Advanced Characterization Techniques for Evaluating Porosity, Nanopore Tortuosity, and Electrical Connectivity at the Single-Nanoparticle Level

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ABSTRACT: We demonstrate quantification of porosity, nanopore tortuosity, and electrical connectivity at the single-nanoparticle (NP) level for NPs synthesized by nanodroplet-mediated electrodeposition. Focused ion beam nanoslice tomography was used to slice NPs with ca. 10 nm slice resolution followed by imaging using scanning electron microscopy (SEM), allowing measurement of these parameters on NPs not amenable to transmission electron microscopy. Slices were reconstructed in three dimensions and revealed pores with an average size of 3 ± 2 nm and relative nanopore tortuosity of 46.8 ± 24.5. We also demonstrate a new technique to evaluate connectivity at the single-NP level by taking advantage of material-selective electrodeposition. The rate of Cu electrodeposition differs significantly on Pt compared to carbon, implying Cu can be selectively electrodeposited onto Pt NPs adsorbed onto a carbon support. Following the Cu electrodeposition step, NP connectivity was determined by the presence of Cu on Pt, as studied by energy-dispersive X-ray spectroscopy and SEM. We demonstrate that NPs synthesized by electrodeposition have >97% connectivity with underlying highly oriented pyrolytic graphite (HOPG) or amorphous carbon electrodes. The same method was employed to study connectivity of citrate-capped Pt NPs (diameter of 70 nm) on HOPG and amorphous graphite adsorbed by drop-casting. Surprisingly, <80% of these NPs had connectivity on HOPG and <40% had connectivity on amorphous carbon. These techniques will find applications in nanomaterials characterization, particularly in the fields of electrocatalysis and energy storage and conversion.

KEYWORDS: nanodroplet-mediated electrodeposition, electrical connectivity, emulsion, nanoparticle, porosity, tomography, tortuosity

1. INTRODUCTION

Over the past several decades, numerous resources have been expended to explore the chemical and physical properties of nanoparticles (NPs) of different shapes and sizes. Recently, many groups have become interested in the electrocatalytic properties of single NPs and how those properties may differ from bulk materials. This avenue of inquiry has been fueled by the heterogeneity in particle size and morphology resulting from general NP synthesis techniques. Ensemble measurements report information only on the average size and morphology of NPs in a population. Therefore, a detailed understanding of how size and morphology affect electrocatalysis at the single-NP level is essential to direct synthetic techniques for electrocatalyst optimization.

Most crucial to this understanding is a diverse set of analytical methods that yield detailed information about the physical properties of NPs. In this article, we present two new techniques to study physical properties of single NPs. The first technique allows single-NP porosity and nanopore tortuosity to be studied without the use of transmission electron microscopy (TEM). The second technique allows quantification of NP electrical connectivity by taking advantage of differences in electrodeposition kinetics on different materials. NP connectivity is defined as the electronic communication across substrateNP and solutionNP interfaces. These techniques are applied here to Pt NPs electrodeposited from water droplets (nanoDroplet-Mediated Electrodeposition), and electrical connectivity is compared to commercially available citrate-capped Pt NPs adsorbed by drop-casting. Scheme 1 depicts the electrosynthesis process followed by the characterization of single NPs using the new techniques developed here.

Our motivation to pursue these new techniques stems from our previous work, where we reported the electrodeposition of Pt NPs (radius ca. 25–250 nm) from water droplets onto amorphous carbon with experimental control over particle size, surface roughness, and surface coverage. Briefly, water droplets containing a controlled concentration of...
chloroplatinic acid were suspended in 0.1 M tetrabutylammonium perchlorate and 1,2-dichloroethane (DCE). When droplets collided with a carbon electrode biased sufficiently negative to drive electrodeposition, NPs formed and were characterized by electron microscopy. One can estimate the theoretical size of an electrodeposited NP by assuming each molecule of chloroplatinate in the water droplet reduces to a Pt atom during electrodeposition. We previously showed that this assumption is valid by studying the collision of these chloroplatinate-filled water droplets on ultramicroelectrodes (UMEs) ($ume < 10 \mu m$), where the complete electrolysis of the droplet can be verified.\textsuperscript{19} In these experiments, Faraday’s Law was used to calculate the size of the droplet by integrating the current-time transient, and these results agreed well with dynamic light scattering results. On the basis of the number of atoms calculated from the metal precursor concentration and the volume of the face-centered cubic unit cell, the resulting NP radius can be estimated. When compared to the observed particle radii synthesized in ref 17, this model consistently underestimated NP size, suggesting some other volume contribution. Figure 1 shows the radius estimation (red) and data we previously reported\textsuperscript{17} (blue) as a function of metal—salt precursor concentration in the droplet. One possible explanation for this volume discrepancy is that the NPs are porous. Unfortunately, single-NP porosity is difficult to probe on amorphous carbon. Generally, TEM is used to study NP porosity\textsuperscript{20--22} however, TEM analysis would necessitate electrodeposition on a TEM grid, which appears to directly influence the NP morphology, as demonstrated in Figure 2.

Furthermore, while we hypothesized that electrodeposited NPs would have a greater probability of having an underlying connection with the substrate because connection is a prerequisite for electrodeposition,\textsuperscript{18} no direct evidence was available to reject the null hypothesis other than an optical method previously reported by Willets and co-workers on a transparent indium tin oxide (ITO) electrode. In that study, the authors describe single Au nanorod electrogenerated chemiluminescence (ECL).\textsuperscript{23} When they compared the rods that displayed ECL to rods observed from dark field scattering, only 82.5% of the rods produced ECL, indicating not all nanorods had a connection with the underlying ITO transparent electrode.

Here, we demonstrate porosity of Pt NPs synthesized by nanodroplet-mediated electrodeposition without the use of
TEM by applying focused ion beam nanoslice tomography (FIB-nST). NPs were sliced with ca. 10 nm resolution with the FIB and subsequently imaged with scanning electron microscopy (SEM). Three-dimensional (3D) image rendering allowed quantification of previously unattainable properties at the single-NP level, most notably nanopore tortuosity and pore density. We further developed a technique to test for an underlying electrical connection with the substrate based on Cu electroplating. Our results indicate that electrodeposited NPs have >97% connectivity, independent of substrate, while drop-cast/adsorbed NPs have <80% connectivity on HOPG and <40% connectivity on amorphous carbon. These techniques will find applications in different fields requiring advanced nanomaterial characterization methods.

2. METHODS

2.1. Chemicals and Materials. All chemicals were of analytical grade unless noted otherwise and were used as received. Nanopure water (18.2 MΩ·cm) was used in all solutions. Hexachloroplatinic acid (HCPA) (99.99%), ferrocenemethanol (98%), potassium ferrocyanide (99%), potassium chloride (≥99%), copper sulfate (99%), hydrogen peroxide, sulfuric acid, nitric acid, hydrochloric acid, and tetrabutylammonium perchlorate ([TBA][ClO₄]) were purchased from Sigma-Aldrich and used without further purification for experiments, electrode characterization, and cleaning. 1,2-Dichloroethane (DCE) was purchased from ACROS Organics. Phosphate buffered saline (pH 7.4) was used for electrodeposition experiments. An aqueous Ag/AgCl reference electrode was used, and a Pt wire or graphite rod was used as an auxiliary electrode. Citrate-capped Pt NPs (diameter of 70 nm) were purchased from nanoComposix (San Diego, CA) and used for drop-casting experiments.

2.2. Electrode Fabrication. Graphite electrodes were prepared by polishing 3 mm radius graphite rods in a figure-eight pattern on a fine grit sandpaper after thorough rinsing with nanopure water. After this treatment, the electrode was buffed to a glassy shine using a beveler (MegNoTek). Connection was made to the electrode via copper tape (3M, Maplewood, Minnesota). HOPG surfaces were exfoliated with adhesive tape between experiments.

2.3. Instrumentation. A CHI 601E potentiostat and a PTFE electrochemical cell with a Viton O-ring of 2 mm diameter were used for electrodeposition of NPs on the substrates. The amperometric i-t curve technique was used, which steps the potential to an applied voltage of choice from the open-circuit voltage. All experiments were performed in a grounded Faraday cage. The emulsion was prepared using a Q500 ultrasonic processor (Quonica, Newton, CT) with a microtip probe (1/16 inch). SEM images and energy dispersive X-ray spectroscopy (EDX) spectra were taken using Helios 600 Nanolab Dual Beam System (FEI, Hillsboro, OR) and INCAPentaFET-x3 (Oxford, Abingdon, United Kingdom) instruments, respectively, at 30 keV and 0.69 nA.

2.4. Emulsion Preparation. To prepare the emulsion for the synthesis of porous NPs, 25 µL of aqueous solution was prepared using 25 mM HCPA in 5 mL of DCE containing 0.1 M [TBA][ClO₄] which15 maintains charge balance during the electrodeposition. The resulting two-phase solution was then ultrasonicated (500 W, amplitude 40%) using a pulse mode method (5 s on, 5 s off, 6 total cycles) to form the emulsion.

2.5. Procedure for Nanoslice Tomography. Reduction of HCPA to Pt NPs occurred as droplets stochastically collided with a polished 3 mm diameter amorphous graphite surface biased at ~0.2 V vs Ag/AgCl QRE for ca. 1000 s. Electrodeposition onto TEM grids was achieved by creating direct contact at the substrate surface above the emulsion with partial substrate immersion. Presence of Pt NPs was confirmed in SEM at 30 keV and 0.69 nA. The stage working distance was brought to 4.1 mm with the electron beam focused on a specific surface feature, and iterative stage rotation and height modulation facilitated sample adjustment to the eucentric height orthogonal to the gallium ion beam. A blind alignment allowed the orientation of ion and electron beams to a coincident point by patterning within a small region, switching to SEM mode, and repeatedly adjusting the ion beam toward the electron beam position. As discussed below, blind alignment was used to protect the NPs from beam damage. Confirming the alignment at increasing magnifications up to 600,000× allowed high confidence in slice resolution. This process was completed within 5 s of the particle of interest to minimize potential alignment shifts. Initiation of slicing with the “cleaning cross section” FIB mode at 30 keV and 1.5 pA allowed 400 × 10 × 500 nm³ patterning of the particle at a working time of one second per slice. After each slice, SEM images captured the cross section and revealed pores and the tomography of the NP. Limitations of this technique are given in section 3.4.

2.6. Image Processing. The open-source ImageJ “Particle Analysis” plugin was employed to obtain pore size and distribution data from SEM slice images using the following procedure. SEM images were obtained at 30 keV and 0.69 nA following FIB milling to produce a series of images corresponding to subsequent slices through the NP. Micrographs were converted to an 8 bit format and uploaded to ImageJ, and the micrograph scale bar was traced with the line tool to calibrate the image under the Analysis → Set Scale function. Micrograph contrast was optimized first with the “Enhance Local Contrast” filter and then with the Image → Adjust → Adjust Threshold function in dark background mode to develop a black/white contrast between the individually resolved nanopores and the bulk NP Pt structure. The number and area of individual nanopores were obtained using the Analysis → Particle Analysis function with a manual minimum area of 1 nm² and a roundness factor of 0.2 to reduce the effects of noise and potential surface defects derived from FIB milling. The total area of the slice was also collected. Individual pore areas were exported from ImageJ and converted to diameter measurements for analysis of pore size and pore density as a function of slice depth. Avizo software was used to further analyze porosity, nanopore tortuosity, and surface-area-to-volume ratio. Analysis of stacked images to obtain a length-per-pixel ratio allows 2D-to-3D conversion at 0.8 mm per pixel. Generated 3D voxels at a resolution of 0.8 × 0.8 × 18 nm³ allowed reconstruction of slices to form the 3D model. Whereas a pixel is a 2D representation of an image, a voxel gives a 3D representation of an image, allowing 3D rendering. The image stack was cropped to include only cross-sectional area and centered to correct for the 52° imaging angle. The Avizo software processing schematic is shown in Figure S2. Image segmentation allowed differentiation between pores, Pt, and blank space. A disc Top-Hat threshold, which allows extraction of tiny elements from an image, with radius 8 was used to identify pore space and Pt. After segmentation, a Watershed function, used to assign different brightness values to image locations, allowed reconstruction of individual segments into a 3D representation. Label Analysis allowed area and volume values to be extracted from each segment. Quantification of tortuosity employed a center-of-mass function, in which the pores in individual slices were weighted into a center-of-mass position and compared to the center-of-mass position in the adjacent slice. Figure S2 shows a representative schematic for this method. Mesher with randomized coloration were generated to add contrast to individual pores. In addition, we applied a Pore Analysis Wizard within the Avizo software to connect pores between slices on the basis of voxel contact (i.e., if a voxel in slice one is located in the same x-coordinate as a voxel in slice two, the program connects them with a single color).

2.7. Procedure for Cu-Deposition Connectivity Analysis. Single-NP electrical connectivity was assessed by a two-step amperometric deposition technique coupled with SEM/EDX analysis. Pt NPs were first electrodeposited onto a HOPG or an amorphous carbon substrate from a water-in-oil emulsion as previously described.17 As a comparative study, commercial Pt NPs were adsorbed onto HOPG or amorphous carbon by drop-casting. A water-in-DCE emulsion was prepared through ultrasonication with HCPA confined to a 30 µL aqueous droplet in a 5 mL DCE continuous phase with or without 1 mM SDS. The presence or absence of SDS did not affect the statistics of particles with underlying connectivity.
Subsequently, HCPA in the aqueous droplet phase was reduced to Pt NPs following stochastic droplet collision with a biased electrode (−0.4 V vs Ag/AgCl QRE). Following 300 s of Pt NP nanodroplet-mediated electrodeposition, the underlying carbon substrate was rinsed for 5 minutes in DCE, ethanol, and nanopure water to remove excess supporting electrolyte, droplet-stabilizing surfactant, and adsorbed metal complexes. Cu electroplating was carried out on these Pt NPs via a conventional potential-step experiment where 50 μM CuSO₄·5H₂O was reduced onto the biased NP-decorated HOPG or amorphous carbon substrate (−0.2 V vs Ag/AgCl) at a time frame sufficient to allow Cu nucleation and growth on Pt while leaving a clean underlying scaffold electrode surface. A schematic representation of this method is given below. This electroplated substrate was rinsed with nanopure water for 15 min and analyzed with SEM/EDX. Single NPs were imaged in SEM (30 keV accelerating voltage and 0.69 nA beam current). Electrical connectivity of single NPs was determined by EDX confirmation of Cu species, based upon the assumption that a NP lacking electrical connection would be unable to electrochemically reduce solution Cu²⁺ to Cu⁰. Negative connectivity results were characterized by total Cu elemental concentrations less than 3% over the surveyed region or when the automatically generated standard deviation in atomic Cu composition exceeded the reported average value. Similar analysis was conducted on Pt NPs deposited on HOPG and amorphous graphite substrates by conventional drop-casting of ligand-capped NPs with subsequent Cu electroplating. Importantly, Pt NPs did not exhibit characteristic Cu X-ray peaks after immersion in CuSO₄·5H₂O without an applied bias, and the carbon substrate in all experiments was sufficiently free of Cu nanostructures. Limitations for this technique are given in section 3.4.

3. RESULTS AND DISCUSSION

3.1. Porosity and Nanopore Tortuosity. Because of our previous results and the discrepancy between the predicted NP size and the observed size shown above,¹⁷ we hypothesized that Pt NPs electrodeposited from water droplets on amorphous graphite substrates were nanoporous. While a number of analytical techniques have been applied to NP characterization, we found it difficult to find a robust technique to quantify porosity at the single-NP level on a variety of substrates. Semiquantitative porosity measurements obtained with techniques such as TEM prohibit clear analysis of pore density and diameter as a function of depth into the particle, especially with larger (>100 nm radius) NPs, which may be opaque to electron transmission (see Figure S1).²⁴ Another important physical property of pores known as tortuosity is also unavailable from TEM analyses. Tortuosity is a measure of the degree of nanopore winding and is generally calculated by dividing nanopore length by displacement, thus requiring individual pore tracking as a function of depth through the NP. By this definition, a perfectly nontortuous nanopore has a tortuosity value of 1, where tortuosity is never less than 1.

TEM also necessitates NP fixation onto TEM grids, which, though generally innocuous for ligand-stabilized NPs suspended in solution, may complicate analysis for NPs synthesized via direct NP electrodeposition. Synthesis of NPs by electrodeposition facilitates the study of chemical and physical properties of NPs unhindered by complicating factors associated with stabilizing ligands (i.e., blocking surface sites for electrocatalytic studies). Unfortunately, the electrodeposition mechanism varies widely depending on the substrate chosen, as shown in Figure 2a−d. Importantly, the particles electrodeposited on boron-doped diamond (BDD, Figure 2a), HOPG (Figure 2b), and amorphous graphite (Figure 2c) differ significantly in morphology from the NP electrodeposited onto a carbon TEM grid, as shown in Figure 2d. Therefore, the ideal tomographical technique effectively probes and quantifies internal porosity and tortuosity of single NPs on a variety of nonspecialized substrates with high resolution. Previously, groups have used FIB to cross-section and image films, particle aggregates, and hollow cavities in microspheres.²³−²⁵ Commonly termed “FIB tomography”, this technique employs a gallium ion beam to slice a material of interest for subsequent imaging by SEM in a dual-beam configuration. To our knowledge, however, FIB tomography has not been used to study porosity and nanopore tortuosity inside individual NPs.

Here, we introduce FIB nanoslice tomography (FIB-nST) for substrate-independent characterization of single Pt NP porosity and nanopore tortuosity. Once the NPs were loaded into the SEM instrument and beam alignment was complete, it took 10−20 min to slice NPs and a further 30 min of software characterization. Further, we also demonstrate that the resolution attained by FIB-nST allows the visualization and tracing of <5 nm diameter pore networks through a single particle with 3D slice resolution between 10 and 20 nm, allowing analysis using the nanoSlice technique of NPs down to 45 nm in radius. In these experiments, the lowest detectable pore size was ca. 2 nm. Figure 3 shows a schematic representation outlining the experimental process and data analysis. NPs were electrodeposited onto an amorphous graphite substrate and loaded into a dual-beam FIB-SEM...
After electron beam alignment, a stage tilt brought the ion beam orthogonal to the particles of interest while the electron beam imaged at $52^\circ$. To preserve our sample, we applied a blind alignment procedure for the ion and electron beams to mitigate possible NP damage by the gallium ion beam, as described previously. The ion beam then directly patterned 10–20 nm slices through the NP for subsequent imaging. Following NP slicing and imaging, direct analysis of the internal pore structure for each image enabled the quantification of pore size and pore density as a function of depth with open-source software ImageJ. Avizo (Thermo Fisher) software was employed to segment the individual components of the particle (i.e., solid Pt, pores) and reconstruct the slices into a 3D representation, which enabled the visualization and extraction of nanopore tortuosity, total particle surface area, and surface-area-to-volume ratio. To our knowledge, these parameters have not been measured before with such resolution at the single-NP level.

Analysis using FIB-nST was carried out on Pt NPs deposited from water droplets to probe single-NP porosity. Tomographical analysis of a 300 nm diameter NP produced the image array presented in Figure 4a, which indicates internal porosity. Generally, dividing the diameter of the particle by the number of slices enabled reasonable estimation of slice depth, indicating ~18 nm depth resolution for the example shown in Figure 4. Figure 4b shows nanopores with arbitrary color to indicate which pores are being counted during the analysis. Figure 4c shows the depth profile results of SEM image analysis yielding information on average pore density and pore diameter as a function of depth. Analysis of average pore density (pores per unit area) and diameter from the ImageJ plugin "Particle Analysis" revealed consistent pore arrangement throughout the particle. The average diameter of pores was $3 \pm 2$ nm and pore density was $3.5 \pm 2.6 \times 10^{15}$ pores per square meter. Pore size also remained stable at $3 \pm 2$ nm in diameter throughout the NPs ($n = 3065$).

![Figure 4. Unprocessed data and depth profile results. (a) Raw image data collected by SEM shows progression of slices through a 300 nm diameter NP. (b) Representative orthoslice illustrates pore identification and quantification with randomized colors for contrast. (c) Analysis of each individual slice with ImageJ plugin "Particle Analysis" allowed quantification of pore density and size. Three representative particles showed stable pore density between slices at $3.5 \pm 2.6 \times 10^{15}$ pores per square meter. Pore size also remained stable at $3 \pm 2$ nm in diameter throughout the NPs ($n = 3065$).](image)
respectively. Whether this extra surface area is externally accessible is currently under investigation.

The visualization and quantification of nanopore tortuosity within NPs achieved by FIB-nST lends another useful characterization technique toward understanding such phenomena as porous NP-mediated drug delivery and electrocatalysis at the single-NP level.\(^\text{36}\) Calculation of nanopore tortuosity by a pore center-of-mass method described in section 2.6 indicated a tortuosity value of 46.8 ± 24.5. Many of the larger pores demonstrate continuity between slices as shown in Figure 5c, allowing visualization of tortuosity within the NP. We believe this method is the first of its kind to begin to quantify tortuosity at the single-NP level.

### 3.2. Electrical Connectivity

NPs are widely used in electrocatalytic studies and in fuel cells\(^\text{17,38}\) because of the enhanced surface-area-to-volume ratio and unique chemical and physical properties observed at single NPs compared to bulk materials.\(^\text{39,40}\) For NPs to have a direct effect on electrocatalysis, it is necessary that NPs have electrical connectivity with the underlying substrate. Conventional synthetic techniques employ homogeneous synthesis of ligand-stabilized NPs with excellent size control. These NPs are subsequently adsorbed onto an electrode surface by drop-casting, and the solvent is evaporated. With this technique, there is no guarantee of electrical connectivity, although the high density of states (DoS) between a metal electrode and a metal nanoparticle increases the probability of electron tunneling (see section 3.3 for further discussion).\(^\text{31,42}\) In contrast, a significant requirement must be met for electrodeposition of NPs: a connection must be made for electrodeposition to occur. This led us to hypothesize that electrodeposited NPs ensure electrical connectivity while adsorbed NPs may display a lower fraction with an underlying electrical connection. This hypothesis was motivated by Willetts’ previous report, where electrogenerated chemiluminescence (ECL) was selectively driven on Au nanorods that were adsorbed on an ITO surface. When ECL images were compared to darkfield scattering, the investigators found that only 82.5% of nanorods generated ECL.\(^\text{25}\) However, this technique to probe electrical connectivity for a NP population requires specialized optical equipment and is limited to transparent/opaque materials that can be used to observe ECL reactions being driven on NPs. As shown in Figure 2, the electrodeposition mechanism can vary greatly depending on the substrate. Thus, it would be helpful to have a technique to test for single-NP activity on a variety of substrates.

Here, we demonstrate a new technique to evaluate NP connectivity independent of substrate. In principle, the proposed technique should be easily extendable to different systems given kinetic criteria described below can be met. As presented in Figure 6, Pt NPs are first electrodeposited from water droplets onto an amorphous carbon or HOPG substrate, as previously reported.\(^\text{17}\) Details of the electrodeposition are presented in section 2.7. Briefly, following emulsion preparation, 2 mL of solution was added to a cell with a 2 mm radius exposed carbon working electrode biased at −0.4 V vs Ag/AgCl QRE,\(^\text{43}\) thereby allowing Pt NP formation at the carbon substrate following droplet–electrode collisions with a total deposition time of 300 s. The Pt NP-decorated carbon electrode was then rinsed with DCE, ethanol, and water for 5 min each. Subsequently, 2 mL of a 50 μM CuSO\(_4\)·5H\(_2\)O solution with 0.25 M KCl supporting electrolyte was added to the cell and the working electrode was biased at −0.2 V vs Ag/AgCl for 25 s to induce preferential Cu electroplating at the Pt NP surface with minimal deposition on the underlying exposed carbon substrate. SEM/EDX was then used to elucidate single-NP elemental composition. Figure 6 shows a schematic representation of the experimental workflow. Nanodroplet-mediated electrodeposition was used to electrodeposit porous Pt NPs onto amorphous carbon and HOPG substrates. These NPs were compared to commercial citrate-capped Pt NPs (diameter of 70 nm) that were adsorbed onto the aforementioned substrates by drop-casting. A Cu electrodeposition step, shown in the figure as a potential-step experiment, was then used to deposit Cu on NPs with an underlying connection, which was analyzed using SEM/EDX. As stated in the previous sentence, each step is associated with a potential-step experiment except for drop-casting, and these potential–time profiles are also shown in Figure 6 for clarity. The lines around 0.4 V indicate discrepancies in the experimental open-circuit potential, which arise from different species dominating the two half reactions at the electrode surface when the cell is at open circuit.\(^\text{44}\)

This two-step electrodeposition technique to probe electrical connectivity at the single-NP level takes advantage of electrochemical kinetic parameters to allow deposition of a Cu film on Pt NPs with underlying connection while leaving the substrate electrode without any deposition. It is important to note that this method takes advantage of two distinct kinetic parameters: the heterogeneous electron-transfer rate and the

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Figure 5. 3D-rendered NP for pore visualization and quantification. (a) Surface rendering of NP by 3D rendering of nanoSlice images shows extensive porosity. Image resolution of 0.8 nm/pixel allows clear visualization of individual <10 nm pores. (b) Surface rendering showing complete pore network within a single NP. Comparing the pore volume to the total particle volume indicates a porosity value of 16.2% for the NP. Individual pore networks are colored to facilitate visualization on the basis of voxel (3D pixel) interaction between slices. (c) Filtered pore network reveals tortuosity of larger pores winding through the NP. A calculated tortuosity factor of 17.4 quantitatively describes the movement of the pores’ center of mass through the NP. (d) Theoretical (red curve) hemispherical NP radii and the observed (blue curve) radii with volume correction from pore analysis. The green curve represents the corrected theoretical curve taking into account the 15% volume correction.
rate at which metal nuclei nucleate (induction time) and subsequent growth ensues. The heterogeneous electron-transfer kinetics of 50 μM Cu²⁺ reduction to Cu⁰ suggests that deposition on a Pt macrodisk electrode would occur at a faster rate than on a similar HOPG electrode, as evidenced in cyclic voltammetry (Figure 7a) by the sharper current increase of copper deposition on Pt compared to HOPG. In addition to this observed difference in heterogeneous electron-transfer kinetics, the kinetics of Cu nucleation was highly substrate-dependent, as evidenced by the difference in induction time of Cu nuclei on Pt (Figure 7b), HOPG (Figure 7c), and amorphous graphite (Figure S3). While Cu electroplating on a Pt macrodisk electrode resulted in characteristic current increase following the familiar nucleation and growth profile after 15 s of electrodeposition, nucleation on HOPG was observed after 800 s, suggesting large differences in the kinetics of nucleation. The background decay is likely an artifact of the potential step experiment (“Amperometric i-t” technique on the CH Instruments potentiostat), which will step from the open-circuit voltage to the applied potential. In these experiments, the open-circuit potential is a mixed potential that is not constant and is governed by undefined half reactions, as mentioned above. While we acknowledge that the background decay is much longer than what is expected for the double-layer relaxation time constant, the origin of the decay is still under investigation in our laboratory and has been observed before in the nucleation and growth literature. Given these results, a deposition window based on the time of nuclei birth can be employed to control electrodeposition of Cu on Pt NPs with underlying electrical connectivity while maintaining a carbon substrate free of Cu NPs or films. From this type of analysis, we chose an electroplating time of 25 s.

Figure 6. Experimental schematic to probe Pt NP electrical connection by two-step deposition pulse technique. Electrosynthesized Pt NPs were fabricated via nanodroplet-mediated electrodeposition following droplet collision at a biased HOPG or amorphous graphite working electrode. Commercial citrate-capped Pt NPs were drop-cast on carbon working electrodes without applied electrical bias. Electrical connectivity was probed by depositing a Cu film from an aqueous solution for a time frame sufficient to induce Cu nucleation at Pt NPs with underlying electrical connection while insufficient to induce nucleation at the carbon electrode. The potential-step profiles for Pt NP electrodeposition and Cu electroplating are presented wherein a constant potential is held for the duration of electrodeposition. The lines around 0.4 V indicate discrepancies in the open-circuit potential, which is dominated by dissimilar half reactions.

Figure 7. Cu²⁺ reduction kinetic data. (a) Cyclic voltammetry of 50 μM CuSO₄·SH₂O reduction indicating sluggish deposition on HOPG compared to Pt. (b) Amperometric i-t curve of 50 μM CuSO₄·SH₂O deposition (−0.2 V vs Ag/AgCl) on a Pt macrodisk electrode with an induction time at t = 15 s. (c) Amperometric i-t curve of 50 μM CuSO₄·SH₂O deposition (−0.2 V vs Ag/AgCl) on a HOPG macrodisk electrode with an induction time after 800 s.
While SEM confirms NP presence, EDX elemental analysis confirms if both Pt and Cu are present. EDX offers adequate elemental selectivity due to the differences in principal Cu, Pt, and C X-ray peaks, thereby offering single-NP quantitative analysis based on elemental composition. As electrical connectivity is a prerequisite for conventional electroplating, Pt NPs with an underlying connection would be predicted to demonstrate distinct Cu and Pt X-ray signals detected by EDX while Pt NPs lacking connection would lack significant Cu X-ray peaks. Importantly, EDX analysis of Pt NPs immersed in 50 μM CuSO₄·5H₂O with 0.25 M KCl without an electrical bias did not indicate Cu X-ray character, confirming electrodeposition as the principal source of Cu signal. A representative EDX map of a single Pt NP following Cu electroplating is presented in Figure 8a, indicating homoge-

![Figure 8](image_url)

**Figure 8.** Cu electroplating on Pt NPs and electrical connectivity. (a) Representative SEM image and EDX elemental mapping of a single Pt NP following Cu electroplating. Importantly, the HOPG electrode does not display significant Cu plating, verifying selective electrodeposition onto Pt NPs. (b) Electrical connectivity fraction of droplet-deposited and adsorbed NPs by drop-casting with subsequent Cu electroplating reveals statistically significant differences in fraction of analyzed NPs with underlying connection (ANOVA with Tukey multiple comparison test).

3.3. Implications of Connectivity Results. The electrical connectivity findings presented in this study have implications to energy storage and conversion devices and fundamental studies of NP–electrode interactions. For instance, electrocatalysis has previously been studied by adsorbing electrocatalytic materials onto conductive surfaces. In these experiments, however, the number of units that have underlying electrical connectivity with the substrate is not reported. Furthermore, the study of NP collisions with UMEs has received great attention in the past decade. In 2007, Bard and Xiao spearheaded the electrocatalytic amplification experiment. In this experiment, a relatively inert electrode is biased at a potential where an inner-sphere reaction will not occur on the inert electrode but will occur on a catalytic nanoparticle that collides and adsorbs to the UME surface. For instance, proton reduction is kinetically hindered on carbon compared to Pt. Thus, if a carbon UME is biased at a potential where proton reduction does not occur in an acidic solution, and a single Pt NP adsorbs to the electrode surface, an increase in current will be observed that corresponds to proton reduction on the Pt NP. Thus, this increase in current is the electrocatalysis at a single Pt NP. These kinetic differences have also been taken advantage of for OCP measurements. Other experiments also exist for the electrochemical observation of single-NP collisions for insulating NPs; conductive NPs that can electrochemically etch; and soft NPs, such as emulsion droplets and single ions and atoms. Historically, the frequency of collision has been difficult to quantify and does not always match what one would expect for freely diffusing NPs following Fick’s Law. Our findings indicate that perhaps not all NP collisions result in an electrochemical response. At this time, it is difficult to understand why NPs lack electrical connectivity, and this is an active pursuit of our laboratory. As stated above, one would expect electrical connectivity between the NP and the substrate electrode because the overlap of DoS

3.4. Limitations of Presented Techniques. While the methods presented above will likely find many applications across different fields, there are some limitations to the demonstrated techniques that should be outlined. The methods described here do not require specialized optical equipment; however, they do require access to a FIB-SEM instrument that is EDX-capable. Implementing the nanoslice method on such small particles requires careful attention to complicating factors, such as particle degradation and compensation for beam drift under both the electron beam and the ion beam. During the necessary control experiments to determine the ion beam effect over the entirety of the NP, we observed a high degree of particle instability (i.e., visible surface deformation after beam exposure) over long exposure times. Even at ion beam currents of 1.5 pA, the minimum for the instrument used in this study, imaging with the ion beam led to obvious degradation of the particle within a one second time frame. To determine the effect of the gallium ion beam on our particles, we subjected particles to the lowest possible beam currents (1.5 pA) and took SEM images to observe the response. Figure 9 shows a series of images and timestamps...
Figure 9. Image progression shows effect of gallium ion beam at 1.5pA, 30KeV over the entire Pt NP as a function of exposure time, as indicated by the time given in each panel. After 2 s, obvious surface deformation occurs. The application of a blind alignment technique outlined in the main text avoids particle beam exposure before patterning.

indicating NP instability over short periods of beam exposure at the lowest current. Because of this instability, we employed the blind alignment method described above to avoid compromising NPs. Blind alignment also requires more user time. Thus, users have to take care not to allow the beam to influence the particles, which could ultimately alter values of porosity. When attempting to image NPs <50 nm in radius, a magnification increase becomes necessary to enable high-resolution images of the internal pore network. However, increasing the magnification tends to exaggerate the effects of the drift in both the ion beam and the electron beam, making accurate patterning time-consuming and unreliable. Despite the aforementioned limitations, this method proved rather robust in this report as a reliable means of extracting information from single electrodeposited NPs, information (i.e., nanopore tortuosity) that has been previously unobtainable. A main limitation in measuring tortuosity using this method is the physical slicing of the NPs using FIB. Currently, the limitation is the resolution of the beam, which was between 5 and 15 nm in this study. Using beams with smaller atoms, such as helium and neon, might mitigate this issue and increase the resolution, which increases the precision of the tortuosity measurement. In this study, NPs down to 45 nm in radius were investigated. We also found that the beam slice resolution was 10 nm, which is consistent with previous reports. This ultimately affects the values of tortuosity. Given the difficulty of blind alignment, the image quality of SEM, and the slice resolution, we found it difficult to slice NPs smaller than 35 nm in radius. Regarding NP connectivity, the analysis necessitates a system where differences in heterogeneous kinetics and electrodeposition kinetics can be exploited to study whether a NP has an underlying connection with the substrate electrode. While these differences in kinetics may not always be obvious, the workflow presented in this report represents a reproducible means of optimizing parameters.

4. CONCLUSIONS

In this report, we have shown that Pt NPs synthesized by nanodroplet-mediated electrodeposition are nanoporous by extending FIB tomography to small NPs, where the slice resolution achieved was ca. 10 nm. FIB-nST offers porosity information as a function of depth independent of substrate, and 3D rendering of these slices allowed for the visualization and quantification of nanopore tortuosity at the single-NP level. The porosity analysis also offered a volume correction for the NPs, which explained their larger deposit size. These 3D representations facilitated the visualization of nanopore tortuosity, surface-area-to-volume ratio, and total particle surface area for comprehensive NP tomographic characterization.

We also showed that NPs synthesized by electrodeposition have >98% underlying connection with the substrate electrode (see Figure 8b). Surprisingly, however, NPs adsorbed onto HOPG by drop-casting had less than 80% connectivity, and NPs adsorbed onto amorphous graphite by drop-casting had less than 40% connectivity. These particular results indicate careful considerations should be taken when quantifying parameters of energy storage and conversion devices as well as fundamental studies of how NPs interact with electrode surfaces.


