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# Carbon-Supported Gold Nanocatalysts: Shape Effect in the Selective Glycerol Oxidation

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Gold nanoparticles were supported on two types of carbon nanofibres with different degree of graphitisation. The investigation of these materials with an aberration-corrected transmission electron microscope showed that the degree of the surface graphitisation strongly influences the structures of the supported gold particles. The more ordered graphitic layers of the carbon nanofibre surface led to Au particles more preferred to immobilise on their {111} plane, exhibiting more facet area. In contrast, disordered carbon nanofibre surfaces

#### Introduction

Since the discovery of Haruta that supported gold nanoparticles (AuNPs) are highly active catalysts for CO oxidation,<sup>[1]</sup> a series of studies have revealed that gold is active in several other catalytic reactions as well, such as hydrochlorination of alkynes, production of hydrogen peroxide, and oxidation of alcohols and polyols in the liquid phase,<sup>[2]</sup> if it is highly dispersed on different supports. Gold catalysts were proved to work also in homogeneous oxidation with various oxidants including air.<sup>[3]</sup> In recent years, gold and gold-based catalysts have attracted more and more interest in their application for catalytic transformation of biomass-derived chemicals; they have potential in "green chemistry" through aerobic oxygen as the oxidant instead of other chemical oxidants that produce waste.<sup>[4]</sup> The origin of activity is still under debate both in gas- and liquid-phase reactions; however, activity is generally attributed to the electronic and geometric structures of nanometre-sized Au particles, which differ from bulk Au.<sup>[5]</sup> In contrast to the limited understanding of the catalytic mechanisms,<sup>[6]</sup> numerous experiments have shown that the catalytic activity is highly dependent on the nanostructures of the particles and the support. Particularly, in the oxidation of CO by Au catalysts hemispherical particles were shown to be more active than spherical ones, which supports the importance of the perimeter interfaces between AuNPs and the support.<sup>[7,2a]</sup> The importance of the interface in the O2 activation has also been revealed by DFT calculation.<sup>[8]</sup> Moreover, dynamic environmental TEM studies have recently shown that AuNPs can wet the support surface differently, depending on the nature of the material, and the wetting can be also influenced by adsorption of O<sub>2</sub>.<sup>[9]</sup> Depending on the O<sub>2</sub> partial pressure and the size of the AuNPs, O<sub>2</sub> adsorption has been shown to modify the structure of the particles by rounding the nanocrystals at elevated pressure, whereas close-packed (111) facets were more stable at low partial pressure.<sup>[10]</sup> The support also plays an essential role in led to random orientation of supported particles. The different shape of similarly sized Au nanoparticles allowed determining the effect of support surface structures on the selectivity of the catalyst in the liquid-phase oxidation of glycerol, highlighting the higher C3 product selectivity on the {111} surface. Based on these results, we could also gain new insight in the effect of Au nanoparticle size on the selectivity in the liquidphase oxidation of glycerol, that is, larger particles were more selective toward C3 products than the smaller ones.

tuning the fine-structures of Au particles. It was also suggested that highly disordered supports lead to high activity and the perimeter interfaces could contain oxidic Au species  $(AuO_x)^{[11]}$  derived from partially charged Au ions binding with OH or  $O_2^-$  species derived from  $O_2$  or the support itself. Therefore, it is expected that several interlocked factors (structure and size, support, and experimental conditions) determine the overall activity of supported metal-based catalysts.

Most of the studies dealing with shape effects concern with gas-phase reactions and, therefore, do not take into consideration the presence of a solvent that could lead to significant variations in terms of both activity and selectivity. Here, we have focused on the effect of the support on the selectivity of glycerol oxidation through modification of the shape of supported AuNPs. This reaction has been studied by many research groups as an important application of gold-based catalysts.<sup>[12]</sup> It has been shown that both reaction rate and path are sensitive to the particle size and the support.<sup>[13, 12c]</sup> The mecha-

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nism of the reaction has been studied for Au-activated carbon (AC) catalysts from theoretical and kinetic viewpoints,<sup>[14]</sup> highlighting the possible active role of the support and of AuNP step and edge sites in O<sub>2</sub> activation. From the activity point of view, Corma et al. have shown that the reaction rate directly depends on the surface atom, thus classifying this reaction as not structure-sensitive.<sup>[15]</sup> The selectivity of the reaction has also been studied with respect to the C-C scission in native H<sub>2</sub>O<sub>2</sub> production, degradation, or both,<sup>[16]</sup> as well as by comparing glyceric acid production to hydroxyacetone production,<sup>[17]</sup> even with some doubts on the analyses emerging recently.[18]

Carbon-based materials, such as AC, carbon nanotubes (CNTs), and carbon nanofibres (CNFs), have been widely used as catalyst support because it is possible to manipulate them by specific chemical and thermal treatments aimed to tune the surface chemistry. Theoretical studies on the interaction between Au clusters and graphite shows that the stability and the structure of Au are highly dependent on the Au cluster size and the defects on graphitic layers.<sup>[19]</sup> We have shown that the exact type of carbon support exerts a strong influence on the catalytic properties (activity and selectivity) even when the Au particles were preformed by sol immobilisation methods.<sup>[20]</sup> Therefore, to study these findings in more detail and the possible role of carbon support in controlling the structures of nanoparticles, supported systems synthesised by a two-step methodology (generation of nanoparticles followed by their immobilisation on the support) with two different types of commercial CNFs were prepared. The correlation between Au particle structure and the selectivity of glycerol oxidation was then analysed by using aberration-corrected high-resolution (HR)TEM.

#### **Results and Discussion**

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Both CNFs used as support in this work have an average diameter of approximately 100 nm. The CNFs denoted as PR24-PS were produced by pyrolytically stripping the as-produced fibre to remove polyaromatic hydrocarbons from the fibre surface. The PR24-LHT were produced by heat-treating the fibre at 1500 °C. This treatment converts any chemically vapour-deposited carbon present on the surface of the fibre into a more ordered graphitic structure.

HRTEM and high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) are very important techniques to study the structure of nanoparticles at atomic level and have been extensively applied to determine the configuration of supported metal catalysts.<sup>[21]</sup> With aberration-corrected HRTEM and HAADF STEM, the atomic configurations of nanoparticles and clusters have been successfully resolved.<sup>[22]</sup> We used a FEI Titan 80-300 microscope operating at 300 kV equipped with a CEOS image Cs corrector to study the structures of two different CNF supports, the termination of Au catalysts surface, and the dependence of Au nanoparticles morphology on the support structure. The revealed different structures of supported Au particles were then directly correlated to the selectivity observed in the aerobic oxidation of glycerol. In the HRTEM image of the PR24-PS nanofibre in Figure 1a, deposited layers of carbon approximately 2 nm thick are shown on the surface, which consisted of highly defective and discon-



Figure 1. HRTEM images of a) PR24-PS and b) PR24-LHT CNFs.

tinuous graphitic layers. In contrast to PR24-PS, PR24-LHT exhibited a more graphitised surface of more ordered layers, as shown in Figure 1b. The layers of deposited carbon were only approximately 0.5 nm thick. At a distance of approximately 20-30 nm from the carbon layer surface, a well-ordered graphitelike structure was seen for both CNFs. This structure had no direct contact with the Au particle subsequently deposited on it and the distance to the surface was relatively large; it is thus expected to have no strong impact on the structure of Au particles on the CNF surface. In a previous characterisation of these two carbon supports by Raman spectroscopy, the ratio of D band (at  $\approx$  1350 cm<sup>-1</sup>) and G band (at  $\approx$  1580 cm<sup>-1</sup>) intensities were measured to indicate the graphitisation degree. A lower D/G band intensity ratio and the appearance of much more prominent 2D band intensity for PR24-LHT than for PR24-PS indicated an increasing degree of graphitisation for PR24-LHT.<sup>[23]</sup> Therefore, our TEM observation is consistent with the previous Raman spectroscopic results.

#### Structures of gold particles supported on CNFs

Pregenerated polyvinyl alcohol (PVA) protected Au nanoparticles were immobilised on CNFs by impregnation and TEM analyses revealed that the distribution and the size of the Au particles were similar on PR24-PS and PR24-LHT CNF supports. Although some CNFs were found with few or no Au particles, most CNFs carried evenly distributed Au particles in a narrow particle size distribution. The respective overviews of the Au/ PR24-PS and Au/PR24-LHT are shown in Figure 2. The measured median particle sizes for these two catalysts were (3.7  $\pm$ 0.2) nm and  $(3.5 \pm 0.1)$  nm, respectively.

We studied the structure of the two catalysts, Au (1 wt%) on PR24-PS and on PR24-LHT CNFs, by aberration-corrected HRTEM and found that the final shape of the Au particles was related to the surface structures of the support, although the Au particles were preformed in the sol. To obtain a good statis-



Figure 2. TEM overview images of a) Au/PR24-PS and b) Au/PR24-LHT.

tic evaluation on the particle morphology, 167 particles with metal-support interface parallel to the electron beam were imaged in the case of Au/PR24-PS. The median size of these particles was  $(3.8\pm0.2)$  nm, which is in good agreement with the evaluation from the overview images. Therefore, the statistic evaluation was representative. The Au particles were attached to the PR24-PS nanofibres without distinguishable orientation relation between Au low-index crystallographic planes and the CNF surface. Among the examined 167 particles, only 36 particles (21.6%) were found to have one set of {111} planes parallel to the CNF surface and the rest were randomly oriented (Figure 3). Most of the particles exhibited a polyhedral shape, for example, cuboctahedron, decahedron, icosahedron, and truncated alternatives. In Figure 4a and 4b, two Au particles of approximately 3 nm size are seen with cuboctahedron and icosahedron shape, respectively. The Au particle in cuboctahedron shape has clean surfaces. However, a closer inspection of the intersection of the two {111} surfaces and two {100} surfaces revealed one missing atom (marked by an arrow). Furthermore, this particle is situated on the CNF surface not with its (100) plane or (111) plane parallel to the CNF surface but it is inclined. Consequently, the atoms around the intersection ridge of the (100) and (111) surfaces in contact with CNF are missing so that the interface between the particle and CNF is smoothed without any sharp edge. Such config-



**Figure 3.** Statistical evaluation of the orientation of 167 particles from Au/ PR24-PS and 218 particles from Au/PR24-LHT imaged by HRTEM. with (111) planes parallel to CNF surface; =: particles with other orientation. The Au/PR24-LHT shows a much higher percentage of particles with (111) planes parallel to the CNF surface than the Au/PR24-PS.



**Figure 4.** Aberration-corrected HRTEM images of Au particles supported on PR24-PS with a) modified cuboctahedral configuration, b) icosahedral configuration showing interaction between particle and CNF surface, and c) surface carbon decoration with uncovered windows (each indicated by arrows).

uration reduces the contacting area. The interatomic distances between the atoms in the bottom layer and the ones in the neighbouring sublayer were measured and compared with the distances between the atoms at inner planes. No systematic contraction or expansion was observed for the carbon-contacting atomic layer, suggesting that no C diffusion into the subsurface layer of Au particles has occurred. In Figure 4b, the icosahedron nanoparticle was imaged on neither its six-fold nor its five-fold axes, therefore it exhibits a complicated projected contrast. Again, the modification of the interface between the particle and the CNF support can be seen. The contacting plane on the particle is more flattened than the side exposed to the vacuum and some carbon decoration is observed at the perimeter of the interface (indicated by the arrow in Figure 4b), which is attributed to either strong metal-carbon interaction or the residual protection agent, PVA. These two examples offer direct evidence that both metal particles and CNF support undergo considerable reconstruction, which modifies the exposed surfaces and interfaces.

It was also frequently observed that the particle was wellcovered by a layer of carbonaceous species, but usually not completely. In Figure 4c such an example of a particle decorated with the layer is seen. In the places indicated by arrows, windows without covering can be distinguished, which owes to the residual PVA applied during the formation of the metallic Au nanoparticles. Besides the particle size control and particle stabilisation, the protecting agent may exert additional effects on the properties of metal catalysts through offering binding between particle and support and acting as "cement". It is therefore apparent that the contact between the metal Au and the support surface is mediated by the nanoparticle pro-

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tector (PVA). This is in agreement with the observation by Hutchings et al. reporting on the different degree of wettability between carbon and  $TiO_{2}$ .<sup>[24]</sup> From Figure 4c, we can see that the surface decoration is bound directly to the CNF support at the perimeter of the interface. The holes in the covering are essential to the accessibility of the reactant to the particle. Moreover, it should be noticed that such carbonaceous surface decoration also makes the particle surface rougher so that it has less flat facets and more uncoordinated sites.

The most noticeable difference between Au/PR24-LHT and Au/PR24-PS was that statistically the {111} planes of Au particles on PR24-LHT are more frequently observed to be parallel to the CNF surface than in the case of PR24-PS. In the case of Au/PR24-LHT, 218 particles were imaged in HRTEM images. The median size of these particles was  $(3.6\pm0.2)$  nm, which is in agreement with the evaluation from overview images. Among these particles, 102 particles (46.8%) were found to have one set of {111} planes parallel to the CNF surface (Figure 3). This percentage was much higher than in the case of Au/PR24-PS (21.6%). The correlation was extraordinarily prominent for Au particles with sizes smaller than 3 nm. Below this size, the percentage of the oriented particles reached 72.1%, in contrast to 44.8% for the particles with size between 3 nm and 4 nm, and only 21.2% for the particles larger than 4 nm. The histogram of size distribution for oriented particles and all particles is shown in Figure 5. In Figure 6a a representative particle with one set of {111} lattice planes on the CNF surface is shown. The particle has a configuration similar to the cuboctahedron shape with {111} and {100} surfaces exposed. A structural model was constructed and is shown in Figure 6b. The particle has a relatively large (111) base plane contacting with the supporting CNF. However, the contact angle is larger than  $90^\circ$  and there is no distinguishable carbonaceous adlayer binding the Au metal particle to the CNF support. Moreover, a stacking fault is observed at the second stacking plane on the CNF. Our observations strongly suggest that the more graphitised CNF surface stabilises the first few layers of Au (111) stacks and the whole particle keeps more or less the regular shape and less surface decorated carbon is found on such particle. This tendency is more prominent for smaller particles. Other examples of such kind of regularly shaped Au particles exposing the low index





b



**Figure 6.** Aberration-corrected HRTEM images of Au particles supported on PR24-LHT. a) A representative 2–4 nm particle with (111) surface epitaxially parallel to the graphitic layer of CNF. b) Structure model derived from the image in part a. c) A larger particle with spherical shape showing carbon binding to the CNF surface.

surfaces are reported in Figure S1 in the Supporting Information. Their {111} planes are more or less parallel to the CNF surfaces, although no strict epitaxial relation with the undulating graphitic layers could be addressed. To further confirm that such tendency is related with highly graphitic carbon surface, Au particles deposited on thin amorphous C film were also investigated and there was no orientation preference between Au particles and amorphous C film (HRTEM image in Figure S2).

Similarly to the case of Au/PR24-PS, the lattice spacing in Au particles was constant from top to bottom within the accuracy of the measurement, which means that no carbon was dissolved in the Au particle. Statistically, particles larger than 4 nm were more inclined to form spherical shape than the one shown in Figure 6 c. Among the 218 imaged particles, 52 particles (25%) were larger than 4 nm, 39 of them (75%) were found in spherical shape. Owing to the relatively low fraction of interface area, carbon binding is essential for the stabilisation of these particles on the support surface against leaching and coarsening. Previous experimental data showed that particle dispersion increased with the number of acidic groups, suggesting that such particles are positioned on top of stable oxygen functional groups owing to the "oxophilicity" of gold.<sup>[25]</sup>

#### Liquid-phase oxidation of glycerol

The two Au/CNFs prepared were very similar in particle size and distribution but showed a prevalent different shape. This finding allowed us to investigate more detailed the wellknown particle size effect observed in the liquid-phase oxidation of glycerol.<sup>[12]</sup> This reaction has been studied by several groups owing to its importance in the valorisation of biomassbased processes.<sup>[12d]</sup> Glycerol can be smoothly oxidised under basic or neutral conditions.<sup>[12a-c, 16c]</sup> On the basis of experimental evidences, it is now accepted that the larger the AuNP size is, the more the activity decreases.<sup>[12a-c, 16a, 26]</sup> The selectivity of the reaction toward C3 products (glyceric, tartronic acids) appears to be related to the particle size as well as the activity but in the opposite sense.<sup>[12a-c, 16a, 26]</sup> We tested the Au/CNFs (PR24-PS and PR24-LHT) under the usual conditions reported in the literature (glycerol 0.3 m, NaOH/glycerol = 4 mol mol<sup>-1</sup>, 304 kPa  $O_2$ , T = 50 °C) to determine the shape effect on the activity and selectivity of the reaction. The results, reported in Table 1, confirmed that the catalyst activities mainly depended

Table 1. Catalytic results of Au/CNFs in the liquid-phase oxidation of $glycerol$ . <sup>[a]</sup>						
Catalyst	Au particle size [nm]	TOF [h <sup>-1</sup> ]	Glyceric acid	Selectiv Formic acid	vity [%] Glycolic acid	Oxalic acid
Au/CNFs-PS	3.7	948	56	19	22	2
Au/CNFs-LHT	3.5	982	22	40	35	2
Au/AC	3.6	950	58	20	21	1
[a] Glycerol solution (0.3 M with a ratio NaOH/glycerol = 4 molmol <sup>-1</sup> ), and the catalyst (ratio substrate/metal = 1000 molmol <sup>-1</sup> ) were mixed in distilled water (total volume 10 mL). The reactor was pressurised at 304 kPa of $O_2$ and thermostatted at 50 °C.						

on particle size and distribution with similar activities of the two catalysts. The activities in both cases were high and full conversion was obtained within 1 h reaction time. However, at closer inspection, we observed strong differences between the two catalysts, which can be mainly addressed to the different shape of the AuNPs, whereas the size and the distribution were very similar. We cannot completely exclude a support effect on the reactivity, but the similarity of the CNF employed made this effect reasonably small. From the data of Table 1, we observed that Au/PR24-PS presents a similar selectivity toward glyceric acid to that observed for similarly sized AuNPs supported on AC (58%). Formate and glycolate, by probing the C–C bond cleavage, were formed with selectivities of 19 and 22%, respectively. Conversely, Au/P24-LHT produced these compounds with considerably higher selectivity (40 and 35%, respectively). Considering, as highlighted before, that the AuNPs were prepared by the same methodology with similar particle sizes and distribution, we concluded that the shape and the configuration of the Au particles are important factors that determine selectivity. In the reaction described herein, the specific particle shapes and configurations were induced by the supports onto the preformed AuNPs. In particular, in glycerol oxidation, the direct contact between PR24-LHT and {111} surface of Au(PVA) nanoparticles led to the exposure of low-

index Au surfaces, suggesting that the active sites on these surfaces could promote the C1 and C2 products, that is, the C–C bond cleavage.

To find a possible explanation of this result, we also investigated the behaviour of AuNPs on amorphous AC. In this case, AuNPs deposited on amorphous carbon as shown in Figure S2 did not show a preferential orientation. In addition, their activity and selectivity (conversion 91%, selectivity to glycerate 58%; see Table 1) were very similar to those of Au/PR24-PS. Therefore, we concluded that a fundamental factor in ruling the overall selectivity is the preferentially exposure facets of the AuNPs. Tentatively we could correlate the high selectivity toward the C–C cleavage shown by low-indexed surface to

the  $H_2O_2$  production. Native  $H_2O_2$  has been recognised as one of the main factors affecting selectivity, which decreases as  $H_2O_2$  production and stability increase.<sup>[16]</sup> It has been shown recently that Au (111) surfaces are the most suitable for  $H_2O_2$ direct synthesis.<sup>[27]</sup> According to the widely accepted mechanism shown in Scheme 1,  $H_2O_2$  is formed through  $O_2$  reduction by metal hydride. In our case  $H_2O_2$  could form faster or decompose to a lesser extent on Au (111) sites than on other sites. Therefore, the local higher presence of  $H_2O_2$ , if there are Au



**Scheme 1.** Mechanism of  $\Pi_2 O_2$  formation on Au through  $O_2$  reduct

(111) facets preferentially exposed as it was the case in Au/ PR24-LHT, could promote the C–C bond cleavage and enhance the selectivity to glycolate and formate. In all cases no leaching of Au was observed by inductively coupled plasma measurements on the collected solution after reaction.

#### Conclusions

In a carefully designed synthesis with preformed Au nanoparticles (AuNPs) from the same batch (i.e., with the same narrow particle size distribution) immobilised onto different carbon supports, we demonstrated that the shapes of the AuNPs depended on the different interaction with the support. The methodology enables the exclusive study of a single factor, for example, particle size, distribution, or support, which are often convoluted in complex catalysts. By aberration-corrected highresolution TEM, the structures of Au particle surfaces, including added or missing atoms, the deviation from equilibrium lattice sites and uncoordinated sites, and the decoration at the interface were imaged directly.

The catalytic performance in the glycerol oxidation reaction could be related directly to the structural difference observed. Particularly, we focused on the activity of the catalysts determined principally by the particle size and distribution because similar activities were observed for the three catalysts Au/ PR24-PS, Au/PR24-LHT, and Au particles on amorphous activated carbon. However, the selectivities in the reaction differed, which was attributed to the preferential orientation of AuNPs and the particle shapes. We concluded that Au/PR24-LHT was more selective toward C-C bond cleavage because more ordered graphitic layers of the CNF surface led to Au particles bonded through their {111} planes thus exhibiting more facet area. These findings demonstrate the importance of particle shape in determining the selectivity of a catalytic reaction and provide new insight into the support in heterogeneous catalytic reactions.

#### **Experimental Section**

The metallic Au nanoparticles was first prepared by the sol method.<sup>[28]</sup> Solid NaAuCl<sub>4</sub>·2H<sub>2</sub>O (0.043 mmol) and PVA solution [2 wt %, 103  $\mu$ L, PVA/Au (w/w) = 1] were added to H<sub>2</sub>O (130 mL). After 3 min, NaBH<sub>4</sub> solution (0.1 m, 1.3 mL) was added to the yellow solution under vigorous magnetic stirring. The ruby-red Au<sup>0</sup> sol was immediately formed.

Within a few minutes of sol generation, the Au nanoparticles (acidified until pH 2 by sulfuric acid) were immobilised by adding the CNF support under magnetic stirring. After additional 18 h, the slurry was filtered and the catalyst washed thoroughly with distilled water. ICP analyses were performed on the filtrate by a Jobin Yvon JV24 to verify the metal loading on carbon. The total metal loading was 1 wt%.

Reactions were carried out in a 30 mL glass reactor equipped with a thermostat and an electronically controlled magnetic stirrer connected to a 5000 mL reservoir charged with oxygen (300 kPa). The oxygen uptake was monitored by using a mass flow controller connected to a PC through an A/D board to plot a flow time diagram. Glycerol oxidation: glycerol (0.3 M), and the catalyst (substrate/ total metal = 1000 mol mol<sup>-1</sup>) were mixed in distilled water (total volume 10 mL) with NaOH (NaOH/glycerol = 4 mol mol<sup>-1</sup>). The reactor was pressurised at 300 kPa of O<sub>2</sub> and set to 50 °C. Once this temperature was reached, the gas supply was switched to O<sub>2</sub> and the monitoring of the reaction started. The reaction was initiated by stirring. Samples were removed periodically and analysed by HPLC with a column (Alltech OA- 10308, 300×7.8 mm) with UV and refractive index (RI) detection to analyse the sample mixture. Aqueous H<sub>3</sub>PO<sub>4</sub> solution (0.1 wt %) was used as the eluent. Products were identified by comparison with the original samples.

CNFs were purchased from Apply Science Company. They have an average diameter of approximately 100 nm and a minimal CVD layer of carbon on the surface of the fibre over a graphitic tubular core. The CNFs denoted as PR24-PS were produced by pyrolytically stripping the as-produced fibre to remove polyaromatic hydrocarbons from the fibre surface. The PR24-LHT CNFs were produced by heat-treating the fibre at 1500 °C. This converts any CVD carbon present on the surface of the fibre to a short-range-ordered structure.

HRTEM images were acquired by using a FEI Titan 80–300 transmission electron microscope with CEOS image Cs corrector. It was operated at accelerating voltage of 300 kV. The TEM samples of both Au/CNF catalysts were prepared by directly putting the powder on Cu grids coated with holey carbon film, without using any ultrasonic dispersion in any solvent to avoid any possible surface decoration on Au particles.

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**Keywords:** carbon  $\cdot$  glycerol  $\cdot$  gold  $\cdot$  oxidation  $\cdot$  transmission electron microscopy

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### **FULL PAPERS**

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Carbon-Supported Gold Nanocatalysts: Shape Effect in the Selective Glycerol Oxidation



**Order, order!** More ordered graphitic layers on the supporting carbon nanofibers surface led to Au particles bonded through their {111} plane, exhibiting more facet area. This catalyst presented higher selectivity toward C–C bond cleavage in the liquid-phase oxidation of glycerol.

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