Supporting Information

Understanding Nanoparticle Porosity via Nanoimpacts and XPS: Electro-Oxidation of Platinum Nanoparticle Aggregates

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Calculation of the number of platinum atoms oxidised per PNP aggregate

For Model 1, the assumption was made that the PtNP is a solid, smooth sphere of radius 25 nm. This was calculated as a possible bound (limiting case). The volume ($\boldsymbol{V}_{\mathbf{solid,full}}$ / m^3) is

$$V_{\text{solid,full}} = \frac{4}{3}\pi R^3$$

where R is the radius of the non-porous, solid spherical PtNP.

The mass can be written as

$$m_{\text{solid,full}} = \rho V_{\text{solid,full}}$$

$$= (21.46 \times 10^6) \times \frac{4}{3}\pi(25 \times 10^{-9})^3$$

$$= 1.4 \times 10^{-15}\ \text{g}$$

where ρ is the density of platinum.[1]

Therefore, the total number of platinum atoms per PtNP is

$$N_{\text{Pt}} = \frac{1.4\times10^{-15}}{195.084} = 7.2 \times 10^{-18}\ \text{mol}$$

$$= 4.3 \times 10^6\ \text{atoms}$$

The surface area ($\boldsymbol{S}_{\mathbf{solid,surface}}$ / m^2) is

$$S_{\text{solid,surface}} = 4\pi R^2$$

Assuming optimal close-packing was adopted by the platinum atoms on a two-dimensional surface plane, the fractional filling efficiency ($\boldsymbol{f}_{\mathbf{solid,surface}}$) is 0.91 for spheres or ellipses[2] and the total surface area of all platinum atoms on the surface ($\boldsymbol{S}'_{\mathbf{solid,surface}}$ / m^2) can be written as

$$S'_{\text{solid,surface}} = 0.91 \times 4\pi R^2$$

The cross-sectional area ($\boldsymbol{a}_{\mathbf{Pt}}$ / m^2) of a platinum atom is

$$a_{\text{Pt}} = \pi r^2$$

Therefore, the number of platinum atoms on the surface of small nanoparticles per PtNP can be determined as

$$N_{\text{Pt}} = \frac{0.91\times4\pi(25\times10^{-9})^2}{\pi(138.5\times10^{-12})^2} = 1.2 \times 10^5\ \text{atoms}$$

For Model 2, each PtNP (ca. 25 nm radius) was considered to an aggregate of identical small nanoparticles (ca. 2.5 nm radius, estimated from Figure 2(b)). As it is difficult to know the inner configuration of the aggregates from the TEM images, these small solid spheres were assumed to arrange in a densest close-packing in space and the fractional filling efficiency ($\boldsymbol{f}_{\mathbf{porous,full}}$) is 0.74.[2] The volume of a spherical PtNP ($\boldsymbol{V}_{\mathbf{porous,full}}$ / m^3) is

$$V_{\text{porous,full}} = 0.74 \times \frac{4}{3}\pi R^3$$

The mass can be written as

$$m_{\text{porous,full}} = \rho V_{\text{porous,full}}$$

$$= (21.46 \times 10^6) \times 0.74 \times \frac{4}{3}\pi$$

$$= 1.0 \times 10^{-15}\ \text{g}$$

where ρ is the density of platinum.[1]

Hence the total number of platinum atoms per PtNP aggregate is

$$N_{\text{Pt}} = \frac{1.0\times10^{-15}}{195.084} = 5.33 \times 10^{-18}\ \text{mol}$$

$$= 3.2 \times 10^6\ \text{atoms}$$

Given fractional filling efficiency $\boldsymbol{f_{\text{porous,full}} = 0.74}$ for three-dimensional close-packing of small nanoparticles in each PtNP aggregate

$$S_{\text{porous,surface}} = 0.74 \times 10 \times 4\pi R^2$$

Therefore, the number of platinum atoms on the surface of small nanoparticles per PtNP aggregate is

$$N_{\text{Pt}} = \frac{0.91\times0.74\times10\times4\pi(25\times10^{-9})^2}{\pi(138.5\times10^{-12})^2} = 8.8 \times 10^5\ \text{atoms}$$

References

1. Haynes, W. M., *CRC Handbook of Chemistry and Physics, 97th Edition*. CRC Press: 2016.
2. Matsumoto, T.; Nowacki, W., On densest packings of ellipsoids. In *Zeitschrift für Kristallographie - Crystalline Materials*, 1966; Vol. 123, p 401.