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Shape-Dependent Electrocatalysis: Oxygen Reduction on Carbon-Supported Gold Nanoparticles

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Cubic, octahedral and quasi-spherical (two different particle sizes) Au nanoparticles are synthesised and dispersed in a carbon-black powder. The size and morphology of the Au nanocatalysts is confirmed by transmission electron microscopy and X-ray diffraction. Au nanospheres are approximately 5 and 30 nm in diameter, whereas the size of Au octahedra and nanocubes is approximately 40–45 nm. The electrocatalytic activity of these carbon-supported particles towards the oxygen

reduction reaction (ORR) is studied in 0.5 M H₂SO₄ and 0.1 M KOH solutions by using the rotating-disk-electrode method. The specific activity (SA) for O₂ reduction is measured, and the highest SA is observed for Au nanocubes supported on carbon. The highest mass activities are found for the smallest Au nanoparticles. Tafel analysis suggests that the mechanism of the ORR on shape-controlled Au/C catalysts is the same as on bulk Au.

1. Introduction

Noble-metal-based nanomaterials have a wide variety of applications in the field of catalysis. In addition, it is well established that the unique properties and enhanced catalytic performance of metal nanoparticles can be tuned by controlling their atomic composition, size and morphology. In particular, the influence of the particle shape is the focus of ongoing research. Several synthetic methods, including seeded growth, electrochemical methods, underpotential deposition, and those that involve the use of selective facet-capping agents, are being continuously developed for the preparation of shape-controlled nanoparticles, that is, nanoparticles with certain crystal facets exposed, as recently reviewed.^[1,2]

Gold nanoparticles (AuNPs) have received a great deal of attention and are being widely used—for their electrochemical properties—in electrochemical sensors, and as electrocatalytic materials in various reactions, such as oxidation of CO,^[3] oxidation of alcohols and reduction of oxygen.^[4]

The oxygen reduction reaction (ORR) is one of the most important electrochemical reactions and plays a role in several applications, including fuel cells and metal–air batteries.^[5,6] The most active electrocatalyst for ORR is Pt, whereas Au possesses rather modest catalytic activity. It has been demonstrated that the ORR activity of these materials can be improved by designing nanoparticles with a certain shape.^[7–14] The electrocatalysis of diO₂ reduction on shape-controlled Pd nanoparticles has also been investigated recently.^[15–18] Studies on Au single-crystal electrodes have shown that Au(100) is the most active low-index plane for ORR in alkaline media.^[19,20] The increased activi-

ty has been suggested to arise from AuOH species that facilitate stronger interaction with O₂, HO₂[–] and O₂[–].^[20] The highest ORR activity of Au(100) among low-index crystal planes in acidic media has been suggested to be caused by structural effects.^[21,22] More recently, it has been shown on the basis of spectroscopic data that the ORR takes place via a series mechanism where peroxide is the reaction intermediate in alkaline media,^[23] and the formation of adsorbed superoxide species is also evident.^[24] In contrast, the reduction of O₂ proceeds only through a two-electron process, yielding H₂O₂ as the final product on all Au single-crystal faces in acidic media.^[23] Polycrystalline Au can be modified so that an Au(100)-type structure would preferentially form, which increases the activity of the electrode in favour of the ORR.^[25] The higher ORR activity on Au(100) has also been shown using the impinging jet system.^[26]

The fact that the ORR activity of Au electrodes depends on the crystallographic orientation suggests a route to synthesise active catalysts by preparing AuNPs with certain shapes, namely nanocubes, as these have preferential (100) facets.^[9–12,27] In comparison with Au nanospheres or nanorods, nanocubes have shown much higher electrocatalytic activity towards the ORR. The final product of O₂ reduction on Au nanocubes and nanospheres was observed to be H₂O, whereas on nanorods the two-electron reduction of O₂ to H₂O₂ dominates.^[9–12] In contrast, triangular Au nanoprisms and nanoperiwinkles, composed mainly of a Au(111) lattice plane, support the two-step, four-electron reduction of O₂.^[13] More recently the ORR activity of Au nanospheres of two different sizes and Au nanorods has been reported.^[14] The highest activity was obtained with Au nanospheres with diameters of 20 nm. Au nanorods were less active, but it was suggested that the size effect of particle size outweighs the effect of shape. It has been shown very recently by Compton and co-workers that the ORR kinetics on citrate-capped AuNPs of 5 nm diameter is

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virtually the same as on bulk Au. However, a strong enhancement of electrocatalytic activity was observed in the presence of small amounts of underpotentially deposited lead.^[28]

Sarapuu et al. studied the electroreduction of O₂ on thin Au films prepared by vacuum evaporation and found that the specific activity (SA) does not depend on film thickness in H₂SO₄ solution, but in KOH solution the SA decreases with film thickness.^[29,30] Zeis et al. have demonstrated the high electrocatalytic activity of nanoporous Au for the reduction of O₂ and H₂O₂.^[31] Ohsaka and co-workers have carried out several studies on O₂ reduction on Au electrodeposited onto various substrates.^[32–38] The resulting electrodes possessed different morphology and thus different activity in the ORR, with AuNPs with Au(100)-like crystal structure showing the highest activity.^[35] In addition to these studies, El-Deab has shown how the deposition time affects the crystallographic orientation of the resulting electrodes—short deposition times yield Au(111)-rich surfaces and longer deposition times result in larger particles with preferred Au(100) and Au(110) surface orientation.^[39] Recently, Compton and co-workers have performed a thorough kinetic study of the ORR on electrodeposited AuNPs of diameters between 17–40 nm, and found small changes of electrode kinetics compared to a bulk Au electrode.^[40]

Studying the reduction of O₂ on unsupported nanoparticles gives important information about their properties, but these are not practical for application to real systems. Thus, AuNPs supported on high-area carbon materials such as carbon nanotubes or carbon black and, more recently, on graphene, have been used as electrocatalysts for O₂ reduction.^[41–54] Tang et al. investigated how Au particle size affects the ORR activity in a basic electrolyte.^[41] They found that 3 nm Au clusters on a carbon support exhibited higher ORR activity, and also a four-electron reduction of O₂ occurred on these particles, whereas on 7 nm AuNPs the two-electron reduction to HO₂[–] predominates. Similarly, Chen and Chen have shown that smaller AuNPs have higher electrocatalytic activity in alkaline solution.^[55] Bron studied the reduction of O₂ in an electrolyte containing sulphuric acid and found that the SA of Au is almost independent of particle size in the range 2.7–42.3 nm.^[48] In contrast, Inasaki and Kobayashi have shown that the SA increases with increasing particle size and the number of electrons transferred per O₂ molecule also increases.^[49] Brülle et al. has reported that electrochemically deposited AuNPs on highly oriented pyrolytic graphite and boron-doped diamond exhibit size–activity effects in sulphuric acid.^[56] Furthermore, Jirkovský et al. have observed particle-size effects in perchloric acid solution.^[51] Thus, the effect of particle size on catalytic activity is evident in alkaline as well as in acidic media, but still remains a topic of interest.^[57]

Alexeyeva et al. prepared AuNP/carbon-nanotube composite materials using different approaches and these catalysts showed high electrocatalytic ORR activity in acidic media.^[42,44–46] Previously, we have also studied the effect of Au/C layer thickness on the electrocatalytic activity for ORRs in acidic and alkaline solutions and found that the SA of Au is independent of catalyst loading.^[47] AuNPs in conjunction with organic compounds have also shown high activity for O₂ re-

duction.^[58,59] Experiments with Nafion-coated bulk Au electrodes showed no clear evidence of the enhancement effects of Nafion coatings on the cathodic O₂ reduction.^[60]

O₂ reduction has been also studied on Au/TiO₂ composite surfaces for which the voltammetric curve was similar to that of an Au(100) plane, and a four-electron O₂ reduction pathway dominated.^[61] Similarly, an Au catalyst has been used to enhance the electrocatalytic activity of SnO₂ for the ORR, showing that a small amount of Au significantly increases the kinetics of this reaction.^[62] An interesting approach has been used to prepare a composite catalyst with AuNPs and MnO particles to yield a four-electron reduction of O₂.^[37] ■ ■ what is the approach? ■ ■ However, despite these previous efforts, and to the best of our knowledge, the ORR activity of shape-controlled AuNPs supported on a carbon material has never been reported. In this work, carbon-supported Au nanocubes, octahedra and spherical AuNPs of two different sizes have been synthesised, and their electrocatalytic activity in ORRs has been studied using the rotating disk electrode (RDE) method.

2. Results and Discussion

2.1. Transmission Electron Microscopy (TEM) Characterisation of Au Nanoparticles and Au/C samples

Figure 1 a shows a set of TEM images of AuNPs prior to the addition of carbon. These images show that AuNPs have their preferred shape and thus are suitable for the preparation of Au/C catalysts.

Figure 2 shows representative TEM images of the carbon-supported AuNPs synthesised and used in this work. Well-dispersed AuNPs were observed in all samples. However, remarkable differences in particle size were found, as expected from

Figure 1. Representative TEM images of unsupported AuNPs. a) ≈ 5 nm Au spheres, b) ≈ 30 nm Au spheres, c) Au octahedra, and d) Au nanocubes.

Figure 2. Representative TEM images of the carbon supported AuNPs. a) ≈ 5 nm Au spheres, scale bar: 20 nm; b) ≈ 30 nm Au spheres, scale bar: 20 nm; c) Au octahedra, scale bar: 50 nm; d) Au nanocubes, scale bar: 50 nm.

the different synthetic methodologies used. The AuNPs prepared by the reduction of HAuCl_4 with ice-cold NaBH_4 in the presence of citrate had a quasi-spherical particle shape with an average particle size of approximately 5 nm (Figure 2a). A similar quasi-spherical particle shape was also found for AuNPs prepared by the standard citrate method, however, as expected, their particle size was much larger at approximately 30 nm (Figure 2b). The AuNPs prepared by addition of NaOH in the presence of cetyltrimethylammonium bromide (CTAB) and ascorbic acid show a well-defined octahedral shape but also a certain degree of truncation. The average particle size of these octahedral AuNPs was approximately 40–45 nm (Figure 2c). This size matches well the expected particle size at the reaction temperature used.^[63] Finally, the AuNPs prepared using the Au seed-mediated method adopted a preferred cubic shape with a particle size of 40–45 nm (Figure 2d).

It is important to point out that TEM data provide valuable information about nanoparticle size and shape, as well as about nanoparticle dispersion on the carbon substrate, but nothing about their surface structure. However, as shown in previous studies,^[64–66] shape is expected to be a prerequisite for a particular surface structure. Thus, quasi-spherical nanoparticles can be considered as polyoriented, non-specifically-surface-structured catalyst materials, as no preferred facets are exposed. However, octahedral AuNPs represent a catalytic material having a preferential (111) surface orientation, and cubic AuNPs can be considered as catalytic material containing a preferential (100) surface orientation. Consequently, electrocatalytic activity is expected to vary across these samples as a consequence of their different surface structure.

2.2. X-ray Diffraction (XRD) Characterisation of Au Nanoparticles

Figure 3 shows the XRD patterns of the different AuNPs. All the diffraction peaks could be indexed with the face-centred cubic (FCC) Au bulk structure, except for a broad peak due to the Si wafer ($\approx 62^\circ 2\theta$) that was observed if the amount of sample was low (Figure 3a and d).

Figure 3. XRD patterns of AuNPs. a) ≈ 5 nm Au spheres. b) ≈ 30 nm Au spheres. c) Au nanocubes. d) Au octahedra.

The relative intensity of the different diffraction peaks is similar in all cases and analogous to that obtained with bulk Au, indicating the absence of a preferential orientation parallel to the substrate.^[67] This was expected because the XRD measurements were performed with clean, unsupported Au samples, that is, samples without the capping agent, which produces a disordered deposition of the AuNPs on the Si wafer substrate.

The average crystal size (D) of the different AuNPs was determined using the Scherrer equation [Eq. (1)]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the X-ray wavelength, K the particle shape factor, taken as 1 in all cases. β is defined as the line-broadening at half-maximum of the peak (full width at half-maximum), after subtracting the instrumental line broadening, and θ is the position (angle) of the peak. For these calculations, the (200) peak has been used. From this analysis, values of D of 5.8, 27.6, 39.7 and 42.7 nm were obtained, corresponding to approximately 5 and 30 nm Au nanospheres and 40–45 nm Au nanocubes and octahedra, respectively. These results are in good agreement with the TEM characterisation of the different samples.

2.3. CO-Stripping on Shape-Controlled Au Nanoparticles in Alkaline Media

Carbon monoxide effectively blocks the underpotential deposition of hydrogen $\blacksquare\blacksquare\text{OK?}\blacksquare\blacksquare$ on Pt and Pd, but on Au there are no hydrogen-related adsorption/desorption processes and thus CO adsorption cannot be confirmed.^[68] However, it is expected that CO adsorbs onto the Au surface and covers the surface. Koper et al. have found an unusual behaviour of adsorbed CO on single-crystalline Au electrodes in alkaline media.^[69] They observed a pair of peaks at around 0.4 V versus reversible hydrogen electrode (RHE) on Au(111) and hex-Au(100), which have been associated with reversible $\blacksquare\blacksquare\text{OK?}\blacksquare\blacksquare$ OH^- adsorption induced by CO adsorption on the surface. This behaviour has not been found on Au(110) single crystal surfaces.^[3,69]

In this work, AuNPs without carbon support were used for pre-adsorbed CO oxidation experiments. The adsorbed CO was oxidised in a single sweep that was confirmed by the absence of peaks in the subsequent sweep (Figure 4). For all shapes of

Figure 4. CO-stripping voltammograms on unsupported 5 nm Au spheres in Ar-saturated 0.1 M KOH solution. $\nu = 20 \text{ mV s}^{-1}$.

AuNPs, the CO-stripping voltammograms were similar. The pair of peaks observed previously by Rodriguez et al. at 0.4 V versus RHE on Au(111) and Au(100) with adsorbed CO in 0.1 M NaOH solution^[3,69] was not present with Au spheres, cubes or octahedra (Figure 4). The CO-stripping peak appeared at approximately 0 V as suggested previously.^[3,69,70] Geng and Lu studied the size effect of AuNPs on the electro-oxidation of CO and observed the CO oxidation peaks in both cathodic and anodic sweeps.^[70] In this study, CO was oxidised by applying a single potential cycle. The second cycle showed the same cyclic voltammetry (CV) characteristics as bulk Au in O_2 -free electrolyte. The electroactive area of Au increased upon CO oxidation, which could be attributed to the improved surface cleanliness, as there was probably some surfactant remaining on the nanoparticles from their synthesis. CO-stripping experiments were also carried out with carbon-supported AuNPs, but with those catalysts the CO-stripping peaks were not well defined probably due to the low Au loading. Further work is in

progress to achieve a better understanding of the CO-stripping reactivity on shape-controlled AuNPs in alkaline media.

2.4. Cyclic Voltammetry of Au/C Catalysts

Cyclic voltammograms were recorded in Ar-saturated 0.5 M H_2SO_4 and 0.1 M KOH solutions. Representative voltammograms are shown in Figure 5.

Figure 5. Cyclic voltammograms of Au/C catalysts in Ar-saturated a) 0.5 M H_2SO_4 and b) 0.1 M KOH solutions. $\nu = 50 \text{ mV s}^{-1}$.

In acidic solution, the anodic peak at $E > 1.1 \text{ V}$ corresponds to the formation of Au surface oxides, and the cathodic peak at approximately 0.9 V to the reduction of these oxides. The large background current was mainly due to the high-area carbon support. The current increase above 1.3 V was partially caused by the oxidation of the carbon support surface. The pair of peaks centred at about 0.4 V is related to the oxidation and reduction of oxygen-containing species on the carbon surface, which were probably quinone-type groups.^[71] In alkaline solution the processes related to Au surface oxidation and reduction are also evident. The anodic wave commenced at $E > 0.1 \text{ V}$ and the cathodic peak of Au oxide reduction is centred at approximately 0.05 V (Figure 5 b).

The real electroactive surface area of Au catalyst (A_r) was determined from stable cyclic voltammograms in acidic solution by charge integration under the oxide reduction peak and by

using a value of $400 \mu\text{C cm}^{-2}$ for the reduction of an oxide monolayer.^[72]

2.5. O₂ Reduction on Au/C Catalysts in H₂SO₄

Au is a modest electrocatalyst for ORR in acidic media, however, its electrocatalytic activity is considerably higher than that of unmodified carbon materials. For all Au/C catalysts studied, single-wave O₂ reduction polarisation curves with no well-defined current plateau were obtained using the RDE method. A typical set of current–potential curves for O₂ reduction on approximately 5 nm Au spheres and Au octahedra measured at various electrode rotation rates is presented in Figure 6.

Figure 6. RDE voltammetry curves for O₂ reduction on carbon-supported ≈ 5 nm Au spheres (a) and Au octahedra in O₂-saturated 0.5 M H₂SO₄ solution (b). $\nu = 10 \text{ mV s}^{-1}$. Inset: K–L plots for O₂ reduction [–0.15 V (■), –0.2 V (●), –0.3 V (▲), –0.4 V (▼)].

The RDE data on O₂ reduction were analysed using the Koutecký–Levich (K–L) equation [Eq. (2)].^[73]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = -\frac{1}{nFkC_{\text{O}_2}} - \frac{1}{0.62nFD_{\text{O}_2}^{2/3}\nu^{-1/6}C_{\text{O}_2}^b\omega^{1/2}} \quad (2)$$

where j is the measured current density, j_k and j_d are the kinetic and diffusion-limited current densities, respectively, n is the

number of electrons transferred per O₂ molecule, k is the rate constant for O₂ reduction, F is the Faraday constant (96485 C mol^{-1}), ω is the electrode rotation rate, $C_{\text{O}_2}^b$ is the concentration of O₂ in the bulk ($1.13 \times 10^{-3} \text{ mol dm}^{-3}$),^[74] D_{O_2} is the diffusion coefficient of O₂ ($1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)^[74] and ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$).^[75] The corresponding K–L plots are shown in Figure 6, inset. From the slopes of K–L lines the n values were found. The value of n was close to 2 at the foot of the polarisation curve, but it increased to approximately 2.5–3.5 at more-negative potentials. This means that at the beginning of the O₂ reduction wave the final product is H₂O₂, but at more-negative potentials the peroxide is further reduced to yield water. Such behaviour is typical for O₂ reduction on nanostructured Au electrodes in acidic media.^[29,30,44,46,52]

A comparison of different Au catalysts is presented in Figure 7. It is important to note that for the nanoparticle-modified electrodes with a fixed mass of nanocatalyst per unit area, the electrocatalytic activity is determined by the size and

Figure 7. Comparison of RDE voltammetry curves for O₂ reduction on Au/C catalysts and bulk Au in O₂-saturated 0.5 M H₂SO₄ solution. $\omega = 1900 \text{ rpm}$, $\nu = 10 \text{ mV s}^{-1}$.

shape of the catalyst particles.^[76] Thus, the half-wave potential ($E_{1/2}$) of O₂ reduction is most positive for approximately 5 nm spherical AuNPs, which is slightly higher than that of bulk Au. The other Au/C catalysts exhibited lower $E_{1/2}$ values. This observation can be explained by the differences in the real electroactive surface area, which is highest for approximately 5 nm Au spheres and bulk Au (Table 1). The other Au/C catalysts studied in this work (≈ 30 nm Au spheres, octahedra and nanocubes) have a smaller electroactive surface area and thus the half-wave potential is more negative. Differences in the $E_{1/2}$ value between larger Au spheres and octahedra apparently arise from differences in crystallographic orientation. Au nanocubes have the smallest electroactive surface area, but similar $E_{1/2}$ value, showing that the crystallographic orientation has a large contribution to the electrocatalytic activity, as previously suggested.^[10–12,27] For a better comparison, the SA values for O₂ reduction were calculated [Eq. (3)]:

Table 1. Kinetic parameters for O₂ reduction on Au/C catalysts in 0.5 M H₂SO₄, $\omega = 1900$ rpm.

Catalyst	A _r [cm ²]	Tafel slope [mV]	E _{1/2} vs. SCE [V]	SA at 0 V vs. SCE [mA cm ⁻²]	MA at 0 V vs. SCE [A g ⁻¹]
≈ 5 nm Au spheres	0.67 ± 0.02	−139 ± 2	−0.05 ± 0.01	0.56 ± 0.06	277 ± 24
≈ 30 nm Au spheres	0.12 ± 0.02	−151 ± 6	−0.14 ± 0.02	0.87 ± 0.03	77 ± 15
Au octahedra	0.14 ± 0.01	−150 ± 4	−0.13 ± 0.01	0.82 ± 0.02	86 ± 3
Au nanocubes	0.06 ± 0.01	−166 ± 2	−0.13 ± 0.01	1.81 ± 0.07	78 ± 1
Bulk Au	0.43 ± 0.02	−141 ± 3	−0.05 ± 0.02	0.75 ± 0.01	–

$$SA = I_k / A_r \quad (3)$$

where I_k is the kinetic current at a given potential and A_r is the real electroactive surface area of Au. Mass activities (MA) were also determined [Eq. (4)]:

$$MA = I_k / m_{Au} \quad (4)$$

where m_{Au} is the mass of Au on the electrode, calculated on the basis of a nominal Au loading (20 wt%). The SA and MA values determined at 0 V versus SCE are given in Table 1. The SA values for larger Au spheres and Au octahedra are similar to that of bulk Au. The smaller Au spheres have a slightly lower SA as compared to larger spheres, which might be related to the particle size effect as demonstrated previously.^[49] The considerably higher SA of Au nanocubes indicates that the crystallographic orientation of AuNPs has a major contribution to the activity of these catalysts. This is in accordance with the previous studies, in which it has been determined that the Au(100) is the most active single-crystal surface for ORR.^[21,22] As expected, the smallest Au particles (5 nm spheres) demonstrated the highest mass activity.

On the basis of the RDE data shown in Figure 7, the mass-transfer-corrected Tafel plots (Figure 8) were constructed and the values of the Tafel slopes were determined (Table 1). The absolute values of the Tafel slope are slightly higher than the typical value of −120 mV, which suggests that the rate-determining step is the transfer of the first electron to an O₂ molecule. Similarly, more-negative slope values have been previously observed for some Au single-crystal electrodes^[21,22] and Au/

Figure 8. Mass-transfer-corrected Tafel plots for O₂ reduction on Au/C catalysts and bulk Au in 0.5 M H₂SO₄ solution. $\omega = 1900$ rpm, $\nu = 10$ mV s⁻¹.

C catalysts.^[47] In addition, more-negative Tafel slope values due to the porosity of the catalyst have been obtained in case of thick catalyst layers,^[77] however, in this work the catalyst loading was much lower and presumably the reaction was not limited by thin-layer diffusion, as confirmed for Au/C catalysts of various loadings.^[47] Therefore, the precise reason for the higher value of slope is not clear at present, but it is expected to be related to the reaction kinetics and not to diffusion effects.

2.6. O₂ Reduction on Au/C Catalysts in 0.1 M KOH

In alkaline media, Au is an active catalyst for ORR.^[57,78] A set of ORR polarisation curves of approximately 30 nm Au spheres and Au octahedra is shown in Figure 9; similar two-wave polarisation curves were obtained for all the Au/C catalysts studied (Figure 10). To analyse the RDE data on O₂ reduction the K-L equation [Eq. (2)] was used with the following values of O₂-diffusion coefficient and concentration in 0.1 M KOH: $D_{O_2} = 1.9 \times 10^{-5}$ cm² s⁻¹ and $C_{O_2} = 1.2 \times 10^{-3}$ mol dm⁻³.^[79] The value of n is a function of electrode potential as is typical for Au-based cat-

Figure 9. RDE voltammetry curves for O₂ reduction on carbon-supported ≈ 30 nm Au spheres (a) and Au octahedra in O₂-saturated 0.1 M KOH solution (b). $\nu = 10$ mV s⁻¹. Inset: K-L plots for O₂ reduction [−0.6 V (■), −0.7 V (●), −0.8 V (▲), −0.9 V (▼), −1.0 V (◆)].

Figure 10. Comparison of RDE voltammetry curves for O_2 reduction on Au/C catalysts and bulk Au in O_2 -saturated 0.1 M KOH solution. $\omega = 1900$ rpm, $\nu = 10$ mV s $^{-1}$.

alysts in alkaline media.^[12] At the current maximum at around -0.4 V, $n > 3$, depending on the Au/C catalyst, but upon scanning to more-negative potentials n first decreases to 2.0–2.5 and then increases again to 3–4. This behaviour suggests that the main product is H_2O_2 , which is further reduced to water at negative potentials.

From the comparison of the O_2 reduction results (Figure 10) it can be seen that the overall electrode activity was the highest for smaller Au spheres and that bulk Au has similar ORR activity to that of larger AuNPs. The differences in the $E_{1/2}$ values are more pronounced in alkaline media than in acid, being approximately 60 and 40 mV between approximately 5 and 30 nm Au spheres and octahedra, respectively (Table 2).

Taking into account that the electroactive surface area of Au nanocubes is considerably smaller than that of 5 nm Au spheres the half-wave potential does not reflect the intrinsic electrocatalytic activity of nanoparticles and thus the SA values were calculated using Equation (3). The SA values were slightly lower for smaller Au spheres, as compared to those of larger Au spheres and bulk Au (Table 2). This might be due to the effect of particle size on the kinetics of the ORR, which has previously been reported also in alkaline media,^[55] however, the difference is too small for that conclusion to be reached. The Au octahedra had a somewhat low SA value, and similarly to the results obtained in acidic solution, the highest SA was determined for Au nanocubes. This order of activities is in agreement with studies on Au single-crystal electrodes,^[21] which show that Au(111) is the least active and Au(100) the most active single-crystal plane, and it confirms the results of previ-

ous O_2 reduction studies on shape-controlled AuNPs.^[12] As expected, the MA increased in the following order: Au octahedra $\approx$ Au cubes $<$ 30 nm Au spheres $<$ 5 nm Au spheres.

The Tafel slope values remained lower than -60 mV for Au spheres and Au nanocubes; for octahedra it was around -60 mV at low current densities, but it increased up to -170 mV in the high-current-density region (Figure 11). The Tafel slope values in the range of -120 to -60 mV suggest that the rate-determining step is the transfer of the first electron to the O_2 molecule.^[78]

Figure 11. Mass-transfer-corrected Tafel plots for O_2 reduction on Au/C catalysts and bulk Au in 0.1 M KOH solution. $\omega = 1900$ rpm, $\nu = 10$ mV s $^{-1}$.

The SA and MA values of AuNPs for O_2 reduction suggest that the particle size of the catalysts should be further reduced for practical applications. Conversely, the results obtained demonstrate that the surface structure of the AuNPs plays an essential role in the performance of these catalysts, which can therefore be improved by using new synthetic methods for controlling the shapes of these nanoparticles.

3. Conclusions

In summary, the shape-controlled AuNPs supported on high-area carbon have been shown to be electrochemically active catalysts in ORRs. The highest SA in both acidic and alkaline media was observed for Au nanocubes, which is most likely due to the crystallographic effect—the prevalence of Au(100) crystal facets on the surface. However, the nanocubes possessed modest MA due to their larger size. The Tafel analysis showed that the mechanism of the ORR is the same on synthesised Au/C catalysts as on bulk.

Table 2. Kinetic parameters for O_2 reduction on Au/C catalysts in 0.1 M KOH, $\omega = 1900$ rpm.

Catalyst	A_r [cm 2]	Tafel slope [mV]	$E_{1/2}$ vs. SCE [V]	SA at -0.15 V vs. SCE [mA cm $^{-2}$]	MA at -0.15 V vs. SCE [A g $^{-1}$]
≈ 5 nm Au spheres	0.67 ± 0.02	-43 ± 9	-0.23 ± 0.03	0.18 ± 0.03	89 ± 9
≈ 30 nm Au spheres	0.12 ± 0.02	-44 ± 4	-0.29 ± 0.02	0.27 ± 0.04	29 ± 9
Au octahedra	0.14 ± 0.01	-60 ± 11	-0.33 ± 0.02	0.15 ± 0.02	16 ± 2
Au nanocubes	0.06 ± 0.01	-48 ± 3	-0.30 ± 0.03	0.36 ± 0.02	15 ± 1
Bulk Au	0.43 ± 0.02	-54 ± 8	-0.27 ± 0.02	0.23 ± 0.02	-

Experimental Section

Preparation of Au catalysts

Carbon supported shape-controlled AuNPs were prepared using different methodologies. In all cases, the nominal metal loading on the carbon support was 20 wt. %.

Quasi-spherical AuNPs (≈ 5 nm) were synthesised using a previously reported method.^[27,80] A freshly prepared ice-cold NaBH_4 solution (0.01 M, 0.3 mL per 20 mL Au^{3+} solution; 99%, Acros) solution was added to an aqueous solution of HAuCl_4 (1.25×10^{-4} M; 99.9+%, Sigma-Aldrich) and trisodium citrate dihydrate (2.5×10^{-4} M; 99%, Sigma-Aldrich) at room temperature with vigorous stirring. After 30 s, stirring was slowed, and the Au colloid solution was stirred gently at $40\text{--}45^\circ\text{C}$ for 15 min to ensure reaction of the excess NaBH_4 . Then, the appropriate amount of carbon powder (Vulcan XC-72R, Cabot Corp., ■■■town? country?■■■) was added under fast stirring for approximately 1 h, alternating both magnetic and ultrasonic, in order to properly disperse the hydrophobic carbon in the aqueous solution, and also to favour the uniform distribution of the nanoparticles on the support surface. Finally, NaOH pellets (Merck) were added to the mixture to precipitate the sample and the synthesis mixture was left to stand overnight. After complete precipitation, the sample was filtered, rinsed with ultrapure water and ■■■oven?■■■ dried at $70\text{--}80^\circ\text{C}$.

Quasi-spherical AuNPs (≈ 30 nm) were synthesised using the standard citrate reduction method.^[81] In brief, aqueous HAuCl_4 (0.25 mM) was heated to boiling. To this, a freshly prepared sodium citrate solution (35 mM, 0.65 mL per 50 mL Au^{3+} solution) was added quickly with vigorous stirring. The mixture was refluxed for 20 min and then allowed to cool to room temperature. As previously described, the appropriate amount of Vulcan XC-72R carbon was added to the solution. Then, NaOH pellets ■■■how many?■■■ were added to the mixture to precipitate the sample and the synthesis mixture was left to stand overnight. Finally, the sample was filtered, rinsed with ultrapure water and finally ■■■oven?■■■ dried at $70\text{--}80^\circ\text{C}$.

Octahedral AuNPs (40–45 nm) were prepared using a methodology previously described by Han et al.^[63,82] In a typical synthesis, aqueous ascorbic acid (100 mM, 100 μL ; Sigma-Aldrich) was added to an aqueous solution (20 mL) containing HAuCl_4 (1.25×10^{-4} M) and CTAB (10 mM; Sigma-Aldrich). To this mixture, aqueous NaOH (100 mM, 100 μL) was rapidly injected to induce particle formation. The reaction temperature was maintained at 25°C and the reaction was allowed to proceed for 20–30 min. Subsequently, the appropriate amount of Vulcan XC-72R carbon was added to the solution. Then, a methanol solution (■■■ vol?■■■), in which ■■■how many?■■■ NaOH pellets were dissolved, was added to the mixture. The sample was filtered, rinsed with ultrapure water and finally ■■■oven?■■■ dried at $70\text{--}80^\circ\text{C}$.

Cubic AuNPs (40–45 nm) were grown from spherical AuNPs using a similar seed-mediated method to that previously published.^[11,12,27,83] In summary, Au seeds were prepared by the reduction of HAuCl_4 (0.01 M, 250 μL) by treatment with ice-cold aqueous NaBH_4 (0.01 M, 0.6 mL) in the presence of CTAB (0.1 M, 7.5 mL). The growth of the nanoparticles to yield the nanocubes was performed in the following way: solutions of HAuCl_4 (0.01 M, 1 mL), CTAB (0.1 M, 8 mL) and L-ascorbic acid (0.1 M, 4.25 mL) were added to water (40 mL). Then, a diluted (1:10) Au seed solution (25 μL) was added to this growth solution. Once the reaction was completed (around 1 h), the appropriate amount of Vulcan XC-72R carbon was added to the solution. Then, a methanol solution (■■■ vol?■■■), in which the NaOH pellets were dissolved, was added to the mixture. The sample was filtered, rinsed with ultrapure water and finally ■■■oven?■■■ dried at $70\text{--}80^\circ\text{C}$.

The corresponding unsupported AuNPs were prepared as described above, but without the carbon addition step. Furthermore,

filtering and drying steps were unnecessary, and the AuNPs were simply washed 3–4 times with ultrapure water after precipitation.

Surface Characterisation

TEM experiments were performed on a JEOL JEM-2010 microscope operating at 200 kV. The samples for TEM analysis were obtained by placing a droplet of the sample solution onto a formvar/carbon-coated copper grid and allowing the solvent to evaporate in air at room temperature.

X-ray powder diffraction patterns of the samples were obtained using a Bruker D8 Advance diffractometer fitted with a copper tube. The optical setup included a Ni 0.5% $\text{CuK}\beta$ filter in the secondary beam so that only $\text{CuK}\alpha$ radiation illuminated the sample ($\text{CuK}\alpha_1 = 0.154059$ nm and $\text{CuK}\alpha_2 = 0.154445$ nm). The clean, unsupported AuNPs were spread onto an Si wafer and measured in reflection geometry over the $30\text{--}90^\circ 2\theta$ range with a step of 0.10° and a counting time of 30 s per step.

Electrochemical Characterisation

Bulk Au and glassy carbon (GC) electrodes were prepared by mounting Au (99.99%, Alfa Aesar) and GC disks (diameter 5 mm, GC20-SS, Tokai Carbon ■■■town, country?■■■) into Teflon holders. The surface of the electrodes was polished to a mirror finish using 1.0 and 0.3 μm alumina slurries (Buehler, ■■■town, country?■■■) and for the bulk Au electrodes additional 0.05 μm alumina slurry was used. After polishing, the electrodes were sonicated in Milli-Q water for 5 min.

The catalyst suspension was prepared by mixing Au/C powder in ethanol containing 1.3% Nafion and an aliquot (5 μL) of this suspension was pipetted onto the GC electrode surface to afford an Au loading of $6.8 \mu\text{g cm}^{-2}$. The electrodes were left to dry overnight, expecting that the ethanol completely evaporates and thus would not affect the ORR kinetics. O_2 reduction was studied in H_2SO_4 (0.5 M, prepared from 96% H_2SO_4 , Suprapur, Merck) and KOH (0.1 M, prepared from p.a. quality pellets, Merck) solutions using the RDE method. The solutions were made using Milli-Q water and were saturated with pure O_2 (99.999%, AGA ■■■town, country?■■■) or degassed with Ar (99.999%, AGA). CV in Ar-saturated H_2SO_4 (0.5 M) was used for the determination of real surface area of Au.

For pre-adsorbed CO oxidation experiments the suspensions of AuNPs without carbon support were transferred onto freshly polished GC electrodes and were left to dry overnight. CO (AGA) was adsorbed by bubbling the gas through KOH (0.1 M) solution for 1 min. Then, the solution was purged with Ar to eliminate CO from the solution and both steps were conducted while maintaining the electrode at a constant -1.2 V versus SCE. The next step was the oxidative removal of the adsorbed CO from the surface by scanning the potential between $-1.2\text{--}0.5$ V.

An SCE connected to the cell through a Luggin capillary was used as a reference and all the potentials performed are referenced to this electrode. A Pt wire served as a counter electrode and the counter electrode compartment of the three-electrode glass cell was separated from the main cell compartment by a glass frit. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., ■■■town?■■■, The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. An EDI101 rotator and CTV101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. All experiments were carried out at room temperature ($23 \pm 1^\circ\text{C}$).

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Keywords: electrocatalysis • gold nanoparticles • nanocatalysts • oxygen reduction • shape-controlled catalysts

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Time to shape up: Electrocatalysis of oxygen reduction on carbon-supported gold nanostructures is mainly determined by the surface structure of the particles. This surface structure can be tuned by changing the shape of the nanoparticle.

H. Erikson, A. Sarapuu, K. Tammeveski,*
J. Solla-Gullón, J. M. Feliu

■■ – ■■

**Shape-Dependent Electrocatalysis:
Oxygen Reduction on Carbon-
Supported Gold Nanoparticles**

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