One-Step Pyrolysis Preparation of 1.1.1 Oriented Gold Nanoplatelets Supported on Graphene and Six Orders of Magnitude Enhancement of the Resulting Catalytic Activity

Iván Esteve-Adell, Ana Primo, Hermenegildo Garcia

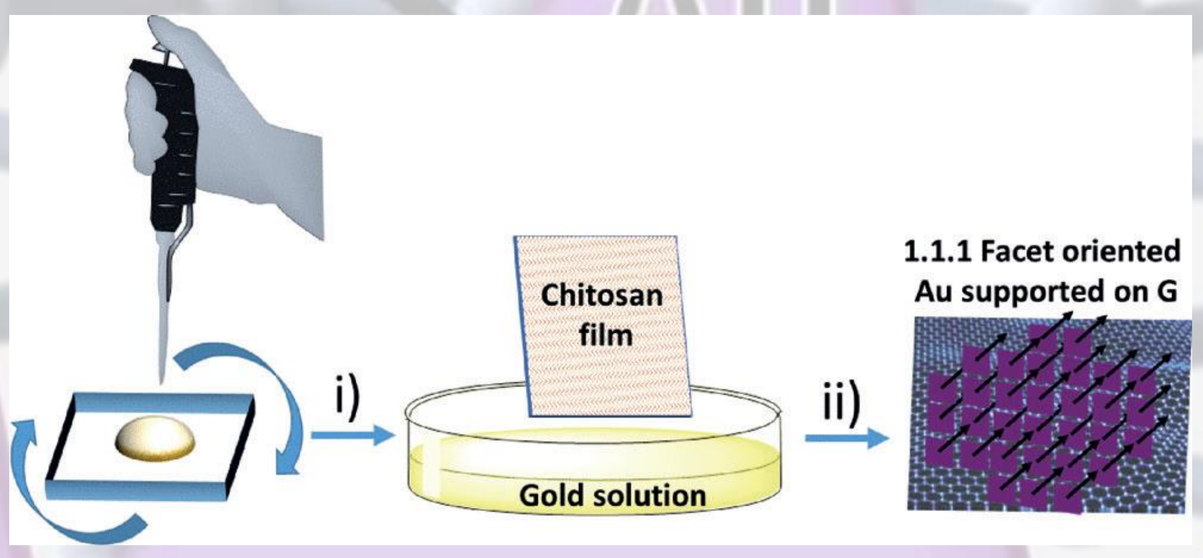
Instituto de Tecnología Química CSIC-UPV, Universidad Politcénica de Valencia

Introduction

Catalysis by supported metal nanoparticles (MNPs) has been a very active field of research in the last thirty years. Remarkable examples of highly active and selective MNP catalysts for organic transformations include aerobic oxidations, couplings, and rearrangements. Catalysis by gold constitutes one of the most salient examples of unforeseen properties for a material that appear exclusively at the nanoscale. A constant target in this area has been the development of more efficient Au catalysts, and this has been generally achieved by changing the support and average particle size. However, according to an existing theory, control of the crystallographic facet exposed by the NP should be a powerful tool to boost catalytic activity. Herein, we report the preparation of 1.1.1 facet-oriented Au nanoplatelets of average lateral dimension 20 nm and 3– 4 nm height, supported on a few layers of N-doped graphene films ($\overline{Au}$/fl-G) that exhibit about six orders of magnitude higher catalytic activity than the analogous unoriented Au catalyst (Au/fl-G) for three different goldcatalyzed reactions.

Experimental

The preparation of $\overline{Au}$/fl-G is based on the formation of N-doped G by simultaneous pyrolysis of nanometric films on quartz under inert atmosphere at 900ºC of a natural biopolymer (chitosan), and Au nanoplatelets by reduction of Au(III). The Au particles are morphologically nanoplatelets, and their dimensions range from 20 nm to larger than 1000 nm, depending on the Au loading on the polymeric precursor.



Scheme 1. Preparation procedure for $\overline{Au}$/fl-G films.(i) Spin coating of an aqueous chitosan solution on quartz (2 x 2 cm^2); (ii) Adsorption of $AuCl_4^-$ on chitosan film before pyrolysis under inert atmosphere at 900ºC.

Characterization

This one-step synthesis of $\overline{Au}$/fl-G contrasts with other reported methods for the preparation of Au NPs supported on G that require prior preparation of G, and even modification of the G surface.
XRD of $\overline{Au}$/fl-G samples exhibit a single peak at 39º, accompanied by a weaker 2.2.2 peak at 82º, characteristic of 1.1.1 oriented crystals. Figure 1 shows XRD of $\overline{Au}$/fl-G compared to Au/fl-G (Au loading 1 wt%) lacking any preferential orientation.

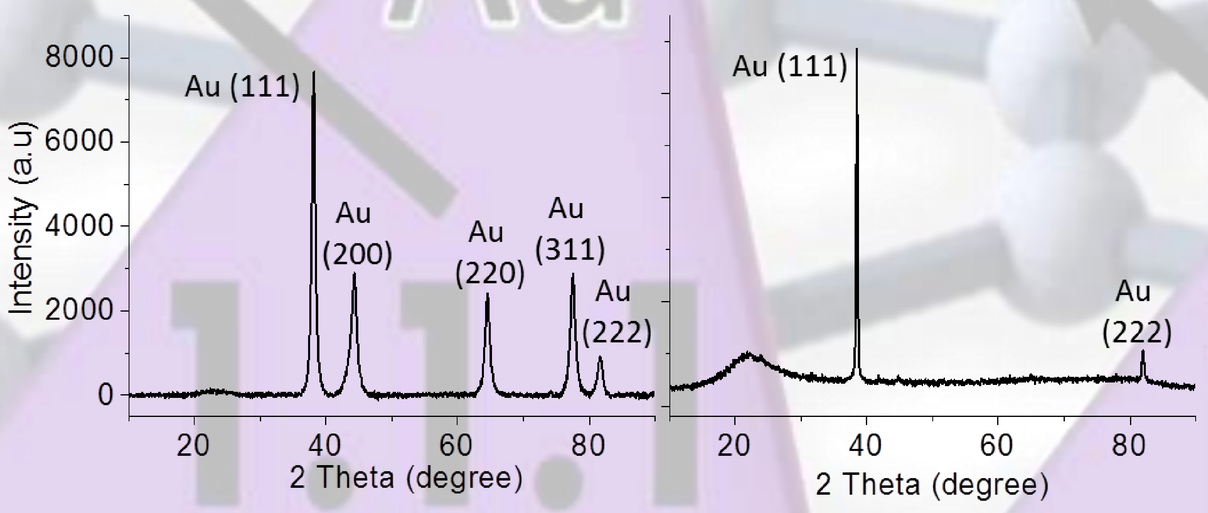


Figure 1. XRD patterns of Au/fl-G (1 wt%; left) and $\overline{Au}$/fl-G (2.4 mg x cm^2; right) showing the different indexation of the peaks. The broad band at about 22º observed in the $\overline{Au}$/fl-G corresponds to the characteristic diffraction of mI-G.

As seen in Figure 1, the consequence of the simultaneous formation of N-doped G and Au NPs is the orientation of the Au NPs crystals
Direct information on the morphology of Au crystals and their preferential 1.1.1 facet orientation, was obtained by electron microscopy

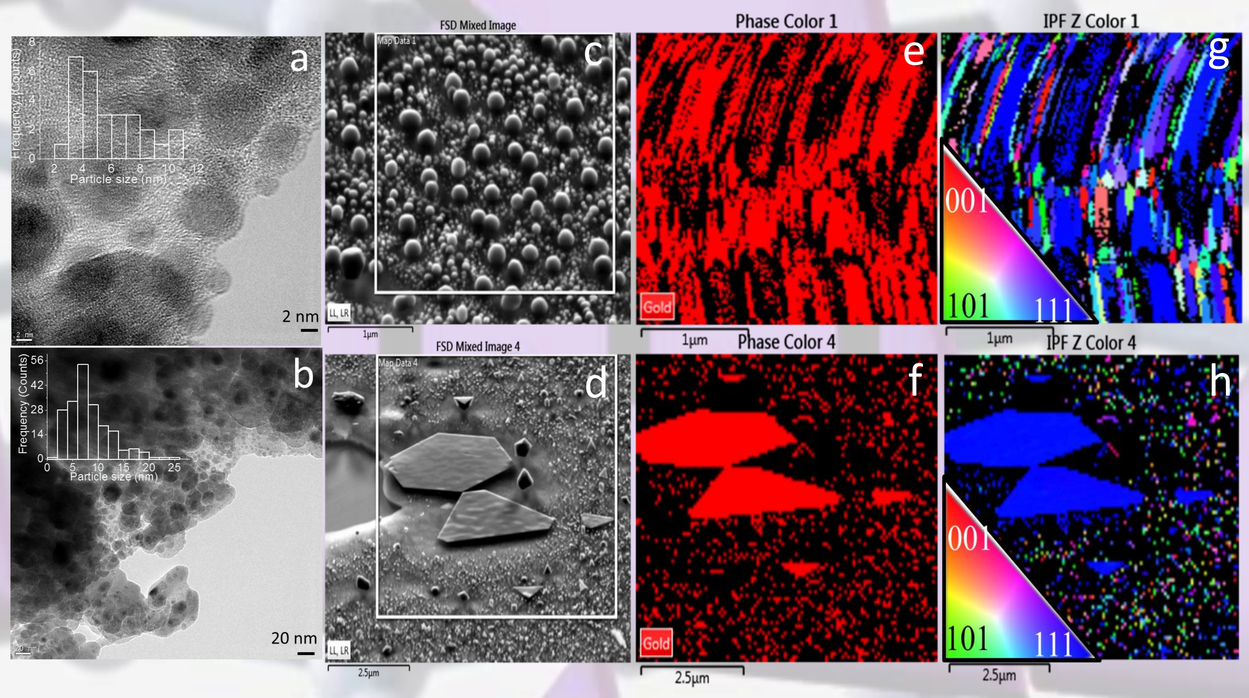


Figure 2. a and b) TEM images of $\overline{Au}$/fl-G (3.2 ng cm^{-2}) at two different magnifications. Insets: corresponding particle size distribution. c and d) SEM images of two films with the selected area for EDS analysis. e and f) EDS analysis of Au of two different films (Au loading= 3.2 ng cm^{-2}) showing the presence of Au in red. g and h) Facet orientation of the nanoplatelets presented the 1.1.1 facet (blue) and the 0.0.1 planes (pink) obtained by transmission Kikuchi diffraction. Insets: color codes.

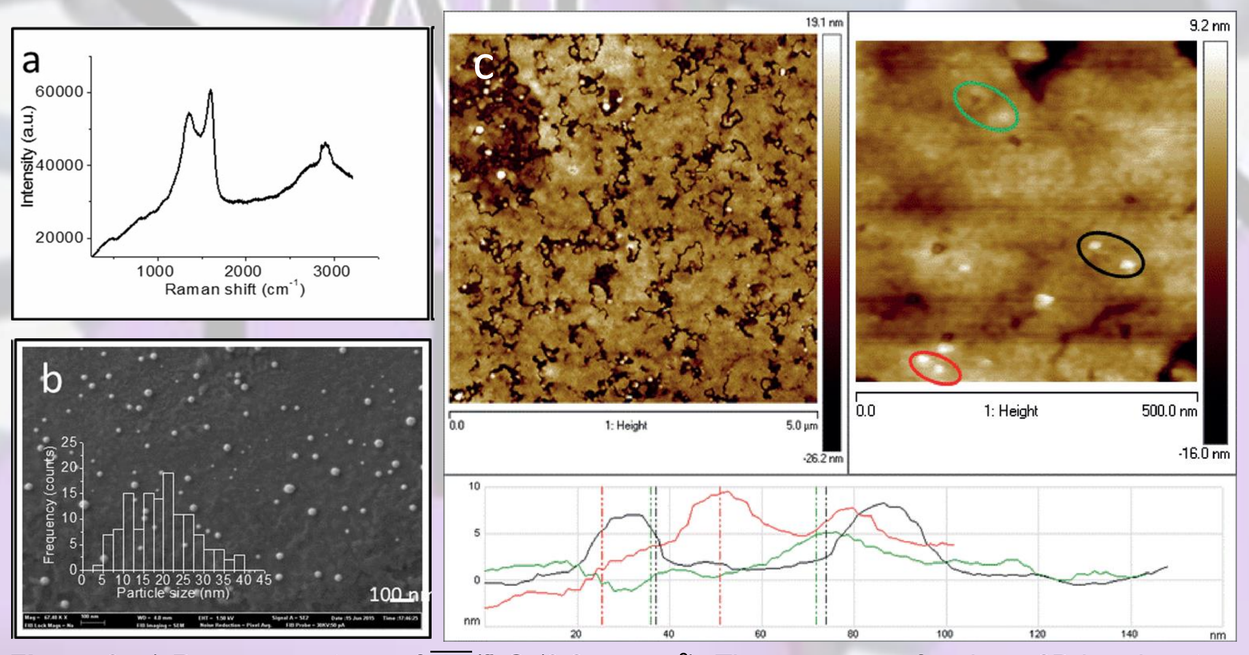
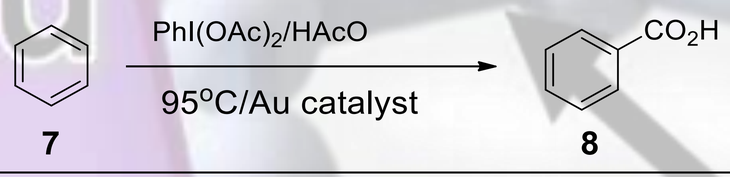


Figure 3. a) Raman spectrum of $\overline{Au}$/fl-G (3.2 ng cm^{-2}). The presence of a sharp 2D band on top of a broad 2D background can be clearly observed at 2850 cm^{-1}. b) SEM image of $\overline{Au}$fl-G (3.2 ng cm^{-2}). Inset: particle size distribution. c) Top view at two different magnifications of the AFM image taken for $\overline{Au}$/fl-G (3.2 ng cm^{-2}). The size (height and lateral dimensions) of five Au nanoplatelets circled in the right frame are presented in the bottom part of the image. Notice that according to the low magnification image shown in the left frame, Au nanoplatelets are consistently located on valleys of the G film of height lower than 10 nm.

Catalytic Activity



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Catalyst	Conversion (%)	Selectivity (%)	Turnover number
$\overline{Au}$/*fl*-G-film	23.9	100	1.4x 10^7
Au-*fl*-G	35.2	100	21.8

[a] Reaction conditions: **7** (10 mmol), PhI(OAc)$_2$ (1mmol), HOAc (17 mL), 95 ºC, 24 h.
Catalyst: $\overline{Au}$*/fl-G* films 1×1 cm^2 (Au 3.2ng) or Au/fl-G powder 10 mg (Au 0.1 wt%).

Conclusions

In conclusion, we have shown a reliable procedure for the preparation of 1.1.1 facet-oriented Au nanoplatelets supported on fl-G by pyrolysis at 900ºC of a chitosan precursor containing $AuCl_4^-$. The resulting $\overline{Au}$/fl-G films exhibit an extremely high catalytic activity for coupling and oxidation reactions compared to unoriented Au/fl-G analogues. Although further work is necessary to fully clarify the origin of the remarkable catalytic activity, it seems that it derives from the combination of strong metal–support interaction and preferential facet orientation.

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