Facile Synthesis of Catalytically Active Platinum Nanosponges, Nanonetworks, and Nanodendrites

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Abstract: In this paper, we report a simple approach for the preparation of various porous Pt nanomaterials (NMs) in aqueous solution. Employing different temperatures and concentrations of sodium dodecyl sulfate (SDS), we obtained Pt nanosponges, Pt nanonetworks, and Pt nanodendrites from the reduction of PtCl$_6^{2-}$ ions via galvanic replacement reactions with Te nanowires (length: 879 nm; diameter: 19 nm). At ambient temperature, Pt nanosponges and Pt nanodendrites formed selectively in the presence of SDS at concentrations of < 10 mM and > 50 mM, respectively. At elevated reaction temperatures, we obtained Pt nanonetworks and Pt nanodendrites in the presence of SDS at concentrations of < 10 mM and > 50 mM, respectively. Transmission electron microscopy images revealed that these Pt NMs were all composed of one dimensional Pt nanostructures having widths of 3.0 ± 1.0 nm and lengths of 17.0 ± 4.8 nm. Cyclic voltammetry data indicated that the as-prepared Pt nanonetworks, nanosponges, and nanodendrites possessed large electrochemically active surface areas (77.0, 70.4, and 41.4 m$^2$/g, respectively). For the electrocatalytic oxidation of methanol, the ratio of the forward oxidation peak current ($I_f$) to the backward peak current ($I_b$) of the Pt nanodendrites, nanosponges, and nanonetworks were all high ($I_f/I_b$ = 2.88, 2.66, and 2.16, respectively). These three NMs exhibit greater electrocatalytic activities and excellent tolerance toward poisoning species for the oxidation of methanol when compared with the performance of standard Pt NMs.

Keywords: electrocatalysis · nanomaterials · platinum · sodium dodecyl sulfate · tellurium

Introduction

The preparation of inexpensive and efficient electrocatalytic materials for the reduction of oxygen (cathode) and the oxidation of methanol (anode) in fuel cells is currently an active research area. Nanomaterials (NMs) are more attractive than their bulk counterparts for use as catalytic materials in fuel cells because of their greater surface areas and higher catalytic activities.[1,2] In fuel cells, NMs are commonly dispersed on carbon supports to provide high electrical conductivity and acceptable chemical stability at low cost.[3-6] Nevertheless, carbon-supported nanocatalysts usually suffer from problems associated with poor loading, low dispersion, easy exfoliation, and aggregation.[7,8] To overcome some of the problems, carbon nanotubes (CNTs) have been used as supporting materials that possess large surface areas, high stability, and good conductivity.[9-11] To provide effective catalytic activity, it is necessary for these CNTs to be of high purity and possess functionalized surfaces, which makes them difficult to prepare and expensive to purchase. Thus, the preparation of cost-effective and highly-active nanocatalysts for fuel cells remains a considerable challenge.

Pt-based NMs are at present the most effective catalysts for fuel cells, mainly because of their high stability and long lifetimes,[12-17] but they suffer from the drawback of being highly expensive. To lower the cost of catalysts, several approaches toward the preparation of Pt-based NMs having high catalytic activity and large surface areas have been demonstrated. Pt nanowires,[18] multipods,[19] cubes, cuboctahedrons, and octahedrons[20] prepared from H$_2$PtCl$_6$ using polyol processes all provide greater catalytic activities relative to that of spherical Pt nanoparticles (NPs), mainly because of their high-index surfaces and abundances of corner and edge sites.[21-23] Alternatively, several porous Pt NMs, which greatly reduce the amount of Pt required, have been
synthesized and applied to electrocatalytic applications.\textsuperscript{[24–28]} Because of their high surface areas and great number of absorption sites, porous Pt NMs are suitable for O\textsubscript{2} reduction in MeOH fuel cells and hydrogen fuel cells.\textsuperscript{[29,30]} Recently, we prepared Te nanowires (NWs) and used them in conjunction with Au\textsuperscript{3+} ions to fabricate Au-Te nanodumbbells, nanopeapods, and Au pearl-necklace nanomaterials at room temperature.\textsuperscript{[31,32]} In addition, Te NWs are useful templates and reducing agents for the preparation of a range of other NMs through galvanic reactions with other metal ions. For example, Xie and co-workers demonstrated that Pt\textsuperscript{4+} ions efficiently oxidize Te NWs in the presence of polyvinylpyrrolidone (PVP), allowing the preparation of Pt NPs on the surfaces of the Te NWs.\textsuperscript{[33]} Because of the formation of a layer of Pt NPs on the Te NWs, it is difficult to prepare single-component Pt NMs using this route.\textsuperscript{[34]}

In this paper, we prepared three different shapes of Pt NMs (nanosponges, nanonetworks, and nanodendrites) from PtCl\textsubscript{6}\textsuperscript{2-} ions in the presence of sodium dodecyl sulfate (SDS) and Te NWs. We have carefully investigated the roles played by the reaction time and temperature, SDS, Te-to-PtCl\textsubscript{6}\textsuperscript{2-} molar ratio, solvent, and the size of the Te NWs on the formation of these variously shaped Pt NMs. Based on our experimental results, we propose possible mechanisms for the formation of these Pt NMs. In addition, we compare the electrocatalytic properties—determined through conducting cyclic voltammetry (CV) measurements—of these variously shaped Pt NMs with respect to their electrochemically active surface areas (EASAs) and electrocatalytic performance in MeOH oxidation reactions.

**Results and Discussion**

**Growth process and formation mechanism of Pt nanosponges:** The transmission electron microscopy (TEM) image in Figure 1A reveals that the Pt nanosponges that we prepared from PtCl\textsubscript{6}\textsuperscript{2-} and Te NWs in the presence of 10 mM SDS over a reaction time of 6 h had sizes ranging from 20 to 60 nm (average: 37.4 ± 5.7 nm). The enlarged image in the inset reveals that the Pt nanosponges were formed through the assembly of one dimensional (1D) Pt nanostructures having diameters of 2–5 nm and lengths of 10–20 nm. The powder XRD pattern (Figure 1B) displays broad peaks for the (111), (200), (220), and (311) lattice planes of the Pt nanosponges, revealing that they comprised face-centered cubic (fcc) Pt crystals; the broadness of these peaks was due to the sample’s nanoscale structural features. The characteristic diffraction peaks of trigonal Te are absent in this pattern. The EDX spectrum of the Pt nanosponges in Figure 1C confirms that the Pt nanosponges were composed purely of Pt atoms, i.e., no Te atoms were present.

To determine the growth mechanism of the Pt nanosponges, we recorded TEM images over a period of 60 min. Figure 2A reveals that the surface of the Te NWs was smooth at a reaction time of 5 min, suggesting that Pt NPs had yet to form on the Te NW surfaces. When the reaction time was 30 min, many ≈3 nm Pt NPs were present on the Te NW surfaces (Figure 2B), having formed through galvanic replacement reactions between Te and PtCl\textsubscript{6}\textsuperscript{2-} ions [Eq. (1)]:

\[
\text{Te} + 6\text{OH}^- + \text{PtCl}_6^{2-} \rightarrow \text{TeO}_3^{2-} + \text{Pt} + 6\text{Cl}^- + 3\text{H}_2\text{O} \quad (1)
\]

After a reaction time of 60 min, we found that sponge-like nanostructures (nanosponges) that have an average diameter of 31 nm were formed on the Te NW surfaces (Figure 2C). In addition to those formed on the Te NW surfaces, some other Pt nanosponges were present in the bulk solution. Figure 2D displays a high-resolution TEM (HRTEM)
image of a Pt nanosponge; the interplanar spacing of 0.226 nm corresponds to the (111) lattice planes of an fcc Pt structure. Based on the images in Figure 2, we suggest that the Pt NPs that formed on the Te NW surfaces acted as seeds for the preparation of 1D Pt nanostructures. As the reaction continued, the Pt nanosponges grew bigger through the assembly of 1D Pt nanostructures. Because no small Pt NPs were present in the solution when the reaction time was greater than 6 h, we cannot rule out that their dissolution occurred through Ostwald ripening. After a reaction time of 6 h, all of the Te NWs had disappeared (Figure 1A). Because Pt-Te NWs form in its absence, it is evident that SDS plays an important role during the formation of the Pt nanosponges. Indeed, SDS assists the formation of several types of Pt NMs. We note that the presence of SDS was essential to stabilize the Te NWs and the Pt nanosponges: for example, the Te NWs were agglomerated when the SDS concentration was less than 10 mM.

Impact of Te NW and PtCl₆²⁻ concentration: We investigated the impact of the concentration of PtCl₆²⁻ ions on the preparation of Pt NMs at a constant concentration of Te NWs (1.0 mM in terms of Te atoms). When the PtCl₆²⁻ concentration was 0.1 mM, we observed that spherical Pt NPs formed on the surface of the Te NWs. These structures were similar to those that formed during the early growth stages of the Pt nanosponges (Figure 2B). At 0.2 mM PtCl₆²⁻ ions, larger and more-spherical Pt NPs formed on the Te NWs, in turn providing core-shell Te-Pt NMs (Figure 3A) having structures similar to those prepared in the presence of PVP. When we increased the concentration of PtCl₆²⁻ ions to 0.4 mM, we obtained sponge-like nanostructures (Figure 3B). More sponge-like Pt nanostructures were prepared when the concentration of added PtCl₆²⁻ ions was greater than 0.6 mM (Figure 3C). EDX data suggested that some Te was present in the sponge-like Pt nanostructures. These results, along with that depicted in Figure 1A, confirmed that the stoichiometry of PtCl₆²⁻ to Te was 1:1.

We then tested the impact of the concentration of Te NWs on the preparation of Pt NMs at a constant concentration of PtCl₆²⁻ ions (1 mM). When the concentration was 0.2 mM (in terms of Te atoms), Pt NPs were deposited on the Te NW surfaces (Figure 3D). At a concentration of 0.4 mM, more Pt NPs aggregated to form larger spheres on the Te NWs (Figure 3E). Some Te NWs still existed when the concentration was 0.6 mM (Figure 3F), but there were no Te NWs when the concentration was 1.0 mM (Figure 1A). These findings confirm that the stoichiometry of the reaction between Te and PtCl₆²⁻ was 1:1 again, as predicted by Equation (1). Because we used different amounts of Te NWs in each case, differential seeding and growth rates had some effect on the sizes and shapes of the Pt NMs that formed. At low Te concentration (<0.2 mM), spherical Pt NPs were formed (Figure 3D); anisotropic Pt nanostructures were formed at higher Te concentration. The inset to
Figure 3E clearly displays that short 1D Pt nanostructures were formed at a concentration of 0.4 mM, quite different from the spherical NPs that formed at a concentration of 0.2 mM (inset to Figure 3D). The average length of the 1D Pt nanostructures and the number ratio of 1D nanostructures to spherical NPs both increased upon increasing the Te concentration from 0.4 to 0.6 mM (inset to Figure 3F).

The effect of the size of the Te NWs on the preparation of Pt NMs was also observed. Figure 4A and B reveal that Pt nanosponges were formed when using two shorter-length (251 and 595 nm) Te NWs, which are displayed in the insets to Figure 4A and B, respectively. From these two TEM images and the one presented in Figure 1A, we determined that using the 251, 595, and 879 nm Te NWs resulted in Pt nanosponges having dimensions of 20.2, 26.4, and 37.4 nm, respectively. Thus, the size of Pt nanosponges increased upon increasing the length of the Te NWs, mainly because a greater number of SDS molecules and micelles were present on the surfaces of the longer Te NWs and also possibly because more Te atoms were available in the longer Te NWs, thereby favoring the growth process.

**Impact of SDS and reaction temperature:** The TEM images in Figure 1A and Figure 5A and B reveal different shapes of the Pt NMs prepared from PtCl$_6^{2-}$/CO ions and 879 nm-long Te NWs in the presence of 10 mM SDS at various temperatures. The reaction rates were faster at higher temperatures: the reactions performed at 30, 60, and 90 ºC were complete after 6, 3, and 1 h, respectively. Figure 1A reveals that we obtained Pt nanosponges at ambient temperature (30 ºC). At 60 ºC, we obtained sponge-like Pt nanostructures comprising a looser assembly of 1D Pt nanostructures at ambient temperature (30 ºC). At 60 ºC, we obtained sponge-like Pt nanostructures comprising a looser assembly of 1D Pt nanostructures (Figure 5A). In contrast, Pt nanonetworks were formed at 90 ºC (Figure 5B). In each of the three TEM images, we observed that the Pt NMs all contained similarly sized 1D Pt nanostructures: widths of 3.0 ± 1.0 nm and lengths of 17.0 ± 4.8 nm. Upon increasing temperature, the stability of SDS micelles decreases and the collision rate among 1D Pt nanostructures increases. Thus, irregular Pt NMs were formed at higher temperature.

To support the role of SDS in controlling the formation of Pt nanosponges, we conducted a similar reaction at 90 ºC in the absence of SDS and obtained aggregates of spherical Pt NPs (4.2 ± 1.0 nm in diameter). To further demonstrate the role that SDS plays in determining the formation of Pt NMs, we conducted similar reactions in the presence of 50 mM SDS at 30, 60, and 90 ºC. At the three different temperatures, SDS micelles were all formed, which would confine the 1D Pt nanostructures to form Pt nanosponges. Figure 5C–E reveal that assemblies of 1D Pt nanostructures did indeed form at each of these three temperatures, but, surprisingly, we obtained only dendrite-like Pt nanostructures (Pt nanodendrites) instead of the expected Pt nanosponges. Upon increasing the temperature from 30 to 60 ºC, the dendrite-like nanostructures (26.2 ± 4.2 nm in diameter) become more characteristic (Figure 5D). At 90 ºC, larger Pt nanodendrites (33.2 ± 7.6 nm) were formed (Figure 5E). In addition to the increased size of the Pt nanodendrites, the number of 1D Pt nanostructures in each Pt nanodendrite increased upon increasing the reaction temperature from 60 to 90 ºC, mainly because of faster collision rates among the 1D Pt nanostructures at higher temperature. From closer scrutiny of the TEM images in Figure 5C–E, we found that the lengths of the 1D Pt nanostructures increased (from 10.2
to 14.2 nm) upon increasing the temperature, mainly because the growth rate dominated at higher temperature, leading to the formation of larger-sized Pt nanodendrites. We further verified the role that SDS played in assisting the formation of the Pt nanosponges by conducting similar experiments in 10 mM SDS aqueous solutions containing 30 or 50% cyclohexane. At 30% cyclohexane, we obtained Pt nanosponges possessing looser structures (Figure 6A). Network-like Pt nanostructures become more apparent at 50% cyclohexane, mainly because the SDS micelles were not present (Figure 6B). The presence of organic molecules affects the size, shape, and aggregation of SDS micelles,[36] which in turn control the formation of Pt NMs.

**Electrocatalytic analysis**: We calculated the EASA of each sample using Equation (2):[37,38]

\[
\text{EASA} = \frac{Q_H}{(0.21 \times \text{[Pt]})} 
\]

In which \([\text{Pt}]\) represents the platinum loading (mg cm\(^{-2}\)) in the electrode and \(Q_H\) the amount of charge exchanged during the adsorption of hydrogen atoms on Pt (mC cm\(^{-2}\)); the correlation constant of 0.21 (mC cm\(^{-2}\)) represents the charge required to oxidize a monolayer of H\(_2\) on polycrystalline Pt electrodes. The values of \(Q_H\) measured under the electroadsoption curves (Figure 7) for hydrogen on the Pt nanonetwork-, nanosponge-, and nanodendrite-coated electrodes were 27.5, 20.7, and 13.9 mC cm\(^{-2}\), respectively; ICP-MS analysis revealed that the Pt NM loadings were 0.14, 0.17, and 0.16 mg cm\(^{-2}\), respectively. Incorporating these values into Equation (2), we calculated the EASA values of the Pt nanonetwork-, nanosponge-, and nanodendrite-coated electrodes to be 77.0, 70.4, and 41.4 m\(^2\) g\(^{-1}\), respectively. These EASA values are larger than that (38 m\(^2\) g\(^{-1}\)) of commercially available Pt black (Johnson Matthey).[39] The main reason for the EASA of the as-prepared Pt nanonetworks being the highest of our three Pt NMs is that their 2D-like structures result in shorter diffusion distances relative to those of the 3D-like structures of the as-prepared Pt nanosponges/nanodendrites. As a result of these shorter diffusion distances, the resistance to the flow of liquid and gas through the 1D Pt nanostructures is shorter in the Pt nanonetworks. Although some recently prepared Pt NMs (mesoporous Pt, Pt nanoflowers, and porous Pt NP froth) have comparable or higher EASAs (74, 99, and 168 m\(^2\) g\(^{-1}\), respectively) than those of our Pt NMs,[15,39,40] their preparation in high purity, with narrow size distributions, and on large scales is not easy.

We conducted CV measurements to compare the electrocatalytic activity of our as-prepared Pt nanosponges, nanonetworks, and nanodendrites (using the samples employed to obtain Figure 1A, Figure 5B and E, respectively) for the oxidation of MeOH. Figure 8A displays the CV curves of carbon electrodes coated with these three Pt NMs in N\(_2\)-saturated H\(_2\)SO\(_4\) (0.5 M) containing MeOH (1.0 M), recorded at a scan rate of 50 mVs\(^{-1}\). The electrode coated with the Pt nanonetworks exhibited a peak current density (124.7 mA mg\(^{-1}\)) higher than those of the electrodes coated with the Pt nanosponges (57 mA mg\(^{-1}\)) or the Pt nanoden-
in N2-saturated 0.5 M H2SO4, we performed chronoamperometry measurements to evaluate the long-term performance of our Pt NM-coated electrodes. The initial current density of Pt nanosponges was smaller, which in turn hindered the diffusion of fresh MeOH. The Pt nanodendrites, the electrode coated with the Pt nanosponges, and the Pt nanonetwork-coated electrodes exhibited I/I0 ratios of 2.88, 2.66, and 2.18, respectively. These values are all greater than those of other reported Pt NMs: electrodes coated with E-TEK catalyst, multi-walled CNTs containing flower-like Pt clusters (10 nm), and aligned arrays of CNTs containing Pt NPs exhibit I/I0 ratios of 0.88, 2.0, and 1.83, respectively. The I/I0 ratios of our Pt nanosponge- and nanodendrite-coated electrodes decreased by less than 10% after 500 scans, whereas that of our Pt nanonetwork-coated electrode decreased by 20%. Based on the results, the electrocatalytic performance for the oxidation of MeOH using electrodes coated with the three Pt NMs follows the order Pt nanodendrites > Pt nanosponges > Pt nanonetworks. We performed chronoamperometry measurements to evaluate the long-term performance of our Pt NM-coated electrodes in N2-saturated 0.5 M H2SO4 containing MeOH (1.0 M) at a fixed potential of 0.6 V (Figure 8B). All three electrodes exhibited current decays during the initial period because of the formation of intermediate species (e.g., COads), similar to the observations previously reported for traditional Pt and PtRu catalysts. The decrease in the initial current density of the three Pt NM-coated electrodes followed the order Pt nanonetworks > Pt nanosponges > Pt nanodendrites. We suggest that this behavior is related mainly to the decreasing size of the EASA. On the other hand, the current decay rates of the three Pt NM-coated electrodes followed the order Pt nanonetworks > Pt nanosponges > Pt nanodendrites. Relative to the electrode coated with the Pt nanodendrites, the electrode coated with the Pt nanosponges provided a higher initial current density, but a faster current decay rate, mainly because the pore size of the Pt nanosponges was smaller, which in turn hindered the diffusion of fresh MeOH into the electrode surface. In conclusion, we suggest that the electrocatalytic performance for the oxidation of MeOH mediated by the three coated electrodes follows the order Pt nanonetworks > Pt nanosponges > Pt nanodendrites.

Conclusions

We have developed a facile approach—galvanic replacement reactions between Te NWs and PtCl6 2− ions in the presence of SDS—for the selective preparation of Pt nanosponges, nanonetworks, and nanodendrites by simply controlling the reaction temperature and SDS concentration. Based on our findings, we suggest that the presence of SDS controlled the formation of the spherical assemblies, whereas the Te-to-PtCl6 2− molar ratio determined the average length of the Pt NMs. Although all three of these Pt NMs have high electrocatalytic activities for the efficient oxidation of MeOH, the Pt nanonetwork exhibited the best performance, primarily because of its larger active surface area. Because of their low cost of preparation, high purity, good stability, and excellent electrocatalytic activities, we believe that our as-prepared Pt NMs will be effective catalysts for use in fuel cells. To further improve the catalytic activity, in a future study we will prepare Pt-M (M = Pd, Ru, and Au) nanocomposites based on the synthetic strategy proposed herein.

Experimental Section

Materials: SDS (≥98.5%), K2PtCl6, hydrazine monohydrate (80%), and cyclohexane (≥99%), and MeOH (≥99.8%) were obtained from Acros. Tellurium dioxide (99.9%) and hydrazine monohydrate (80%) were purchased from Showa. Nafion 117 (5%) was obtained from Fluka. Deionized water (18.2 MΩ cm) from a Milli-Q ultrapure system was used throughout this study.

Synthesis of Te NWs: Three differently sized Te NWs (diameters/lengths: 8/251, 15/595, and 19/879 nm, respectively) were prepared through the reduction of TeO2 with hydrazine and through the deposition of Te atoms (either oxidized from telluride ions or dissolved from amorphous Te NPs) onto trigonal Te nanocrystallites. Typically, hydrazine (10 mL) was added slowly to a beaker containing TeO2 (0.016 g) at room temperature under constant magnetic stirring. The solution changed color from colorless to blue after 40 min, indicating the formation of Te NWs. Reactions times of 40, 80, and 120 min were required for the preparations of the 251, 595, and 879 nm-long NWs, respectively. To terminate the reactions, the solutions were diluted 10-fold with 10 mM SDS, which also stabilized the as-prepared Te NWs.

Preparation of Pt NMs: Prior to their use in the preparation of Pt NMs, the as-prepared Te NWs were subjected to a centrifugation/wash cycle to remove most of the matrix (e.g., hydrazine). In a typical process for the synthesis of Pt nanosponges, the Te NW pellet was re-dispersed in 10 mM SDS. After 10 min, K2PtCl6 (final concentration: 1 mM) was added to the mixture, which was then left at ambient temperature for 6 h. Heating the mixture at 90°C for 1 h led to the synthesis of Pt nanonetworks. For the synthesis of Pt nanodendrites, the Te NWs pellets were re-dispersed in 50 mM SDS and heated at 90°C for 1 h or at ambient temperature for 6 h.

Characterization: JEOL JSM-1230 and FEI Tecnai-G2-F20 transmission electron microscopes (TEMs) were used to measure the sizes and shapes of the prepared Te NWs and Pt NMs. Prior to TEM measurement, the synthesized NMs were subjected to a centrifugation/wash cycle to remove most of the matrix. The redispersed NMs were then placed on formvar/carbon film Cu grids (200 mesh; Agar Scientific) and dried at room temperature. An EDAX energy dispersive X-ray (EDX) system was used to confirm the composition of the as-prepared Pt NMs. For X-ray diffraction (XRD) measurements were performed using a PANalytical X’Pert PRO diffractometer and CuKα radiation (λ = 0.15418 nm); the samples were prepared on glass substrates. Inductively coupled plasma mass spectrometry (ICP-MS) using an Elan 6000 instrument (Perkin-Elmer) revealed that the concentration of Pt nanosponges, nanonetworks, and nanodendrites in the redispersed solutions were 0.1, 0.12, and 0.11 μg mL−1, respectively.

Electrode modification and electrocatalytic analysis: Prior to electrocatalytic analysis, the as-prepared Pt NMs (100 mM) were subjected to two centrifugation/wash cycles: centrifugation at 12,000 rpm for 10 min and re-dispersion of the pellet with deionized water (10 mL). Each of the solutions was used to prepare Pt-coated electrodes. Representative processes for electrode modification are described as follows. A drop (10 μL) of the solution was placed onto the surface of a clean glassy carbon electrode (3 mm in diameter) and dried in the air for 2 h at room temperature. A drop of 0.5% Nafion solution (5 μL) was placed onto the electrode surface. The electrocatalytic performance was evaluated using a
CHI 802 electrochemical workstation and a conventional three-electrode electrochemical cell: a Pt wire as the auxiliary electrode, an Ag/AgCl electrode as the reference, and a Pt NM-coated carbon electrode as the working electrode. The EASA of each Pt NM was measured in 1 M H$_2$SO$_4$ over a potential range from $-0.25$ to $+1.2$ V at a scan rate of 50 mVs$^{-1}$. The electrocatalytic oxidations of MeOH mediated by the Pt NMs were performed in 0.5 M H$_2$SO$_4$ containing 1.0 M MeOH over a potential range from 0 to 1 V at a scan rate of 50 mVs$^{-1}$. Prior to CV measurements, the solutions were purged with N$_2$ gas for 30 min to remove O$_2$. The V/I data were recorded after 50 equilibrium scans for EASA measurements and 100 scans for the electrocatalytic oxidations of MeOH.

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