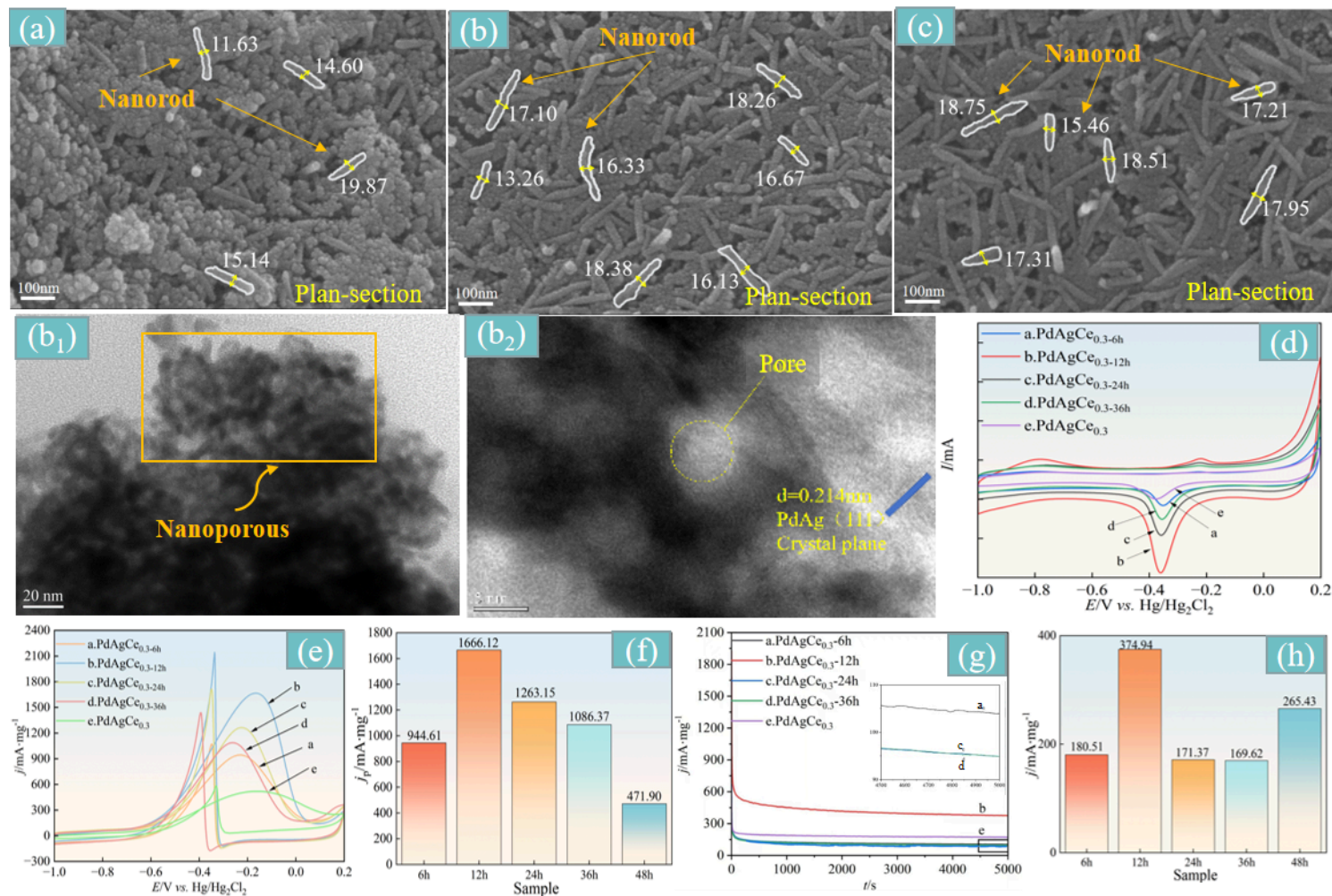


Figure 7

SEM images of the PdAgCe_{0.3-6h} (a), PdAgCe_{0.3-12h} (b), and PdAgCe_{0.3} catalysts (c), TEM (b₁) and HRTEM (b₂) of the PdAgCe_{0.3-12h} catalyst, (d) CV curves of the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalysts with different dealloying times scanned at a rate of 50 mV · s⁻¹ in 1 M KOH solution, The cyclic voltammetry curves (e) and corresponding j_p (f) of the nanoporous Pd-Ag/CeO₂ catalysts with different dealloying times in 1 M KOH solution at a scan rate of 50 mV s⁻¹, i - t (g) and after 5000 seconds j (h) of the nanoporous Pd-Ag/CeO₂ catalysts with different dealloying times in 1 M KOH+1 M methanol solution.

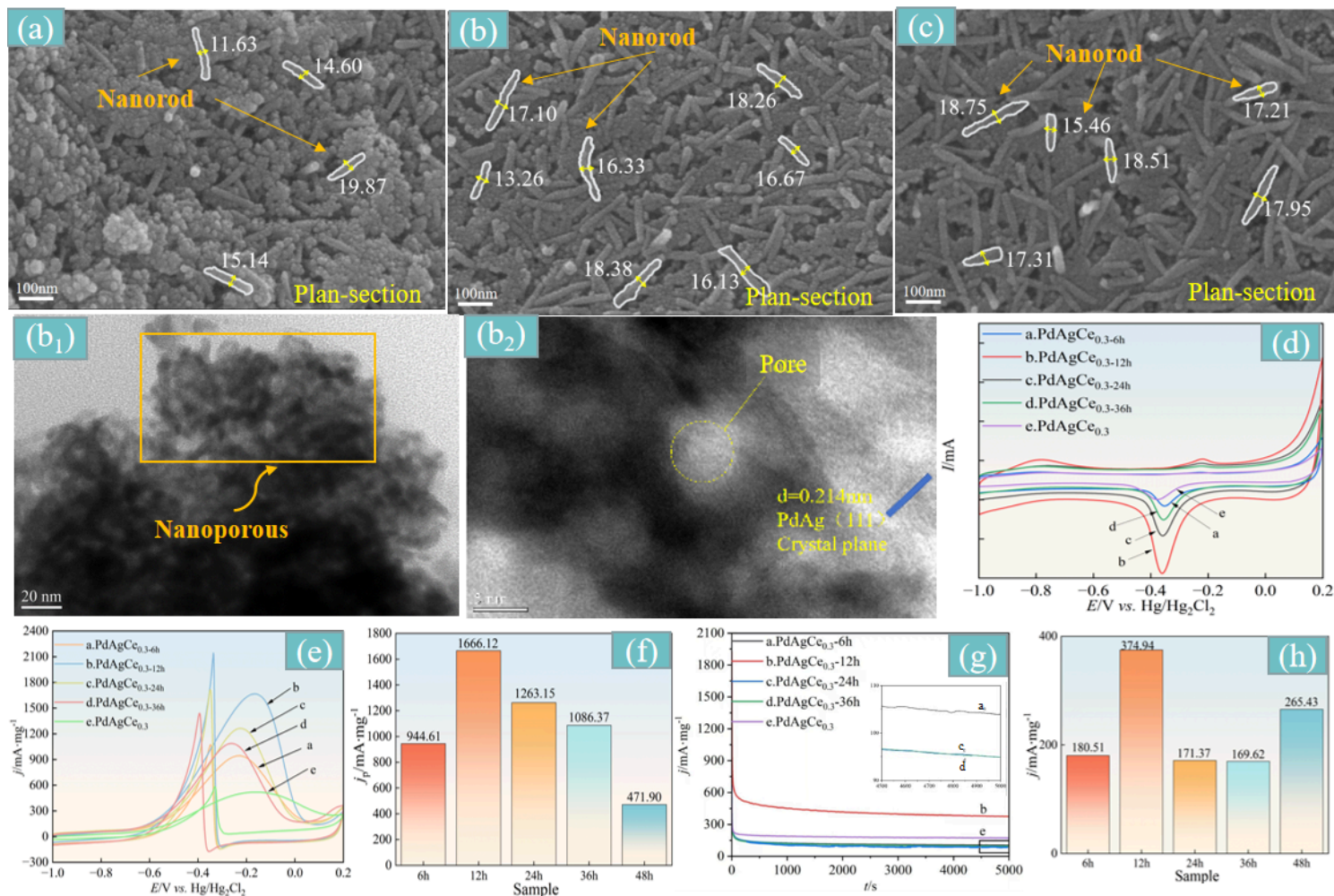


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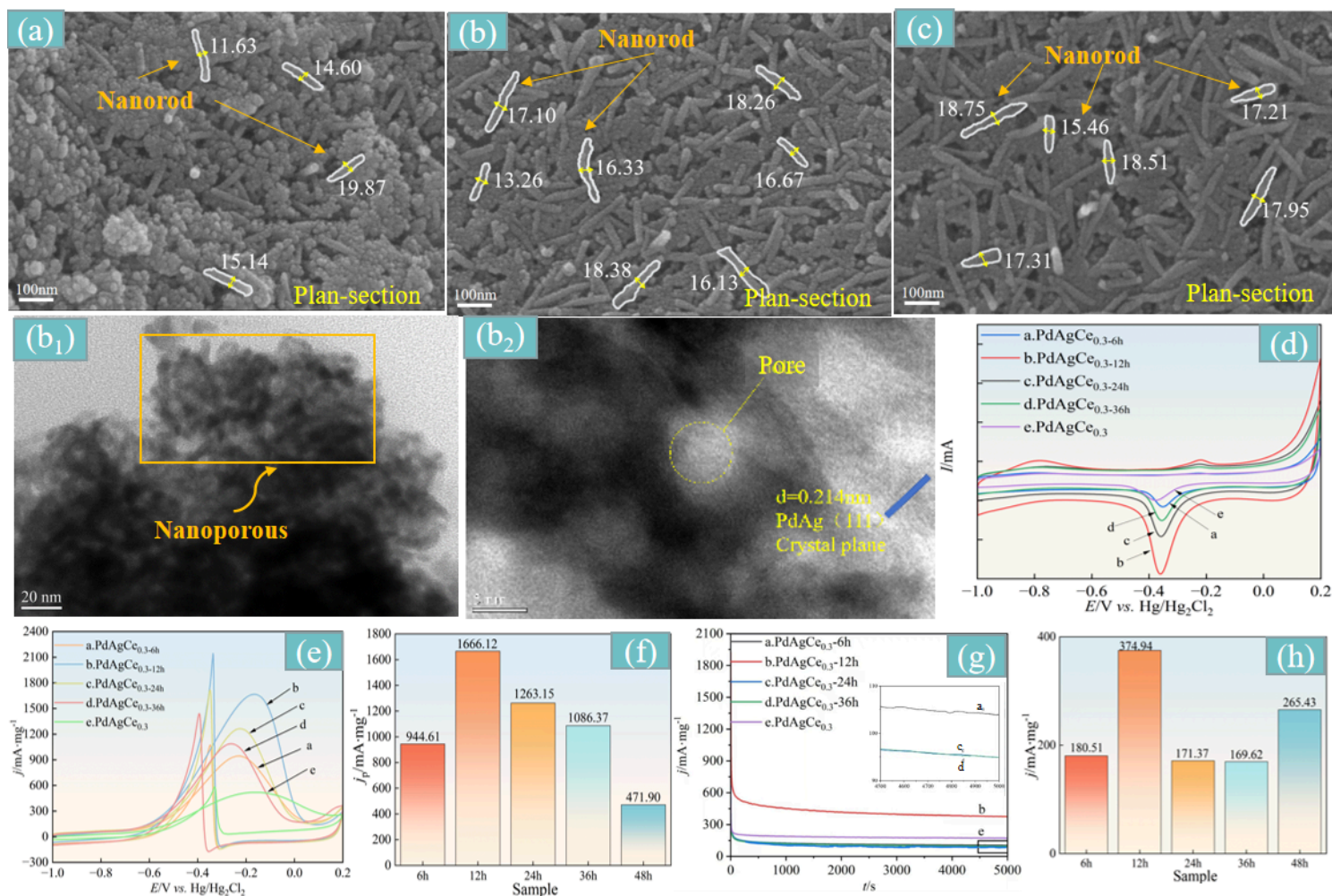


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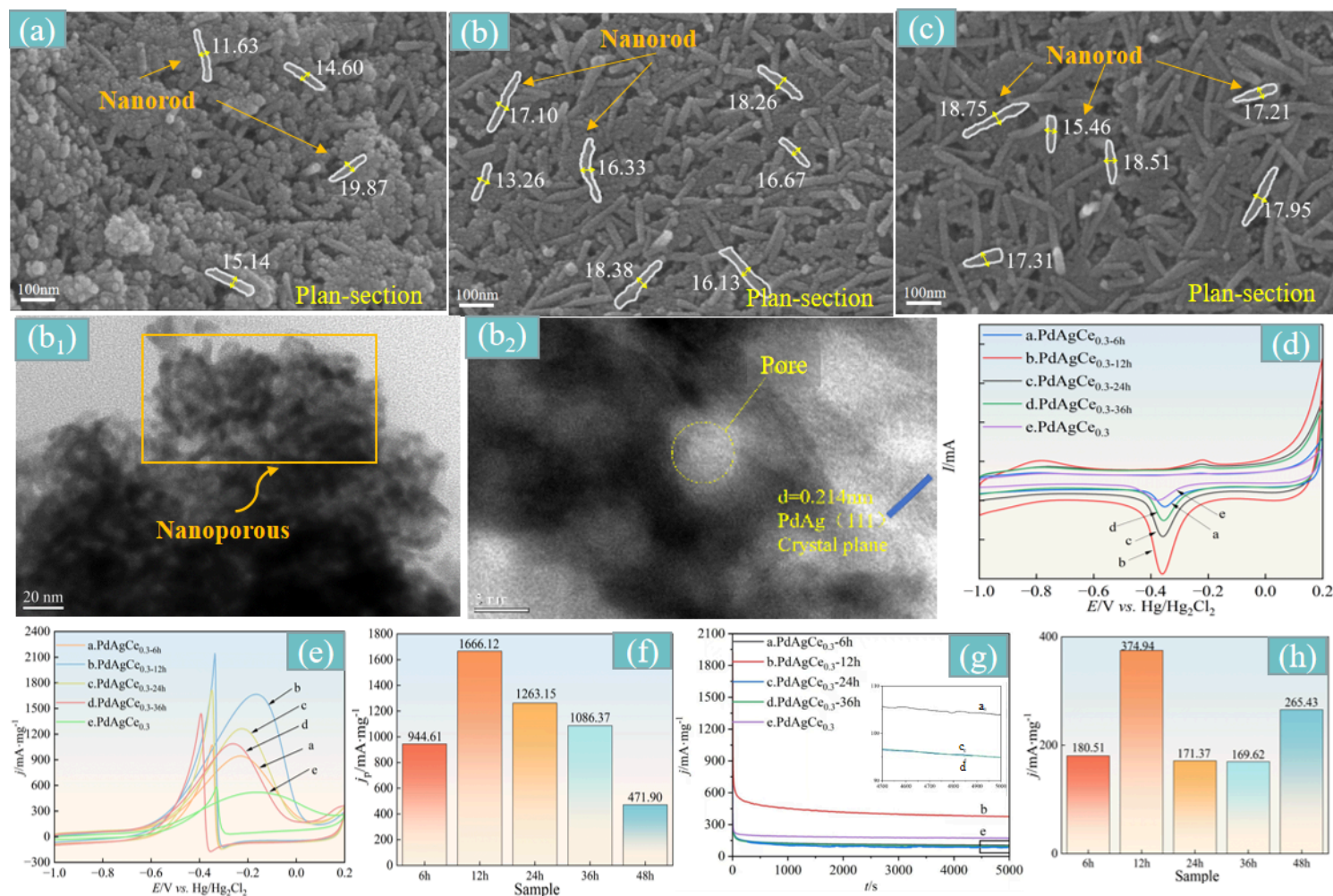


Figure 7

SEM images of the PdAgCe_{0.3-6h} (a), PdAgCe_{0.3-12h} (b), and PdAgCe_{0.3} catalysts (c), TEM (b₁) and HRTEM (b₂) of the PdAgCe_{0.3-12h} catalyst, (d) CV curves of the nanoporous Pd-Ag/CeO₂ (PdAgCe_{0.3}) catalysts with different dealloying times scanned at a rate of $50\text{ mV} \cdot \text{s}^{-1}$ in 1 M KOH solution, The cyclic voltammetry curves (e) and corresponding j_p (f) of the nanoporous Pd-Ag/CeO₂ catalysts with different dealloying times in 1 M KOH solution at a scan rate of 50 mV s^{-1} , $i-t$ (g) and after 5000 seconds j (h) of the nanoporous Pd-Ag/CeO₂ catalysts with different dealloying times in 1 M KOH+1 M methanol solution.

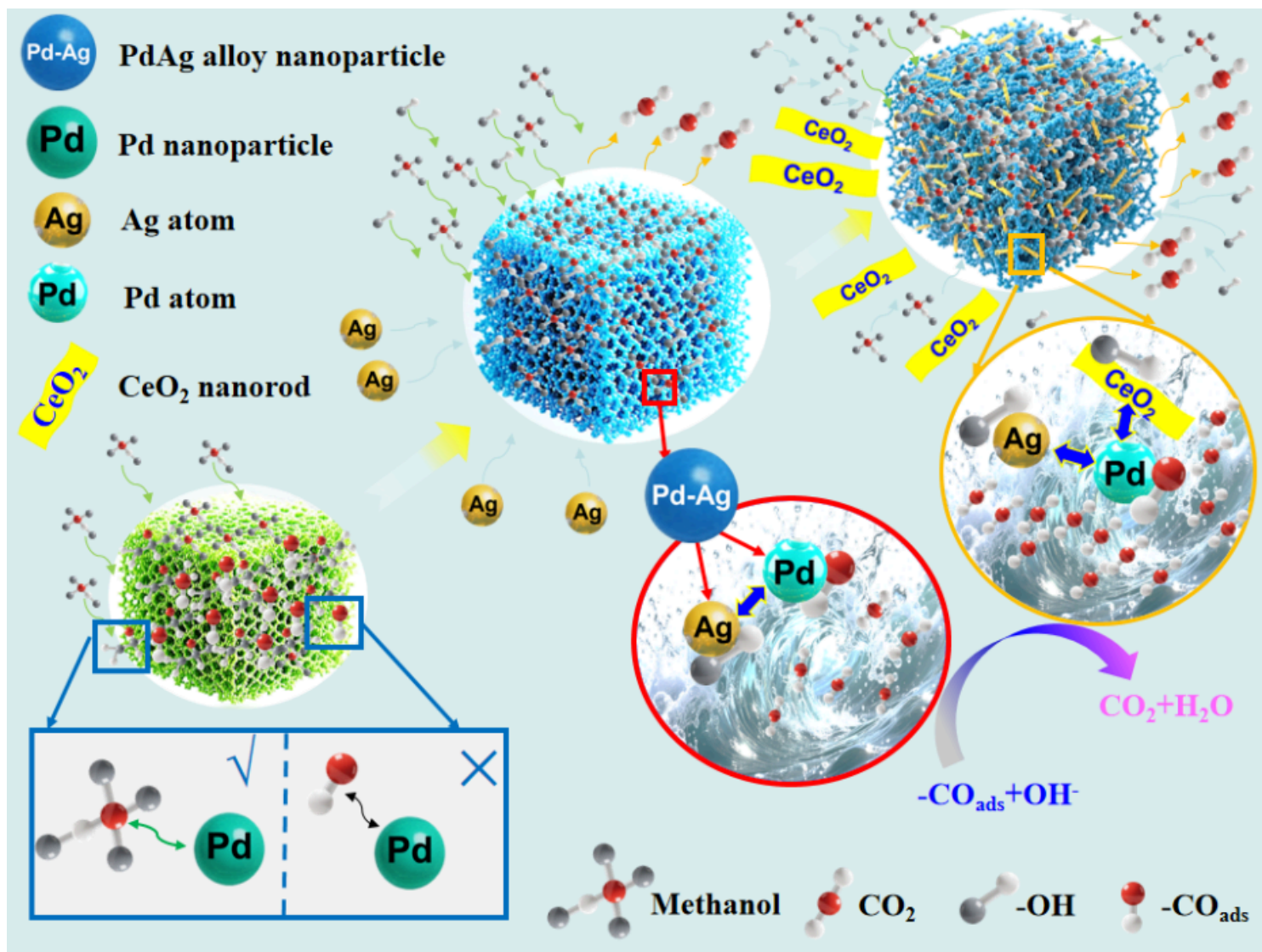


Figure 8

The mechanism diagram for the electrocatalytic oxidation of methanol by the nanoporous Pd-Ag/CeO₂ catalysts.

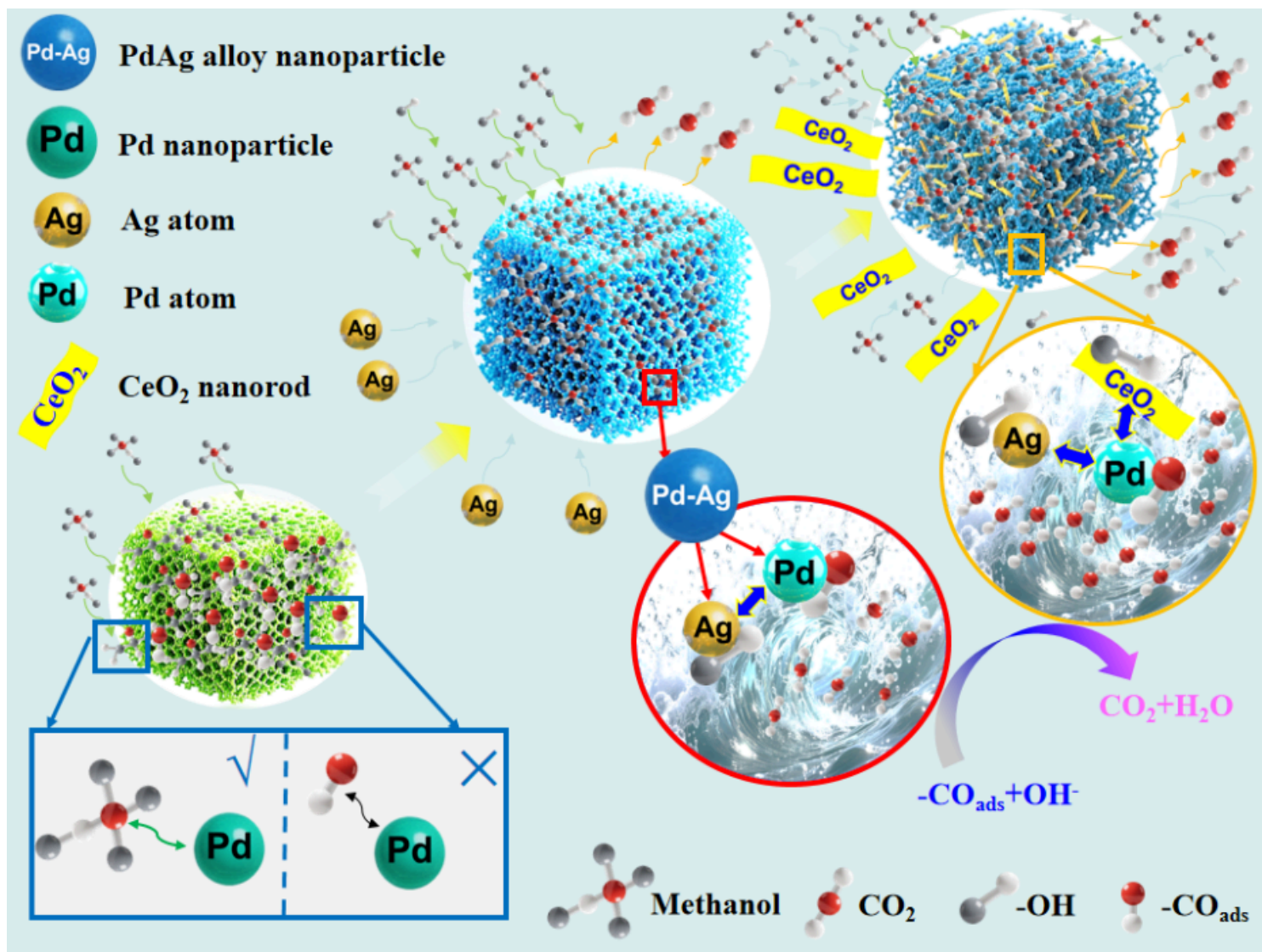


Figure 8

The mechanism diagram for the electrocatalytic oxidation of methanol by the nanoporous Pd-Ag/CeO₂ catalysts.

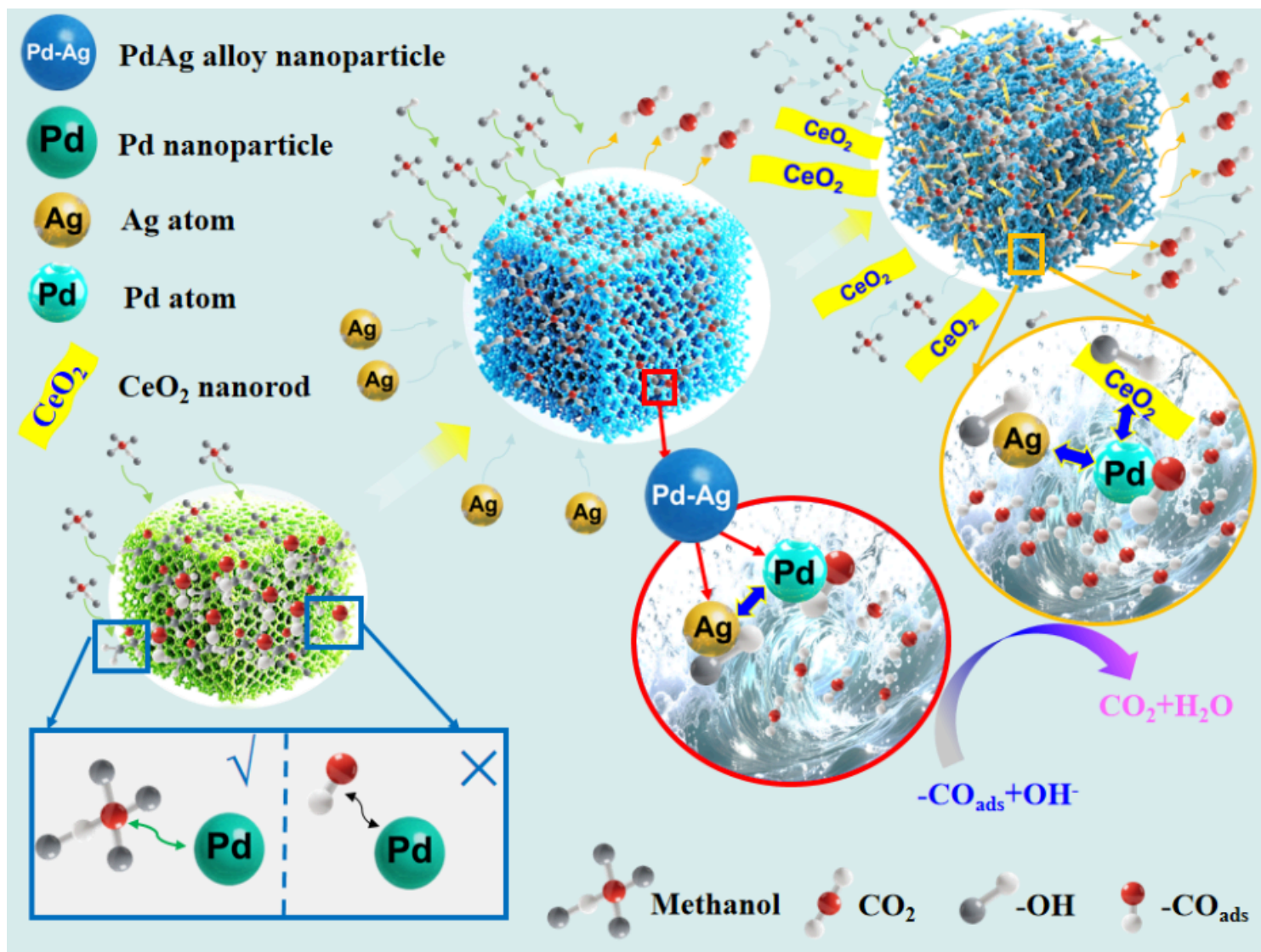


Figure 8

The mechanism diagram for the electrocatalytic oxidation of methanol by the nanoporous Pd-Ag/CeO₂ catalysts.

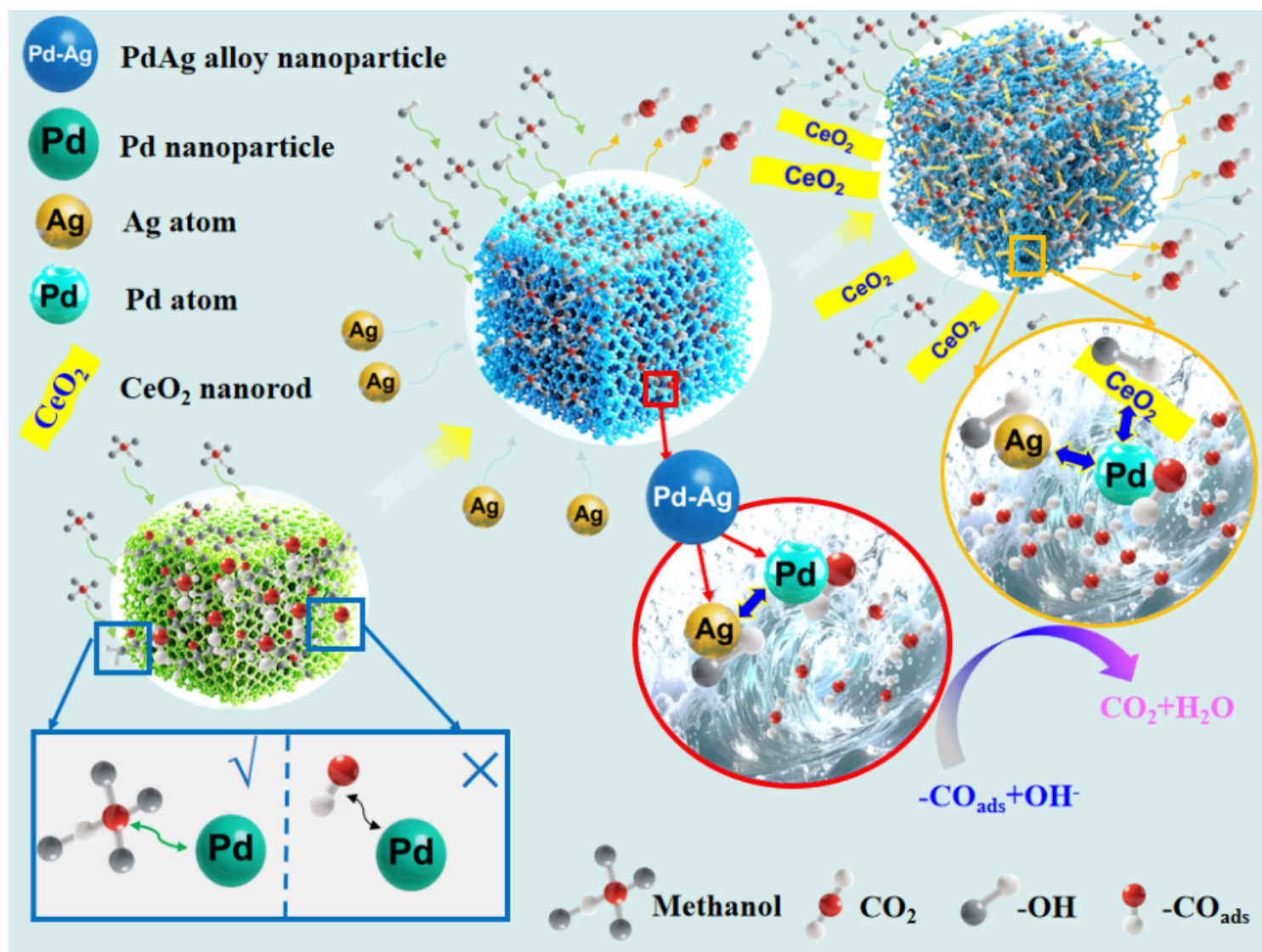


Figure 8

The mechanism diagram for the electrocatalytic oxidation of methanol by the nanoporous Pd-Ag/CeO₂ catalysts.

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