Ultrasonic-assisted synthesis of two dimensional coral-like Pd nanosheets supported on reduced graphene oxide for enhanced electrocatalytic performance

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ABSTRACT

Two dimensional (2D) Pd nanosheets supported on reduced graphene oxide (Pd/rGO) were prepared through a sonochemical routine induced by cetyltrimethylammonium bromide (CTAB). Coral-like porous Pd nanosheets (Pd/rGO-u) were obtained under the sonication condition (25 kHz, 600 W, ultrasonic transducer), while square Pd nanosheets (Pd/rGO-c) were produced via traditional chemical reduction. The size of Pd nanosheets of Pd/rGO-u and Pd/rGO-c are 69.7 nm and 59.7 nm, and the thickness are 4.6 nm and 4.4 nm, respectively. The carrier GO was proved to be partially reduced to rGO with good electrical conductivity and oxygen-containing groups facilitated a good dispersion of Pd nanosheets. The interaction between GO and CTAB made the alkyl chain assembles to a 2D lamella micelles which limit the growth of Pd atoms resulting in the formation of 2D nanosheets. A high ultrasonic power promotes the reduction and the formation of porous structure. Additionally, Pd/rGO-u exhibited a favorable electrocatalytic performance toward oxygen reduction reaction (ORR) in alkaline condition, which provided a potential synthetic strategy assisted by sonication for high-performance 2D materials.

1. Introduction

The crisis of global energy and environment due to the rapid consumption of fossil fuels have drawn growing concerns to renewable and eco-friendly energy sources [1,2]. Fuel cells are considered as a perfect alternative eco-friendly power source owing to the high efficiency [3–5]. Oxygen reduction reaction (ORR), as a fundamental step, plays a vital part in fuel cells [6–8]. Platinum is the most widely applied electrocatalyst in ORR owing to the unique intrinsic structure [9–11], but a high cost of scarcity and unsatisfied durability limit the commercial applications [12,13]. Recently, palladium catalysts have received much attention based on the structural analogy with Pt at a relatively lower cost and higher anti-CO poisoning ability [14,15].

With the aim of enhancing the utilization efficiency and catalytic performance of Pd catalyst, increasing specific surface area and construction of specific crystal facets exposed through structural-controlled synthesis are two common approaches [16,17]. According to previous reports, ultrapure Pd nanoparticles with large specific surface area [18] and Pd nanocrystals with specific morphology such as nanocubes [19], nanorods [20] and concave nano-structures [21] both have been reported to obtain superior catalytic performances. Two dimensional metal nanomaterials with large proportion of unsaturated atoms exposed on surface have gained increasing consideration owing to the excellent catalytic performance compared to bulk nanoscale counterparts [22–26].

Capping agents like polymers, surfactants, and organic ligands are basic components in shape-controlled preparation of metal NPs [27]. Surfactant as a soft template can self-assemble into mesoscopic phases with distinct dimensions [28,29]. Recently, some novel surfactants have been reported to facilitate the formation of Pd nanosheets. Xu et al. [30] prepared ultrathin 2D Pd nanosheets with specific facets exposed on surface by utilizing the lamellar mesophases of novel functional surfactants of C\textsubscript{22}N-COOH (Br'), docusalpyridinium bromide and docosalkyltrimethylammonium bromide. They found that long-chain surfactants (C > 20) with functional groups and halide counter ions are both very crucial in the formation of ultrathin Pd nanosheets. However, 2D assemblies of conventional surfactants like cetyltrimethylammonium bromide (CTAB) are not far effective for the
preparation of Pd nanosheets although they have been effectively introduced to the synthesis of nanocubes, nanorods and so on.

The performance of a catalyst is not only determined by the metal materials, carrier is also crucial for the catalyst design [31–33]. Graphene oxide (GO) has great hydrophilicity and dispersivity in water in terms of massive oxygen-containing functional groups (–OH, –COOH and epoxides, et al) decorated on the basal plane [34]. Metal nanoparticles (NPs) can be bound on these oxygen-containing functional groups to achieve a good dispersion on surface. Furthermore, the reduced graphene oxide (rGO) exhibits better electrical conductivity and electrochemical activity, which provides extensive possibility as an electrode material [35–38]. It has been reported that there are electrostatic interaction between CTAB and GO.

Ultrasonication has gained vast attention in nanoparticle syntheses and catalysts in recent years [39–41], which has successfully used in the fabrication of fuel cell materials [42,43]. Based on above, we designed a lamellar template between CTAB and GO to realize the formation and loading of 2D Pd nanosheets on GO at the same time by a facile sonochemical routine. The 2D coral-like Pd nanosheets supported on monolayered rGO (Pd/rGO-u) were synthesized and characterized. Meanwhile, we also prepared Pd/rGO utilizing traditional chemical reduction (Pd/rGO-c) to explore the formation process of porously coral-like Pd nanosheets and the effect of ultrasonification. A possible formation process was proposed according to a series of experiment results. The electrocatalytic performance of Pd/rGO was measured by ORR in alkaline medium and their activities were compared with commercial Pt/C.

2. Experimental

2.1. Materials

NaCl, PdCl₂, L-ascorbic acid (AA), KOH and CTAB were supplied from Sinopharm Chemical Reagent and used directly. Graphene oxide (monolayered) was bought from Nanjing XFNANO Material Technology Co. Ltd. Commercial Pt/C (40.0 wt%) was acquired from Johnson Matthey Catalysts.

2.2. Synthesis of Pd/rGO nanocatalysts

GO (26.67 mg) was dissolved in DI water (84 mL) under magnetic stirring by an ultrasonic irradiation (300 W, 25 kHz) for 30 min. 2 mL of CTAB (0.1 M) and 0.1 M AA (4 mL) were added to above clear brown solution. Then, 10 mL of Na₂PdCl₄ solution (0.01 M) was injected through a microinjection pump under ultrasonic irradiation (600 W, 25 kHz) at a speed of 5 mL/h at 30°C along with magnetic stirring. Once the Na₂PdCl₄ solution had been all injected, ultrasonic irradiation was turn off and the above mixture was placed only under magnetic stirring for 1 h at 30°C. The black product was separated via centrifugation from the colloidal solution and washed by DI water to obtain Pd/rGO-u. The synthesis of Pd/rGO-c was the same as the process above except no ultrasonic irradiation when injecting precursor solution.

2.3. Characterization

Pd/rGO were characterized by UV–vis spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), thermogravimetric analyses (TGA), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and X-ray photo-electron spectroscopy (XPS). Transmission electron microscopy (TEM) images were observed through a JEM-2100FX microscope working at 200 kV. Atomic force microscopy (AFM) images were captured by a Dimension Icon. Detailed information is presented in Supporting information.

2.4. Evaluation of electrocatalytic performance

The electrocatalytic properties of Pd/rGO and Pt/C were evaluated using a typical three-electrode system (detail in Supporting information). 10 μL of catalyst suspension containing 1 mg of catalysts and Nafton solution (0.5 wt%, 10 μL) in 1 mL ultrapure water dispersed by ultrasanification for 30 min was pipetted onto GCE and dried in air. Linear sweep voltammograms (LSV) were obtained in O₂-satured KOH (0.1 M, scan rate: 10 mV s⁻¹) at a rotation rate from 400 to 1600 rpm by rotating disk electrode (RDE). The durability of catalysts was measured through chronoamperometry at 0.3 V (vs. RHE) for 30000 s.

3. Results and discussion

3.1. Characterization results of Pd/rGO

To monitor reduction process, the time-course UV–vis absorption analysis were employed to track the reaction (Fig. 1). An intense absorption peak at 245 nm of AA (Fig. S1) appears. The peak intensity apparently decreases over time, which indicates that AA was consumed by reacting with Pd²⁺ and oxygen-containing groups of GO. Comparing the two different reduction process of ultrasound and conventional chemical method, the reduction rate under ultrasound (Fig. 1a) is obviously faster than conventional process (Fig. 1b). Ultrasonic irradiation and cavitation accelerate reaction rate by promoting mass transfer and...
reactant diffusion [44].

Fig. 2 reveals the crystallographic structures of Pd/rGO and GO by XRD analysis. The diffraction peak at 2θ degree of 9.8° corresponding to GO (001) [45] is not observed in Pd/rGO compared with GO, indicating the reduction of GO. The peaks at 2θ degree of 40.1°, 46.6°, 68.1°, and 82.0° are well-indexed to (111), (200), (220) and (311) planes of fcc Pd (JCPDS 65-2867) [46], which proves that Pd0 are successfully produced by the reduction of Pd2+ and loaded on the rGO surface.

TEM was employed to observe morphologies of both Pd/rGO (Fig. 3). Pd nanoparticles of Pd/rGO-u in Fig. 3(a) and (b) exhibit a porously coral-like nanosheets with an average size of 43.7 nm, and are uniformly dispersed on the surface of rGO. The continuous diffraction rings in Fig. 3(c) corresponding to (111), (200), (220) and (311) facets are consistent with XRD patterns in Fig. 2 [47]. The lattice fringe spacing in Fig. 3(d) are 2.23 Å and 1.94 Å, respectively, which are corresponded to (111) and (200) planes [30]. Pd nanosheets of Pd/rGO-c show a good dispersion on the rGO without noticeable aggregation with a lamella-like cubic structure (Fig. 3e). It is due to the abundant binding-sites of Pd2+ with oxygen-containing groups attached to GO surface. The interaction between PdNPs and oxygen-containing groups hinders the aggregation of PdNPs. The difference of Pd/rGO-c and Pd/rGO-u is because of the sonication effect, which alters the adsorption state of Br− on surface of PdNPs and subsequently affects the depositing sites of Pd atoms and crystal growth direction. To explore the influence of ultrasound on the formation process, we carried out relevant experiments and discussed the mechanism in-depth in section 3.2 and 3.3.

To further confirm the 2D structure and the dispersion of Pd nanosheets on rGO, AFM analysis are presented in Fig. 4. It indicates that Pd nanosheets are successfully loaded on rGO sheet with evenly dispersion in both of Pd/rGO. The Pd nanosheets of Pd/rGO-u and Pd/rGO-c are 69.7 nm and 59.7 nm in size, and the thickness are 4.6 nm and 4.4 nm, respectively. Combined TEM analysis in Fig. 3 reveals that both of the PdNPs are 2D Pd nanosheets. As for the rGO carrier, the monolayer thickness is about 0.7–1.0 nm [48]. However, the thickness of rGO in Pd/rGO-u and Pd/rGO-c are 1.5 nm and 1.2 nm, which suggests that there is a functionalized interaction between CTAB and GO. The ammonium ions with positively charge of CTAB interact with negatively charged GO through electrostatic interaction [49,50]. The alkyl chains of CTAB on GO surface lead to an increase thickness of carrier. The rGO-u is thicker than rGO-c because the collapse of cavitation bubbles caused by sonication generates shock waves leading to a weaker electrostatic interaction. Therefore, the alkyl chains bind less tightly to GO resulting in the increase of thickness. In addition, Pd nanosheets of Pd/rGO-u are also slightly thicker than that of Pd/rGO-c,
which is also attributed to the larger space between CTAB micelles and GO under ultrasound.

The changes of functional groups before and after Pd nanosheets loading on GO surface were analyzed by FT-IR shown in Fig. 5. The characteristic peaks for GO appear in all of the three samples. The peaks at wavenumbers (cm\(^{-1}\)) of 3264, 1716, 1606, 1362 and 1034 are corresponded to the stretching vibration of hydroxyl group of adsorbed water on GO, C=O, C-O, C-OH and C-O epoxy, respectively [51,52]. Comparing with GO, the peak intensities of –OH, C-O and C=O decrease in both of Pd/rGO, which suggests the decrease of oxygen-containing groups. The –OH and C=O peaks in Pd/rGO-u are weaker than that of Pd/rGO-c, proving the less amount of functional groups on GO surface under sonication. These groups may be decomposed by ultrasound down to organic radicals like phenols, acids and CO\(_2\) mediated by -OH radicals from water sonolysis due to acoustic cavitation [53,54]. However, the peaks at C=O and C-OH always exist, suggesting the incompletely reduction of GO. In addition, Pd/rGO-u and Pd/rGO-c show characteristic peaks of CTAB at 2918 cm\(^{-1}\) and 2848 cm\(^{-1}\) caused by the symmetric and antisymmetric stretching vibrations of CH\(_2\), respectively, and 963 cm\(^{-1}\) and 912 cm\(^{-1}\) caused by C-H out-plane bending vibration [55]. The peak appeared at 1463 cm\(^{-1}\) of both Pd/rGO is corresponding to C-H in-plane bending vibration, and the peak appeared at 719 cm\(^{-1}\) suggests that there are four or more CH\(_2\) groups in the compounds. It proves the functionalization of CTAB on GO through electrostatic interaction. The peak intensity of CTAB in Pd/rGO-u is weaker than that in Pd/rGO-c, suggesting a weaker interaction between CTAB and GO under sonication, which is consistent with AFM analysis about the thickness of rGO. Acoustic cavitation creates local high-energy through liquid jets with high velocity, shockwaves with high pressures and temperatures up to 5000 K [39,56], leading to a relatively weaker functionalization of CTAB.

Thermogravimetric analyses of Pd/rGO and GO performed at air atmosphere in the temperature range of 30-900\(^\circ\)C were shown in Fig. 6. For GO, the weight loss below 150\(^\circ\)C is the removal of adsorbed water because of the existence of oxygen-containing groups in large amounts. At 200\(^\circ\)C, the weight loss is 38%, which is on account of the oxygen-containing groups removing [57]. The weight loss between 450 and 550\(^\circ\)C is 43% because carbon layer of GO reacts with O\(_2\) in the air. After Pd loading, there are four stages of weight loss in both of Pd/rGO. Besides of the same three stages as GO mentioned above, the weight loss at 770\(^\circ\)C is due to thermal decomposition of PdO. Firstly, the weight loss of adsorbed water below 150\(^\circ\)C in both Pd/rGO decreases suggesting oxygen-containing groups are reduced by AA. Secondly, the weight loss temperature of Pd/rGO-c (150\(^\circ\)C) and Pd/rGO-u (160\(^\circ\)C) are both lower than GO (200\(^\circ\)C), while the weight loss of pure CTAB begins at 180\(^\circ\)C with a weight loss of 93% (Fig. S2 in Supporting information). It indicates the functionalization of CTAB on GO facilitates the removal of functional groups. And a lower weight loss temperature of Pd/rGO-c suggests a stronger interaction between CTAB and GO, which is in accordance with FT-IR analysis in Fig. 5. Moreover, a less weight loss of

![Fig. 4. AFM images of Pd/rGO-u (a) and Pd/rGO-c (b).](image1)

![Fig. 5. FT-IR analyses of Pd/rGO and GO.](image2)
The ratio of ID/IG is often employed to specify the defect degree [61]. The band is caused by the in-plane vibration of sp² graphitic C, and D band wavenumber of 1337.7 cm⁻¹ to Pd/rGO-c, and the D bands of Pd/rGO-u and Pd/rGO-c shift to high G band (1585 cm⁻¹) groups can be partially reduced by AA. The ID/IG of Pd/rGO-u is similar to GO aqueous solution under sonication) is 1.23 (Fig. S3), which increases when CTAB functionalized on GO. However, the ID/IG of both Pd/rGO-u and Pd/rGO-c are 45% and 27%, indicating the successful load of Pd sheets. The higher residual weight of Pd/rGO-u than Pd/rGO-c also suggests the reduction degree of GO under sonication is higher than that of chemical reduction. Thirdly, the weight loss temperature of carbon layer consumption in the air in Pd/rGO-c (480 ℃) is higher comparing with Pd/rGO-u and GO (450 ℃), which may be attributed to a more stable carbon layer caused by the stronger functionalization of CTAB. Additionally, the residual weights of Pd/rGO-u and Pd/rGO-c are 45% and 27%, indicating the successful load of Pd sheets. The higher residual weight of Pd/rGO-u than Pd/rGO-c indicates the higher reduction degree of Pd⁡²⁺ under sonication.

Raman spectroscopy is an informative technique for investigating disorder in carbon materials [58]. Two characteristic peaks of GO observed from the Raman spectrum shown in Fig. 7 are corresponding to G band (1585 cm⁻¹) and D band (1333 cm⁻¹), respectively [59]. G band is caused by the in-plane vibration of sp² graphitic C, and D band reflects the sp² defects and disorders [60]. Generally, the peak intensity ratio of I_D/I_G is often employed to specify the defect degree [61]. The value of I_D/I_G of the sample CTAB-GO obtained without AA (only added CTAB to GO aqueous solution under sonication) is 1.23 (Fig. S3), which is greater than that of GO (1.21). It indicates that the defect degree increases when CTAB functionalized on GO. However, the I_D/I_G of both Pd/rGO are less than GO, which signifies that the oxygen-contain groups can be partially reduced by AA. The I_D/I_G of Pd/rGO-u is similar to Pd/rGO-c, and the D bands of Pd/rGO-u and Pd/rGO-c shift to high wavenumber of 1337.7 cm⁻¹ and 1336.0 cm⁻¹ comparing with GO, respectively, which may be due to the load of Pd [62]. The Pd atoms may bond to defect sites or oxygen-containing groups on GO, leading to a structural diversification. More Pd atoms bonding on GO due to the higher reduction degree of Pd⁡²⁺ under sonication leads to a higher D band wavenumber of Pd/rGO-u.

XPS analysis were employed to investigate varied chemical states. As the full spectra shown in Fig. 8(a), besides C1s at 286.1 eV and O1s at 532.1 eV of GO [63], Pd3d and N1s also appear at 338.1 eV [64] and 402.1 eV [65], which proves the successful load of Pd and the functionalization of CTAB on GO. It is found that the O/C atomic ratio of Pd/rGO-u (0.33) and Pd/rGO-c (0.34) are both less than that of GO (0.50), which suggests GO is partially reduced to rGO by AA and the reduction degree assisted by sonication is slightly higher. Meantime, the N/C atomic ratio of Pd/rGO-u (0.040) and Pd/rGO-c (0.049) are greater than that of GO (0.019), proving the existence of CTAB and a stronger CTAB functionalization in Pd/rGO-c. Fig. 8(b), (c) and (e) show the C1s core level narrow-scan XPS peaks of GO, Pd/rGO-u and Pd/rGO-c, which appear 284.5 eV (C–C), 286.1 eV (C–O), 287.0 eV(C–N) and 288.4 eV (C=O) [58,66]. The intensities of C–O and C=O have an obvious decrease in both of Pd/rGO, which further verifies the reduction of oxygen-containing groups. An increase of C–N also further proves a stronger CTAB functionalization in Pd/rGO-c. The Pd3d XPS spectrum (Fig. 8d and f) presents two peaks of Pd3d⁵/₂ and Pd3d⁷/₂ at 335.9 eV and 340.9 eV, respectively [67]. Based on the peak areas of Pd²⁺ and Pd⁰, the reduction degrees are calculated to be 53% and 51% in Pd/rGO-u and Pd/rGO-c, which verifies that sonication promotes the reduction of Pd⁡²⁺ due to the acoustic cavitation.

3.2. Effect of sonication

To further explore the impact of sonication on structure of Pd/rGO-u, a series of samples at different ultrasonic power (300 W, 400 W, 500 W and 600 W) were synthesized. XRD analyses of these samples were presented in Fig. 9. The five diffraction peaks of metallic Pd are all observed, indicating Pd²⁺ are successfully reduced to Pd⁰. The diffraction peaks weaken at higher ultrasonic power, which suggests the degree of crystallinity decreased. The mechanism of sonication in the solvent is based on acoustic cavitation, which concentrates sound field energy and releases rapidly [68]. When the cavitation collapse occurs, a high temperature and a high pressure can be generated instantaneously in a very small space around the cavitation bubble, accompanied by a strong shock wave and a high-speed jet flow. The maximum radius of cavitation bubbles increases when ultrasonic power increased, resulting in a decrease of bubble number. The impact force generated during cavitation collapse increases gradually, which makes the intact crystal surface suffer from concave corrosion [69], resulting in the decrease of crystallinity of Pd. Additionally, high-speed micro-jet can cause material surface damage, and cavitation pit is the most typical damage feature [70]. The damages may also cause a decreased crystallinity of Pd nanoparticles.

The morphology evolution of Pd/rGO-u affected by ultrasonic power was shown in Fig. 10. The amount of coral-like Pd nanosheets increases with the increase of ultrasonic power, which indicated a greater ultrasonic power facilitates the formation of porous structure. The reasons for this phenomenon are two-fold. On the one hand, the absorption of Br⁻ on Pd(100) facets is weakened when ultrasonic power is increased. The deposition and growth direction of the newly reduced Pd atoms are not fixed, which is conducive to the formation of coral-like structure. On the other hand, the impact force produced from cavitation is gradually increased with the increase of ultrasonic power, leading to a concave corrosion on the surface, and then the deposition and growth of Pd atoms are more likely to form dendritic structure. Additionally, the particle size of Pd nanosheets increases gradually, which may be due to the acoustic cavitation. The cavitation bubble is flat on the side near the surface of Pd nanosheets under a greater ultrasonic power, so that when cavitation collapses, the liquid directed at the crystal surface

![Fig. 7. Raman spectra of Pd/rGO and GO.](image-url)
is conducive to the movement of Pd atoms to be crystallized along the dendrite growth direction, resulting in the particle size increase.

Fig. 11 shows the TGA of Pd/rGO-u synthesized at different ultrasonic power. The weight loss of the removal of oxygen-containing functional groups at 150-200°C decreases with the ultrasonic power increased, which suggests that a higher power benefits the decomposition of functional groups of GO. The residual weight is greater at a higher ultrasonic power, proving that a higher power also increases the reduction degree of Pd²⁺. Cavitation creates hot spots at GO surface and organic radicals can be generated, promoting the reduction of Pd²⁺ [54]. The value of $I_d/I_g$ in Raman spectra in Fig. 12 decreases when the ultrasonic power increased, which further confirms a decrease of structural diversity and a high reduction degree of GO at high ultrasonic power.

Fig. 8. (a) XPS full spectra of Pd/rGO and GO; (b) C1s narrow-scan XPS spectrum of GO; (c) (d) C1s and Pd3d narrow-scan XPS spectra of Pd/rGO-u; (e) (f) C1s and Pd3d narrow-scan XPS spectra of Pd/rGO-c.
3.3. Formation mechanism of coral-like Pd/rGO

A train of experiments under sonication were performed to get deep insight into the possible formation mechanism of Pd/rGO-u, and TEM images of samples synthesized under different conditions were shown in Fig. 13. Spherical Pd nanoparticles with severe agglomeration are obtained without addition of CTAB when other conditions are maintained (Fig. 13a). In contrast, Pd nanosheets both formed when CTAB was introduced (Fig. 3), which suggests CTAB has a crucial role in the forming process of 2D nanosheets. Based on this, the effect of different concentration of CTAB on morphology are investigated and shown in Fig. 13(b), (c) and (d). There are still some agglomerated particles at a low concentration of CTAB (Fig. 13b) and the proportion of coral-like Pd nanosheets increases with the increased concentration of CTAB (Fig. 13c). However, when CTAB concentration increased to $n_{\text{CTAB}}/n_{\text{Pd}} = 8:1$, uneven particle size of Pd nanosheets are observed, which may be due to the uneven distribution of CTAB micelles. To further explore whether the alkyl chain is the reason for the formation of 2D nanosheets or the capping effect of Br ions, we changed CTAB to the same concentration of KBr while all other conditions unchanged (Fig. 13e). The 2D Pd nanosheets are not formed, indicating the micelles assembled by alkyl chain in CTAB is the determinant for the construct of 2D structures. Moreover, the 2D structure can't form when without the presence of carrier GO, and an apparently agglomeration is observed in Fig. 13f. It illustrates that the oxygen-containing groups promotes a good dispersion of Pd nanosheets, and the interaction between GO and CTAB micelles is the root cause of the formation of 2D nanosheets. Scheme 1 demonstrates a possible formation mechanism.

The charge on the GO surface appears negative (-52.90 ± 1.73 mV), because massive oxygen-containing groups exist [71]. The ammonium ions in CTAB with positively charge can interact electrostatically with the negatively charged GO surface, and the alkyl chain assembles to a 2D lamella micelles which limit the growth of Pd atoms for the formation of 2D nanosheets [72]. The coral-like structure has been produced at 0.5 h, and most of the particles are small. With the reaction time prolonging, Pd$^{2+}$ are gradually reduced and Pd$^0$ atoms are deposited on the coral-like seeds, which leads to larger coral-like

![Fig. 9. XRD patterns of Pd/rGO-u synthesized at different ultrasonic power.](image)

![Fig. 10. TEM images of Pd/rGO-u synthesized at different ultrasonic power. (a) 300 W; (b) 400 W; (c) 500 W and (d) 600 W.](image)
structure nanoparticles (Fig. S4). Furthermore, Br⁻ is a well-known capping agent in structure-controlled synthesis of Pd nanoparticles [73]. It is able to specifically absorb onto Pd (100) facets, thereby slowing down the growth rate along ⟨100⟩ of reduced Pd atoms and forming cubic structure enclosed by (100) facets [74]. Therefore, square Pd nanosheets are formed in Pd/rGO-c prepared by chemical reduction without sonication. As for the Pd/rGO-u synthesized assisted by sonication, the possible reason for the formation of coral-like nanosheets may be attributed to the effect of cavitation. It concentrates the sound field energy and releases rapidly, which may break the stable adsorption of Br⁻ ions on (100) plane and original slow growth along ⟨100⟩ weakens. From HRTEM image of Pd/rGO-u in Fig. 3(c), the spacing of 1.94 Å and 2.23 Å also confirms that the (110) facets exposed on the surface of Pd nanosheets besides (100) facets. In addition, the impact force generated from the cavitation collapse also promotes a concave corrosion on the surface of the crystal, leading to a deposition of dendrite of newly reduced Pd atoms and growing into a coral-like porous structure gradually. Compared with the traditional chemical method, the high-energy environment generated by cavitation changed the adsorption state of Br⁻, resulting in the final morphology difference of products.

3.4. ORR catalytic performance of Pd/rGO

Since the 2D coral-like structure has abundant active sites on account of the large specific surface area, an enhanced performance of Pd/rGO-u is worth expected in catalyzing ORR. The performance of commercial Pt/C (40 wt%) and Pd/rGO-c were measured as well for comparison. Fig. 15(a) and (b) shows the LSV curves of Pd/rGO acquired in oxygen-saturated KOH at a series of rotation rates. To investigate ORR kinetics, the Koutecky-Levich (K-L) equation is employed for calculating the number of electrons transferred per O₂ molecule n (detail in Supporting information). Fig. 14(c) and (d) demonstrate K-L plot fittings at different potentials. The value of n of Pd/rGO-u is calculated to be 3.8, revealing a four-electron pathway on Pd/rGO-u similar as commercial Pt/C. However, the n of Pd/rGO-c is 2.6, which reveals a complex pathway with H₂O₂ produced to some extent and a lower activity in ORR than Pd/rGO-u.

To comparing the electrocatalytic activity, Fig. 15(a) shows LSV curves of three catalysts recorded at room temperature (ω = 1600 rpm). Pd/rGO-u exhibits a similar onset potential to Pd/rGO-c, but the half-wave potential, which is often employed to estimate electrocatalytic activity, shows a positive shift. Meantime, the diffusion current of Pd/rGO-u is much higher than Pd/rGO-c, indicating a more superior electrocatalytic activity of Pd/rGO-u toward ORR in alkaline condition. Its better electrocatalytic activity may be due to a larger surface area and rich active sites of porous Pd/rGO-u than Pd/rGO-c, but a gap still exists comparing with commercial Pt/C. Tafel plots are constructed in Fig. 15(b) based on the LSV data. The value of Tafel slopes of Pd/rGO-u and Pt/C are −65 mV and −61 mV, which are close to the typical value for nanostructured Pt catalysts. However, the Tafel slope of Pd/rGO-c (−85 mV) suggests a complex mechanism. Finally, the stabilities of catalysts are evaluated by chronoamperometric method (Fig. 15c). The current loss of Pd/rGO-u and Pd/rGO-c are 63% and 69% of the initial at 20000 s respectively, while that of Pt/C is 77%. It
indicates that Pd/rGO shows a good durability, but it is still worth further optimization compared to Pt/C.

4. Conclusion

In summary, the coral-like Pd nanosheets Pd/rGO-u were successfully prepared through a facile sonochemical method. The carrier GO was partially reduced to rGO and functionalized by CTAB. The reduction degree of Pd\(^{2+}\) increases with the ultrasonic power increasing. The interaction of CTAB with GO promotes the formation of 2D Pd nanosheets, and the impact force generated by the acoustic cavitation of ultrasound facilitates the generation of coral-like structures. Compared with Pd/rGO-c prepared by conventional chemical methods, Pd/rGO-u shows a better catalytic performance in ORR reaction, and follows a four-electron reaction mechanism. This article provides a new idea for synthesizing 2D metal composite materials, and is expected to expand to a wider range of applications.

CRediT authorship contribution statement

Zelin Cui: Methodology, Investigation, Validation, Formal analysis, Writing - original draft. Xuefeng Bai: Conceptualization, Methodology,
**Scheme 1.** Formation mechanism of Pd/rGO.

Fig. 14. LSV curves and K-L plots of Pd/rGO-u (a)(c) and Pd/rGO-c (b)(d) at different potentials in oxygen-saturated 0.1 M KOH (scanning rate: 10 mV s$^{-1}$).
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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2020.105309.

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Z. Cui and X. Bai

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