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Assembling Palladium and Cuprous Oxide Nanoclusters into Single Quantum Dots for the Electrocatalytic Oxidation of Formaldehyde, Ethanol, and Glucose

Jasper Biemolt, Dylan van Noordenne, Jianwen Liu, Elise Antonetti, Manon Leconte, Stefan van Vliet, Roland Bliem, Gadi Rothenberg, Xian-Zhu Fu, and Ning Yan*

ABSTRACT: To effectively manipulate the electronic structure of the catalysts, we present here a simple bottom-up synthesis protocol for agglomerating palladium and cuprous oxide ultrasmall nanoclusters into single nanoparticles, forming so-called quantum dot assemblies (QDAs). Our synthesis is based on the galvanic displacement of copper with palladium cations under O2-free conditions, rendering the simultaneous and unique crystal growth of ∼3 nm Cu2O and Pd clusters. Such assemblies, comprising ultrasmall nanoconstituents, offer much more phase boundaries, where the interfacial electronic effect becomes prominent in catalysis. This is demonstrated in the electrocatalytic oxidation of formaldehyde, ethanol, and glucose. In all three cases, the QDA catalyst, despite its similar Pd loading, outperforms the monometallic palladium catalyst. Indeed, complementing the oxidation of formaldehyde, ethanol, and glucose. In all three cases, the QDA catalyst, despite its similar Pd loading, outperforms the monometallic palladium catalyst. Indeed, complementing the oxidation of formaldehyde, ethanol, and glucose.

KEYWORDS: electronic structure, ultrasmall nanoparticles, synergistic effect, electrocatalyst, electroless deposition

1. INTRODUCTION

Engineering the topology of catalysts at the nanoscale is one of the most effective approaches for optimizing their performance. It allows the construction of hybrid systems comprising different components within the same nanostructure.1–3 Such assemblies can result in the formation of optimized active sites thanks to the physical and chemical interactions of constituent components. The synergistic effect is often prominent at the interface, where the electronic and geometric interactions start affecting one another.6–8 Thus, creating more of these boundaries can be beneficial for catalysis.

Intuitively, decreasing the size of the nanoclusters in the assemblies will create more interfaces. In particular, when the clusters become small enough to be considered as quantum dots (d < 3 nm, also called ultrasmall nanoparticles), quantum effects start influencing the catalytic properties significantly.9–13 There are various ways for making nanoclusters. Based on the pioneering work by LaMer and Dinegar,14 monodisperse nanoclusters are produced by controlling the different colloidal growth phases. Surfactants are typically used to influence these growth phases, offering control over the particle size, shape, and crystal structure. This can yield well-defined and highly active catalysts.15–18 Alternatively, one can also use physical methods such as atomic layer deposition or vapor phase deposition.19,20 These gas-based methods give even better control over the final catalyst structure.21–23 They are excellent for lab-scale catalyst synthesis and are often used for making model catalysts for fundamental studies. However, the high cost hinders their practical application in industry.

Notwithstanding the progress in nanocluster synthesis, hybridizing multiple types of nanoclusters to form quantum dot assemblies (QDAs) remains a difficult challenge. Now, motivated by the prospect of strengthening the interfacial electronic effect in such assemblies, we show that simple galvanic displacement is an effective approach for making QDAs. In the literature, this method is often used to grow conventional nanostructures such as core–shell, dumbbells,
nanotubes, and nanospheres. Their structure dimensions are typically larger than 50 nm. By taking advantage of the competing crystal growth of the Cu$_2$O and Pd, we succeeded in preventing the overgrowth of the two types of nuclei. The resulting quantum dots of Cu$_2$O and Pd are both ca. 3 nm in diameter, agglomerating into QDAs of 10–25 nm. Thanks to the maximized interfacial electronic effect as supported by the simulation results, our Cu$_2$O-Pd QDAs are excellent catalysts for the electro-oxidation of small organics (formaldehyde, glucose, and ethanol), outperforming even pure Pd nanoparticles. In the electroless copper deposition (ECD) process, which is industrially relevant for the fabrication of printed circuit boards (PCBs), the new catalysts accelerate the displacement (as illustrated in Figure 1 and eq 1). Each oxide particles grow simultaneously during the galvanic displacement. The five catalysts are denoted using their Pd/Cu percentage mass ratios in subscript before the element symbol (e.g., 0.2Pd-8Cu/C refers to a QDA with 0.2 wt% palladium and 8 wt % copper supported on Vulcan). Additional monometallic palladium catalysts (Pd/C) were prepared as control samples.

X-ray diffraction (XRD) was used to determine the bulk crystal phases of the Pd–Cu/C, Pd/C, and Cu/C catalysts.

Figure 2a shows the diffraction patterns of the 5Pd-8Cu/C, 5Pd/C, and 8Cu/C catalysts (for clarity and brevity, we discuss here only the XRD of 5Pd-8Cu/C; other results are shown in Figure S1 in the Supporting Information). The 5Pd/C sample shows the characteristic peaks of Cu$_2$O (36.6° (111) and 42.5° (200), COD 1000063), while no Pd peaks are observed. This pertains to the formation of ultrasmall Pd nanoparticles, and these local structures of the catalyst were further examined using other techniques (vide infra). Only peaks for metallic copper (43.5° (111) and 50.7° (200), COD 9011604) are observed in the diffractogram of the Cu/C catalyst, showing that the cuprous oxide in the Pd-Cu/C QDAs formed during the galvanic displacement, and not by air oxidation. The control catalyst Pd/C shows peaks for metallic Pd (40.2° (111) and 46.8° (200), COD 1011106).

Further insight into the surface composition was gained via XPS performed ex situ on the 5Pd-8Cu/C QDA. The Cu 2p and Pd 3d spectra of the 5Pd-8Cu/C QDA are shown in Figure 2b and c and are used for the chemical interpretation. The Cu 2p$_{3/2}$ peak suggests that the sample surface is rich in Cu$^{2+}$ oxide, as shown by the peak position and the characteristic strong satellite peaks. The peak at 933 eV (gray in Figure 2b) was assigned to the Cu$^{2+}$ oxide, which accounts for approximately 2.6% of the sample volume probed by XPS. The discrepancy between the XRD and XPS results is attributed to the oxygen spillover from Pd to Cu$_2$O on the material surface when the catalyst is exposed to air for a long period of time. This hypothesis was supported by the Pd 3d peak, showing 86% palladium oxide and 14% metallic Cu.

2. RESULTS AND DISCUSSION

2.1. Synthetic Strategy and Materials Characterization. The geometric structure and the synthetic strategy of Cu$_2$O/Pd QDAs are illustrated in Figure 1. After obtaining the copper nanoparticles (8 wt %) supported on Vulcan XC-72R, QDAs were synthesized through the galvanic displacement reaction shown in eq 1 in the absence of O$_2$ (see the Supporting Information for details). The redox potential difference between palladium and copper (eqs 2 and 3) results in copper oxidation and Pd$^{2+}$ reduction. Usually, the copper atoms would be oxidized following a two-electron process all in an O$_2$-free environment.30 The palladium and the cuprous oxide particles grow simultaneously during the galvanic displacement, and not by air oxidation. The control catalyst Pd/C shows peaks for metallic Pd (40.2° (111) and 46.8° (200), COD 1011106).

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2Cu$^{0}$ + 2OH$^-$ + Pd$^{2+}$ → Cu$_2$O + H$_2$O + Pd$^{0}$

$E_0$ = +1.275 V

Cu$^{2+}$ + 2e$^-$ → Cu$^{0}$

$E_0$ = +0.342 V

Pd$^{2+}$ + 2e$^-$ → Pd$^{0}$

$E_0$ = +0.915 V

Cu$_2$O + H$_2$O + 2e$^-$ → 2Cu$^{0}$ + 2OH$^-$

$E_0$ = −0.360 V

We then varied the size and number of the nanoclusters in the Pd–Cu$_2$O QDAs, to optimize their catalytic activity. Our hypothesis was that using a low concentration of palladium solution during galvanic displacement would give less Pd and more Cu$_2$O clusters, and vice versa. Thus, we prepared QDAs with different Pd/Cu mass ratios (0.2:8, 0.5:8, 1:8, 2:8, and 5:8) from the same Cu/C (8 wt % Cu loading) with varying amounts of palladium in the solution during galvanic displacement. The five catalysts are denoted using their Pd/Cu percentage mass ratios in subscript before the element symbol (e.g., 0.2Pd–8Cu/C refers to a QDA with 0.2 wt% palladium and 8 wt % copper supported on Vulcan). Additional monometallic palladium catalysts (Pd/C) were prepared as control samples.

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palladium (Figure 2c, green and pink peaks, respectively). A palladium to copper ratio of 0.72:1 was determined in the Pd$_x$Cu$_y$/C QDA using the Pd 3d and Cu 3p peaks (see Figure S2). As Cu 3p is closer in kinetic energy to Pd 3d than Cu 2p, the probing depths will be similar. This ratio is comparable with the theoretical one of 0.63:1 based on the synthetic procedure, which is also verified by the microscopy analysis (vide infra).

Transmission electron microscopy (TEM) studies of the Pd$_x$Cu$_y$/C catalyst reveal that the QDAs, with the size between 10 and 25 nm, uniformly distributed on the carbon surface (see Figure 3a). A clear view of the metallic QDAs was obtained via high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM, Figure 3b) imaging. All the QDAs contain both palladium and copper, as shown by the elemental mappings obtained using energy-dispersive spectroscopy (EDS, see Figure 3c). No monometallic species were observed. This confirms that Pd grows from Cu nanoparticles during the galvanic displacement. We also performed the EDS line scan of the QDAs at the nanoscale (Figure 3d). The scan profile in Figure 3e shows alternating signals for Cu and Pd, implying the formation of the QDA structure as illustrated in Figure 1. In particular, the size of all Cu and Pd domains is less than 3 nm, which corroborates the quantum-dot nature of both Cu$_2$O and Pd particles. Since Cu is not in the metallic but oxide form, the direct bond formation between Cu and Pd is unlikely (see our simulation model below). We thus relied on high-resolution TEM (HRTEM) to understand the local structure and the interface of the cluster. The HRTEM micrograph shown in Figure 3f reveals that the particles are assemblies of multiple quantum dots, showing that Pd and Cu$_2$O are strongly bound at the interface. The interplanar spacings in these nanoclusters are ~0.22 nm, corresponding to either Pd (111) or Cu$_2$O (200) with a small lattice expansion.34,35

**Figure 3.** Microscopy characterization of Pd$_x$Cu$_y$/C QDA: (a) TEM micrograph; (b) HAADF-STEM micrograph; (c) EDS elemental mapping; (d) TEM image of the QDA where the EDS line scan was performed, and the inset shows the EDS spectrum of the entire area; (e) TEM-EDS line scan analysis of Cu and Pd; (f) HRTEM micrograph.

The conversion of formaldehyde is also relevant in the ECD process. For the formaldehyde oxidation reaction, we used a classical 3-electrode setup with an alkaline electrolyte containing KOH, ethylenediaminetetraacetic acid (EDTA), and formaldehyde. EDTA was added to simulate the environment of the ECD process (it is commonly added to ensure the stability of Cu$^{2+}$ and the quality of the deposited layer). The Pd/C catalyst was tested in both the blank bath (formaldehyde-free) and formaldehyde bath (see Figure 4a; Figure 4b).

**Figure 4.** (a) CV curves of Pd/C and Pd$_x$Cu$_y$/C in HCOH-free and HCOH bath; (b) comparison of linear sweep voltammetry (LSV) curves of Pd$_2$Cu/C QDAs (solid lines) with the corresponding Pd/C (dashed lines) with the same Pd content in formaldehyde oxidation; (c) comparison of peak current density of different catalysts in formaldehyde oxidation; (d) CV curves of Pd/C and Pd$_x$Cu$_y$/C for both glucose and ethanol oxidation; (e) schematic structural comparison of QDA with the conventional Pd catalyst with varying Pd ratios. Test conditions are specified in the Supporting Information.
versus the SCE and the other one in the backward scan at −0.43 V versus the SCE. The former is attributed to the oxidation of glucose, while the latter is attributed to the oxidation of bound intermediates, which are not oxidized during the forward scan. The peaks have a small positive shift (0.04 and 0.03 V for the forward and backward scan, respectively) for Pd/C. The peak current density for glucose oxidation of Pd–Cu/2/C is ~3 times higher than that of Pd/C (7.90 mAc−2, 17.6 mAc−2 vs 2.67 mAc−2, 5.93 mAc−2 respectively). A similar result was obtained in the ethanol oxidation reaction performed in 1.0 M ethanol and 1.0 M KOH electrolyte. The superior performance of QDA in the oxidation of these small organic molecules emphasizes the importance of the interaction between the Pd and Cu2O domains.

We hypothesize that the catalytic advantages of QDAs come from the maximized interfacial electronic effect between Pd and Cu2O quantum dots (see the illustration in Figure 1). Such an effect is prominent only when the size of Pd and Cu2O dots is the same, maximizing the phase boundaries. When the Pd ratio decreases, this effect diminishes accordingly and the QDA will perform similar to pure Pd (1 wt % Pd). However, at extremely low Pd loadings (e.g., 0.5 and 0.2 wt % Pd, see Figure 4d), the low Pd2+ ion concentration in the galvanic displacement bath results in the formation of much less Pd nuclei, which subsequently undergo nonpittingal and continuous growth. Therefore, nonuniformly dispersed, localized and large Pd dots are observed on the Cu particles (see Figure 4e). Hence, these QDAs perform worse than the corresponding Pd/C with well-distributed Pd nanoparticles.

To understand and verify the interfacial properties, we have constructed a Pd–Cu2O QDA model and performed density functional theory (DFT) calculations. Figure 5a shows the optimized heterostructure containing a 46-atom Pd cluster on the Cu2O (111) surface. This structure is thermodynamically favorable, as the interface has more interfacial bonds and less strain stress. Because of the formation of the interfacial Pd–O and Pd–Cu bonds, charge accumulation at the boundary is observed. This has substantially changed the projected density of states (PDOS) in the interface (see Figure 5b). The d-band center (εd) of the QDA was upshifted to ~2.53 eV toward the Fermi level compared to ~2.75 eV of Cu2O. The catalytic benefits of the optimized electronic structure are shown in the potential energy diagram, Figure 5c. We used the optimized Meerakker’s model in alkaline media in which HCHO is in equilibrium with CH2OOH−:

\[
\text{HCHO} + \text{H}_2\text{O} \leftrightarrow \text{CH}_2\text{(OH)}_2
\]

\[
\text{CH}_2\text{(OH)}_2 + \text{OH}^- \leftrightarrow \text{CH}_2\text{OOH}^- + \text{H}_2\text{O}
\]

The elementary reactions are as follows:

\[
\text{CH}_2\text{OOH}^- + \text{OH}^- \rightarrow \text{CH}_2\text{O}_2^{2-} + \text{H}_2\text{O}
\]

\[
\text{CH}_2\text{O}_2^{2-} + -* \rightarrow \text{COOH}^- + -\text{H} + e^-
\]

\[
-\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^-
\]

where eq 8 is the rate-determining step. The calculation indicates that the activation energy barrier from CH2O2 to COOH decreased by 0.21 eV when the catalytic surface is switched from Pd to the Pd–Cu2O QDA model.

2.3. Industrial Application in Electroless Deposition. We then tested the performance of the Pd–Cu2O QDAs in ECD. This industrially relevant technique plates a surface with a copper layer for anticorrosion applications or PCB manufacturing. The plating is performed in a bath containing metal ions and a reducing agent (eq 10). Although this reaction is autocatalytic, it must be initiated by a catalyst. The state-of-the-art Pd initiator is rather expensive, and replacing it with cheaper and more active materials is industrially important.

\[
\text{M}^{3+} + \text{Red} \rightarrow \text{M}^0 + \text{Red}^{n+x}
\]

In the traditional alkaline formaldehyde bath, the reduction of EDTA-stabilized Cu2+ cations proceeds through the adsorption of formaldehyde hydrate on the catalyst surface followed by anodic oxidation to formate (eq 11). The electrons liberated from this process are transferred for cathodic Cu deposition (eq 12). The combination of both reactions gives the overall cell reaction (eq 13). The initiator catalyzes this reaction via facilitating the oxidation of formaldehyde.

\[
\text{HCOO}^- + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{HCOH} + 3\text{OH}^-
\]

\[
\text{[CuEDTA]}^{2-} + 2e^- \rightarrow \text{Cu}^0 + \text{EDTA}^{4-}
\]

\[
\text{HCOOH} + 3\text{OH}^- + \text{Cu}^{2+} \rightarrow \text{HCOO}^- + 2\text{H}_2\text{O} + \text{Cu}^0
\]

We have shown that the Pd–Cu2O QDAs are excellent catalysts for formaldehyde oxidation (vide supra). Yet, monitoring both the formaldehyde oxidation and copper reduction gives a much clearer picture. Thus, we first used the mixed potential theory to further analyze the activity of both Pd/C and Pd–Cu/C QDA catalysts in ECD. The mixed potential theory concludes that the maximum electrochemical reaction rate is achieved when both the anodic and cathodic reactions occur at the same rate, resulting in no buildup of electrons at the interface. The kinetics can be derived from the intersection between the two half-reaction Tafel curves. Here, we measured the Tafel curves for copper reduction and formaldehyde oxidation for both the Pd/C catalyst and Pd–Cu/C QDA (Figure 6a,b). For Pd/C, the curves intersect at ~0.41 V vs SCE with a current density of 0.28 mAc−2. In contrast, the Pd–Cu/C QDA intersects at a lower potential (~0.52 V vs SCE), while showing a substantially increased current density of 0.53 mAc−2. We hence conclude that the Pd–Cu/C QDA also outperformed the monometallic Pd/C catalyst in the ECD.
As the mixed potential theory only gives an indication of the initial activity of the catalyst, we also used an electrochemical quartz crystal microbalance (eQCM) to monitor both the deposition rate and surface potential. The quartz crystals were coated with the catalysts and then subjected to the ECD bath (see Table S2 for both compositions). During ECD, the frequency variations of this crystal were monitored, which are correlated to the mass change. Simultaneously, the potential was also recorded, revealing more information about the electrochemical nature of the plating process. Both the \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) and \( \text{Pd} \) \( \text{C} \) catalysts were examined in this eQCM system. A plot of the potential and mass change versus time is shown in Figure 6c. Deposition rates of 35 and 21 \( \mu \text{gCu} \text{mgPd}^{-1} \text{ s}^{-1} \) are derived from the total plating time for \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) and \( \text{Pd} \) \( \text{C} \), respectively (deposition rates are denoted as the amount of plated copper per mg of palladium per second). For both catalysts, a linear increase for the mass change is observed after the first 150 s. This linearity comes from the uniformly plated copper on the surface, which autocatalytically grows at a constant rate. The differences in the deposition rate for 150–1200 s period come from the surface area differences of the predeposited copper film.

We thus obtained the plating kinetics of the \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) and \( \text{Pd} \) \( \text{C} \) catalysts from the first 150 s of ECD. The first 15 s is an induction period in which the system equilibrates to the plating bath. After this period, the \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) achieved a deposition rate of 41 \( \mu \text{gCu} \text{mgPd}^{-1} \text{ s}^{-1} \). This is faster than that of the monometallic \( \text{Pd} \) \( \text{C} \), which had a deposition rate of 15 \( \mu \text{gCu} \text{mgPd}^{-1} \text{ s}^{-1} \). Furthermore, the initial deposition rate of \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) is faster than that during autocatalysis, which is catalyzed by the deposited Cu layer, whereas this rate for \( \text{Pd} \) \( \text{C} \) is lower than that during the autocatalysis. This implies that the activity order is \( \text{Pd}_x\text{Cu}_y \text{QDA} > \text{Cu} > \text{Pd} \) \( \text{C} \). This trend is also reflected by the potential profiles of the two materials. From the autocatalysis region in Figure 6c, we found the potential for autocatalyzed ECD is in the range of −0.75 to −0.8 V versus Ag/AgCl. After the initial induction period, the potential of the \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) became lower than the autocatalytic ECD potential, whereas that of \( \text{Pd} \) \( \text{C} \) remained higher than the autocatalytic potential.

We finally demonstrate the excellent mechanical and electronic properties of the Cu deposit layer initiated by the \( \text{Pd}_x\text{Cu}_y \) \( \text{QDA} \) by plating copper wires on a flexible silicon rubber substrate. The QDA catalyst was airbrushed onto the substrate using a simple mask with the logo of the University of Amsterdam. After ECD, the copper layer was uniformly and exclusively deposited within the pattern where catalyst was spray-painted (Figure 7a). The copper pattern is highly conductive and could be used as wires to successfully power a light-emitting diode (LED) assembly (Figure 7b). This shows the potential of using the new catalyst in the context of industrial applications.

3. CONCLUSIONS

We developed a novel QDA catalyst via a galvanic displacement approach, consisting of 3 nm Cu\(_2\)O and Pd clusters. These QDAs are better electrocatalysts for the oxidation of formaldehyde, glucose, and ethanol, outperforming equivalent monometallic catalysts. Together with the DFT simulations, we conclude that the activity enhancement originated from the maximized interfacial electronic effect between Pd and Cu\(_2\)O quantum dots. The industrial relevance of the new catalyst was demonstrated by the excellent performance in initiating the ECD, yet reducing the Pd-Cu\(_2\)O metal loading in the future will make the supported catalyst even more promising for industrial processes. We believe that this catalyst structure opens opportunities for designing better catalytic materials at the ultrasmall nanoscale.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c02162.

Protocols of materials synthesis, electrochemical test, and materials characterizations; additional XRD, XPS, and electrochemical results (PDF)

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Notes

The authors declare no competing financial interest.

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