A One-Pot Route to Faceted FePt-Fe₃O₄ Dumbbells: Probing Morphology–Catalytic Activity Effects in O₂ Reduction Catalysis

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The design and synthesis of faceted nanoparticles with a controlled composition is of enormous importance to modern catalyst engineering. Faceted FePt-Fe₃O₄ dumbbell nanoparticles are prepared by a simple, one-pot technique that avoids the need for expensive additives or preformed seeds. The faceted product consists of an FePt octopod and a cubic Fe₃O₄ lobe, of mean diameter 13.6 and 14.9 nm, respectively. The mass normalized activity for electrocatalytic oxygen reduction shows that this new structure types outperforms related catalysts in alkaline media. This work illustrates the power of morphology control and tailoring crystal facet abundance at the nanoparticle surface for enhancing catalytic performance.

1. Introduction

The synthesis of metal nanoparticles (NPs) with precisely controlled shapes that express selected crystal faces is highly desirable.[1] Such morphology manipulation can be a powerful way of tailoring electronic, optical, catalytic,[2–5] and magnetic properties.[6–8] Anisotropic NPs show asymmetric morphology, with one recently reported subset being nanopods,[9] in which NPs demonstrate a distinct branched morphology. An octopod (OP) is a cube-like nanopod with overgrowth at the corners giving eight branches.[10] Considering the wealth of desirable properties of Pt and its base-metal alloys, they are ideal candidates for morphology development with the aim of generating catalytically active and/or magnetically recyclable nanopods.[2,11–13]

When developing anisotropic NP syntheses, morphology can be controlled[14] to minimize the surface free energy of a material by allowing the movement of newly deposited atoms to alternative lower-energy facets during particle growth. While this often results in pseudospherical NPs, there are several simple parameters that can be manipulated to favor an anisotropic growth mechanism. These include temperature,[15,16] pressure,[8,14,17] stabilizing agents,[9] reducing agent,[18] monomer concentration,[8,16,19] accessible polymorphs,[15] and the presence of seed NPs[20] or metal additives.[15,11] However, these also influence particle size, dispersity, and composition.

Three approaches recur in attempts to increase the activity and/or selectivity of Pt-based NP catalysts. First, the synthesis of faceted NPs[21,22] with increased surface area. Controlling growth at specific facets can induce branched NPs that may provide high surface areas and hence catalytic activity even at larger particle sizes.[23] Moreover, it has been suggested that NPs preferentially store surface charge at the tips and edges of branches during catalysis.[24] Thus, for example, Ma et al. found the activity of branched Pt structures in formic acid oxidation to improve with the number of branches.[25] Other work has yielded NPs that express unnatural abundances of high-reactivity surface facets. For example, within the NiPt bimetallic alloys, oxygen reduction reaction (ORR) activity varies with faceting according to the trend (100) < (110) < (111),[26] where the (111) facet shows a tenfold increase in ORR activity compared to monometallic Pt.[27] As a consequence, highly active ORR catalysts have been achieved through the synthesis of NiPt polyhedra, such as octahedra[28] and icosahedra[29] with exclusively (111) surface termination, or truncated octahedra[30] dominated by (111) terminating facets. However, the syntheses of these has typically necessitated the complexity of adding preformed morphology-directing seeds[31,32] or the expense of including Au or Ag additives.[33] Second, the formation of bimetallic alloys. This enables charge transfer between atoms[34] that yields unique active surface sites, allows the manipulation of substrate adsorption/desorption kinetics,[34,35] and can introduce surface strain.[36] The extent of alloying has been shown to dramatically affect the overall ORR activity of individually bimetallic FePt NPs, with the optimal composition reported to be Fe₇₅Pt₂₅ for pseudospherical NPs.[37] Third, heterojunction formation, which can yield bimetallic active centers. Hence, Sun and co-workers used dumbbell-structured NPs to improve...
catalytic ORR activity by adding an iron oxide phase to small Pt NPs.\cite{38} They also harnessed the electron-donating ability of the oxide lobe in FePt-Fe$_3$O$_4$ dumbbells to improve sensitivity for the electrocatalytic detection and reduction of dopamine.\cite{19}

Some work has attempted to combine the points above. For example, NiPt hexapods synthesized by a complex oxidative etching and CO gas adsorption methodology\cite{40} proved viable for ORR. Likewise, CoPt$_3$ OPs showed impressive activity in CO hydrogenation.\cite{24} Meanwhile, although anisotropic FePt NPs have seldom been prepared, Paez-Pérez et al. reported FePt OPs for theranostics.\cite{41} Although this synthesis required neither an initial seed particle nor expensive metal additives to induce branching, compositional control proved difficult; in spite of using a 2:1 Fe:Pt molar ratio, mean OP composition was Fe$_{35}$Pt$_{65}$. Indeed, reports of cubic or pseudospherical FePt NP syntheses have typically used a 2–3 molar excess of Fe precursor. This helped offset the formation of unreactive iron(III) oleates, which caused a lack of Fe in the final product.\cite{42}

In this work, the synthesis is reported of a range of complex heterobimetallic NPs through the simultaneous polyol reduction of Pt(acac)$_2$ and thermal decomposition of Fe(CO)$_5$, as previously reported by Sun and co-workers.\cite{42} Uniquely, it is shown for the first time that control can be exerted over faceting and alloying within NPs that demonstrate a dumbbell heterodimer structure. A simple and reproducible one-pot methodology is employed, which avoids the need for acidic etching or expensive additives. Not only is the selective generation of a faceted heterostructure reported, but also it proves possible to systematically vary the morphology of either dumbbell component through simple changes to synthetic parameters. The new morphology incorporates a unique combination of traits considered beneficial for catalysis. The advantages offered are explored for ORR in alkaline media and structure-property relationships for a range of morphologies are compared.

### 2. Results and Discussion

#### 2.1. Nanoparticle Synthesis

To the authors' knowledge, varying the availability of Fe for alloy formation during NP synthesis through simple surfactant variations has not been explored. Given the simplicity of faceted NP formation demonstrated using an equimolar mixture of oleic acid (OA) and oleylamine (OAm),\cite{41} the preparation of FePt alloys was targeted under a range of surfactant ratios. Simultaneous reduction of Pt(acac)$_2$ and thermal decomposition of Fe(CO)$_5$ in exclusively OA (see Figures S1 and S2, Supporting Information) immediately achieved a morphology drastically different to OPs expected following previous FePt syntheses that used 50:50 OA:OAm.\cite{41} Transmission electron microscopy (TEM) analysis of the products obtained shows a mixture of pseudospherical ($d_{\text{ave}} = 4.7 \pm 0.88 \text{ nm}$), cubic and rod ($l_{\text{ave}} = 11.3 \pm 3.0 \text{ nm}$) NPs. The introduction of OAm (OA:OAm 75:25, Figures S3 and S4, Supporting Information), gave only polydisperse pseudospheres ($d_{\text{ave}} = 4.8 \pm 0.9 \text{ nm}$). Meanwhile, equimolar OA:OAm (Figures S5 and S6, Supporting Information) gave particles consistent with previously reported OPs\cite{41} ($d_{\text{ave}} = 14.2 \pm 1.5 \text{ nm}$) with a Pt-rich composition, denoted OP$_{Pt}$. Finally, using an excess of OAm (OA:OAm 25:75, Figures S7–S10, Supporting Information), remarkably gave faceted heterodimeric dumbbells, as shown by scanning TEM-high angle annular dark field (STEM-HAADF) imaging in Figure 1a. STEM-HAADF data reveal that the brighter phase has maintained OP morphology, while the darker phase is cubic (OP $d_{\text{ave}}$ (tip to tip across the diagonal OP face) = 13.6 ± 1.4 nm; cubic $d_{\text{ave}} = 14.9 ± 2.1 \text{ nm}$). This unprecedented morphology will be referred to as OPD$_C$. Finally, when using exclusively OAm (Figures S11 and S12, Supporting Information), brightfield (BF) TEM revealed predominantly pseudospheres ($d_{\text{ave}} = 3.5 ± 0.4 \text{ nm}$) containing also some nanowires. In both structures, a lighter phase surrounds a darker particle, suggesting a Pt$_x$Fe$_{1-x}$ core and a Fe$_3$O$_4$ shell.

Overall, these data reveal a strong influence of surfactant ratio on both product morphology and composition. In terms of developing anisotropic NPs, either a 50:50 (OP$_{Pt}$) or 25:75 (OPD$_C$) OA:OAm ratio proves desirable. This outcome agrees with reports by Chou et al.,\cite{10} where a mixture of OA and OAm was required to modulate the relative growth between the (111) and (100) facets of FePt. Chou found that OAm preferentially bound to the (100) facet (cube face). This allowed significantly faster growth on the (111) facet (cube corners) of a cuboctahedral seed and so produced branches. Alternatively, OA was found to interact with both facets indiscriminately, and so to produce a highly symmetric cuboctahedral morphology. Similarly, Chen et al. previously noted the preferential formation of FePt nanocubes in OA:OAm mixtures with the sequential addition of OA and OAm. Nanocubes were exclusively formed, with OA addition first allowing the overgrowth of the (100) cube face.\cite{43} However, further to the purely morphology-directing nature of the surfactant mixture, the current work now demonstrates that varying OA and OAm concentrations can also allow tailoring of the final NP composition within these faceted structures. Such enhanced composition control can be achieved using excess OAm when higher levels of Fe inclusion are required. Hence, when OAm is in excess (OPD$_C$) or is used exclusively there is evidence of a lighter iron oxide phase in a dumbbell or core@shell structure, respectively. These data are expected based upon the limited or nonexistent capability of forming unreactive Fe oleates in OAm-rich systems, leading to a higher concentration of reactive Fe precursor in the reactions in spite of the initial Fe(CO)$_5$ concentration being constant in all syntheses.

The structure observed in OPD$_C$ particles provides a unique combination of both anisotropic NPs that offer an unusual variety of crystalline facets, and dumbbells that allow access to multiple chemical surfaces within single uniform NPs. From Figure 1a, the octopod and cubic lobes are lighter and darker, respectively. The former is logically monometallic Pt or bimetallic FePt, with the latter expected to consist solely of Fe, which passively oxidizes upon atmospheric exposure. High-resolution (HR) TEM data in Figure 1b show a representative OPD$_C$ particle with indexed atomic planes (also Figure S13, Supporting Information). The octopods and cubic lobes show atomic spacing consistent with fcc Pt or FePt [111] and Fe$_3$O$_4$ [113], respectively. While it is challenging to distinguish microscopically between Fe$_3$O$_4$ and γ-Fe$_2$O$_3$, passive oxidation will likely form Fe$_3$O$_4$, whereas γ-Fe$_2$O$_3$ needs strongly oxidizing conditions.\cite{44} Figure 1c,d shows the STEM energy dispersive X-ray (EDX) analysis of OPD$_C$ NPs (also Figures S14 and S15, Supporting Information). This establishes that, of the two possible
products. OPDc consists of FePt-Fe₃O₄ and not Pt-Fe₃O₄; these
data are consistent with the linescan in Figure 1f (Figure S16,
Supporting Information). Area pointscans of either region of
the OPDc (Figure S17, Supporting Information) confirm that
the Fe₃O₄ lobes do not contain Pt, whereas the octopod lobe
shows an Fe:Pt atomic ratio of 0.8:0.7, suggesting Fe₅₃Pt₄₇-
Fe₃O₄. These data are corroborated by analysis of multiple OPDc
structures in the sample (Figure S18, Supporting Information).

Though the octopod synthesis performed by Pazos-Pérez et al.
(OPₙ) used Fe and Pt precursors in a 2:1 ratio, a mean Fe₁₂Pt₈₈
composition resulted. However, the current work reveals that
Fe contribution to the product can be controllably increased by
reducing the quantity of OA used and introducing OAm instead.

This understanding led to the targeting of an OP structure with
an ≈Fe₅₀Pt₅₀ composition by repeating the OPDc synthesis by
retaining a 25:75 OA:OAm ratio but using only half as much
Fe(CO)₅. Of the three rational outcomes of this experiment—1)
Pt-Fe₃O₄ OPDs, 2) FePt-Fe₃O₄ OPDs containing less Fe, or 3) FePt
OPs—the desired outcome was realized; Figure 1e shows the
product to be octopods (OPFePt, dave = 17.7 ± 2.0 nm; Figures S19
and S20, Supporting Information). This gives an indication of
the OPDc growth mechanism, suggesting initial FePt octopod
formation, with any remaining iron precursor forming the
Fe₃O₄ component of the dumbbell structure. Furthermore,
manipulating the surfactant ratios makes it possible for the first
time to create an FePt octopod with a controlled morphology and
a) Reaction scheme illustrating the transition from DD to OPD morphology in FePt octopod formation using 25:75 OA:OAm and varying intermediate reaction temperature. b–e) STEM-HAADF images of NPs synthesized with initial temperatures of 180, 200, 240, and 260 °C. All scale bars 25 nm.

Figure 2. a) Reaction scheme illustrating the transition from DD to OPD, morphology in FePt octopod formation using 25:75 OA:OAm and varying intermediate reaction temperature. b–e) STEM-HAADF images of NPs synthesized with initial temperatures of 180, 200, 240, and 260 °C. All scale bars 25 nm.

=Fe_{50}Pt_{50} composition starting with a 1:1 metal precursor ratio. Hence, STEM-EDX point scan analysis of an individual OP gives a composition of Fe_{25}Pt_{75}, while the interrogation of three additional OPs gives a mean atomic composition of Fe_{47}Pt_{53} (Figure S21, Supporting Information). This represents a significant increase in Fe contribution compared to that in OP_{Pt} (Fe_{25}Pt_{75}, Figure S22, Supporting Information). Finally, Figure Ig compares the powder X-ray diffraction (PXRD) patterns of OPD, and OP_{FePt}. These data illustrate a lack of Fe_{3}O_{4} within the octopod component of the former, supporting TEM analysis.

While focusing on parameters that can achieve the desirable OPD, structure, the influence of temperature on morphology and composition has also been investigated. Initial preparation of OPD NPs involved heating a reaction mixture to the intermediate temperature of 240 °C for 1 h followed by 260 °C for 2 h (X = 240 in Figure 2a). Figure 2b–e shows STEM-HAADF images of NPs synthesized with intermediate temperatures of 180–260 °C. At 180 °C the dumbbell structure is maintained but, rather than an octopod, the brighter Pt-containing phase is shown by STEM-HAADF imaging to have a dendritic morphology. Figure 2b shows such dendrite-dumbbell, DD, structures (Figures S23 and S24, Supporting Information). Increasing this intermediate temperature to 200 °C in Figure 2c (Figure S25, Supporting Information) maintains the dendritic Pt-rich phase. However, the ability of the Fe_{3}O_{4} lobe to form a dumbbell is inconsistent throughout the sample. Finally, raising the temperature immediately to 260 °C gives a structure, in Figure 2e and Figure S26 (Supporting Information), similar to the OPD, structure produced in the original 240 °C synthesis (Figure 2d). Additional studies conducted on composition and morphology relationships within FePt OPs (Figures S27–S31, Supporting Information) reinforce the conclusion of the temperature study above. Namely, reactions in which the concentration of active Fe is reduced, either by lowering intermediate reaction temperature or using less Fe(CO)_{5}, yield products that incorporate a dendritic component. Indeed, dendrite formation within an Fe-depleted reaction mixture (see the Supporting Information) indicates a possible mechanism for DD growth at 180 °C and is evidenced in Figure 2b. In this case, the Fe(CO)_{5} is present within the reaction mixture, yet the low temperature restricts decomposition from generating reactive iron in situ. Thus, the DD structure more closely resembles the morphology of Pt dendrites formed in the absence of Fe(CO)_{5}.

Upon increasing the temperature of the 180 °C system to allow reaction completion, the final DD structure (Figure S23, Supporting Information) is achieved, containing an intermixed FePt dendrite phase. Taken together, data illustrate how the synthetic method developed here can selectively manipulate the FePt component of a dumbbell to give the highly desirable faceted OP structure whilst also maintaining that component’s \(\approx\)Fe_{50}Pt_{50} composition.

2.2. Oxygen Reduction Electrocatalysis

As noted earlier, the activity of modern Pt catalysts can be improved by faceting, increasing surface area, and creating heterostructures with modulated electronic properties and reactive heterojunctions. With this in mind, the potential of the newly created OPD, morphology offered in terms of manipulating all these key traits was tested in electrocatalytic ORR. The use of alkaline media for ORR is an emerging area and offers higher stability for the Fe_{3}O_{4} component compared to traditionally employed acidic media. To understand the influence of the unique morphology, chemical composition and dual surface of the OPD, their activity was compared with those of structures exhibiting only one trait with the potential to improve ORR activity. To interpret the role of morphology within a dumbbell structure, pseudospherical FePt-Fe_{3}O_{4} dumbbells (denoted PSD) were made based on a reported method (Figures S32 and S33, Supporting Information). Interestingly, when this methodology was modified to use 25:75 OA:OAm, echoing the synthesis of OPD, a OPD product resulted (Figures S34 and S35, Supporting Information). The key difference between OPD and OPD is in the morphology of the Fe_{3}O_{4} phase; that in OPD is uniform and cubic, whereas that in OPD is globular and indistinct. Meanwhile, a comparison of OP_{FePt} and OPD probed the effect of the Fe_{3}O_{4} lobe. In addition, the influence of octopod composition was studied by comparing OP_{FePt} with OP_{FePt}. Finally, a comparison of FePt-Fe_{3}O_{4} PSDs and OPD elucidated the importance of a faceted structure. NPs used for electrocatalytic ORR testing are summarized in Figure 3.

Figure 4a shows linear scan voltammograms for ORR at potentials of −0.05 to −0.3 V versus saturated calomel electrode (SCE; for conversion to reversible hydrogen electrode see the Experimental Section) for the five morphologies summarized in Figure 3 and also industry standard Pt. The electrocatalytic tests were performed in a three-electrode setup with a rotating-ring disk working electrode in 1 M aqueous KOH under saturated oxygen conditions. Each sample was measured at room temperature using an identical Pt loading of 0.5 µg per disk. At −0.06 V, the onset potential of the OPD is competitive with the commonly used industrial standard 40% Pt on C (Sigma Aldrich), and is at a substantially more positive potential than for the other samples. This points to a more active morphology that enables the reduction of oxygen while requiring less voltage at the same mass loading of platinum. The remaining NP morphologies show similar onset potentials, with the OPD morphology being slightly more favorable. Taken together, these data point to OPDs being a promising morphology for ORR. Figure 4b shows mass activity normalized for Pt at −0.2 V.
versus SCE. The performance of OPD_c exceeds those of OPD_g and Pt. The 300% increase in mass activity suggests either that the morphology of the Fe₃O₄ phase is a critical determinant of mass activity or that active sites are generated at the FePt-Fe₃O₄ interface. Moreover, it is noteworthy that the activity of Fe-rich OPFePt is boosted by 400% by introducing a monodisperse cubic Fe₃O₄ phase (OPD_c vs OP FePt). This can be explained by Fe within Fe₃O₄ donating electron density to Pt, as shown by work on nonfaceted systems. [38] Similarly, Figure 4b also allows a comparison of OPPt (high Pt content) and OP FePt (≈50:50 FePt), showing a significant increase in mass activity with increased Fe content. These data provide further support for the desirable composition of the octopod phase within OPD_c.

Finally, FePt-Fe₃O₄ PSDs[24] show relatively low activity. This is surprising since they are substantially smaller than the OPD particles, so for an equivalent mass of Pt a larger surface area and a higher activity would be expected. Further experimental data can be found in the Supporting Information (Figures S36–S41, Supporting Information). ORR can proceed via a 2e⁻ or 4e⁻ reduction to yield H₂O₂ or H₂O as final products, respectively. The corrosive nature of H₂O₂ renders its production undesirable in fuel cell technologies. ORR activity was therefore tested on a rotating-ring disk electrode to simultaneously measure peroxide production (Figures S44 and S45, Supporting Information, for Faradaic efficiencies). [46] At −0.2 V, there is little difference between the selectivity of each morphology for a 4e⁻ reduction. However, at more negative potentials, a greater selectivity for H₂O is demonstrated by catalysts that incorporate a higher concentration of Fe. Overall, the OPD_c particles show far superior activity with a minimal compromise in selectivity for H₂O. A comparison of the mass activity of the new OPD_c with both PSD Pt-Fe₃O₄[38] and industrial standard Pt shows that OPD_c has a far greater mass activity at −0.2 V versus SCE. This superior morphology can be prepared by a one-pot technique that avoids the need to isolate and purify Pt seeds, ensuring both greater reproducibility and atom efficiency. A combination of density functional theory (DFT) and spectroscopic studies are being initiated to explore the effects of faceting and the nature of active sites in the OPD_c morphology.
3. Conclusion

In conclusion, a facile one-pot reaction that achieves uniform and complex NPs is reported. These data reveal not only a bimetallic alloy, but also a dumbbell morphology that shows selective faceting on both lobes. Through temperature control, it is possible to selectively manipulate the morphology of the FePt lobe while maintaining a desirable Fe₉₀Pt₃₀ composition. In ORR under alkaline conditions, this new material, FePt-Fe₉₀Pt₃₀ octopod dumbbells, substantially outperforms a series of comparable samples, illustrating the importance of composition, morphology, and interface control as a means of enhancing catalytic activity.

4. Experimental Section

Materials: Fe(CO)₅ (99.99%), Nafion perfluorinated resin, oleic acid (99%), oleylamine (70%), octadecene (90%), KOH (semiconductor grade), and Pt on graphitized carbon (20 wt%) were purchased from Acros Organics. Water was reagent grade deionized milliQ water (Ultrapure Type 1, Merck Simplicity ultrapure water system, 18.2 MΩ cm at 25 °C).

**OPD, Synthesis:** Pt(acac)₂ (0.25 mmol, 98.32 mg), oleic acid (5 mmol, 1.585 mL), and oleyl amine (15 mmol, 5.88 mL) were added followed by the temperature being increased to 240 °C for 1 h and 260 °C for 2 h. Upon cooling to room temperature, the NPs were sedimented in EtOH (30 mL) and redispersed in hexane (10 mL).

**Pt(acac)₂ Synthesis:** Pt(acac)₂ (0.25 mmol, 98.32 mg), oleic acid (2 mmol, 0.64 mL), oleylamine (2 mmol, 0.66 mL), and octadecene (5 mmL) were mixed under Ar at room temperature. The temperature was increased to 105 °C for 10 min to remove H₂O and ensure dissolution of the precursors. Fe(CO)₅ (0.1 mL) was added at 120 °C and the temperature increased to 300 °C at a heating rate of 5 °C min⁻¹, where it was maintained for 1 h before cooling to room temperature.

**Materials Characterization:** For TEM analysis, extensive washing of NPs by sedimentation in EtOH was followed by sonication in hexane and drop-casting on a lacey carbon copper grid. The grid was plasma cleaned for 40 s before TEM analysis was performed using a Thermo Scientific (FEI) Talos F200X G2 TEM or FEI Philips Tecnai 20, 200 keV cleaned for 40 s before TEM analysis was performed using a Thermo Scientific (FEI) Talos F200X G2 TEM or FEI Philips Tecnai 20, 200 keV.

**ORR Electrocatalysis:** Fe₉₀Pt₃₀/C ink was prepared following a published literature method for Pt-Fe₉₀Pt₃₀ dumbbells to aid comparison.[38] Inductively coupled plasma-optical emission spectroscopy analysis was used to determine the concentration of Pt within the Fe₉₀Pt₃₀/C inks, which were then diluted as necessary to generate a Pt loading of 1–2 orders of magnitude lower. The low loading was chosen in line with work on similar heterobimetallic dumbbell particles for ease of comparison.[39] SCE to RHE conversion was achieved using Equation (1)

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.124 \, V \approx (\text{pH} \times 0.059 \, V) \]  

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrocatalysts, faceted nanoparticle, heterodimers, octopods, oxygen reduction

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