

# ORCA - Online Research @ Cardiff

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository:https://orca.cardiff.ac.uk/id/eprint/130404/

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Liu, Shikai, Gow, Isla, Davies, Thomas, Barnes, Alexandra, Meenakshisundaram, Sankar, Gong, Xiaoxiao, Howe, Alexander G. R., Dixon, Michael, Hutchings, Graham J., Kiely, Christopher J. and He, Qian 2020. Probing composition distributions in nanoalloy catalysts with correlative electron microscopy. Journal of Materials Chemistry A 8, pp. 15725-15733. 10.1039/D0TA00334D

Publishers page: http://dx.doi.org/10.1039/D0TA00334D

### Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <a href="http://orca.cf.ac.uk/policies.html">http://orca.cf.ac.uk/policies.html</a> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



# Supplementary Information

# Probing Composition Distributions in Nanoalloy Catalysts with Correlative Electron Microscopy

Shikai Liu,<sup>a</sup> Isla Gow,<sup>b</sup> Thomas Davies,<sup>b</sup> Alexandra Barnes,<sup>b</sup> Meenakshisundaram

Sankar,<sup>b</sup> Xiaoxiao Gong,<sup>b</sup> Alexander G. Howe,<sup>a</sup> Michael Dixon,<sup>c</sup> Graham J.

Hutchings,<sup>b</sup> Christopher J. Kiely,<sup>b,d</sup> and Qian He<sup>a,\*</sup>

- a. Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Block EA #03-09, 117575, Singapore.
- b. Cardiff Catalysis Institute, Cardiff University, Main Building, Park Pl, Cardiff,
   CF10 3AT, United Kingdom
- c. Hitachi High-Technologies Europe, Daresbury, Warrington WA4 4AB, United Kingdom
- d. Department of Materials Science and Engineering, Lehigh University, 5 E Packer
   Avenue, Bethlehem, Pennsylvania, 18015, United States

<sup>\*</sup>Email: heqian@nus.edu.sg

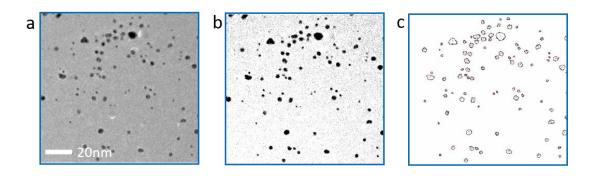
## **Table of Contents**

- **Table S1.** Overall composition of AuPd nanoalloys examined by ICP-AES.
- **Figure S1.** (a) A representative BF-TEM image of AuPd colloids; (b) Image after local threshold filtering using ImageJ; (c) Particles measured by ImageJ with outlines highlighted.
- **Figure S2.** The raw X-ED spectrum (black, *top*) after signal smoothing (red, I) and after background removal (blue, *bottom*).
- **Figure S3.** SEM image of the large area having a high particle density that was used for the 'average' EDS analysis and the corresponding (background subtracted) spectrum acquired from the area highlighted ed by the red box.
- **Figure S4**. BF-TEM images before and after the X-EDS analysis, showing no sign of particle growth, provided the particles were reasonably isolated, which is a prerequirement for the SEM analysis in the first place.
- **Figure S5**. Monte Carlo simulation of the interaction between a 20 keV electron probe (1nm) with Au nanocubes with different dimensions (*i.e.*, 20 nm, 10 nm, 5 nm and 2 nm). The blue lines represent individual electron trajectories travelling downwards, while red lines correspond to back-scattered electrons.
- **Figure S6**. (a-e) A series of BF-TEM images demonstrating how to locate the particles. The arrows indicating the zoom-in sequence from the area of interest (highlighted in red). (f) is the corresponding SEM-BSE image of the same field of view compared to (e). Some isolated particles (such as those highlighted in yellow) can be analysed using EDX using the method described in the paper.

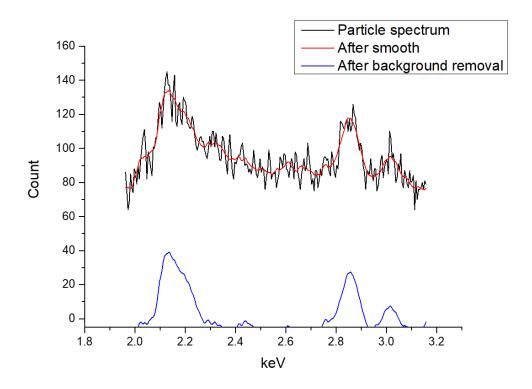
**Table S1.** Composition of the AuPd nanoalloys as determined ed by ICP-AES.

	Pd	Relative	Au	Relative	Pd:Au wt
Catalyst	content	error	content	error	ratio
	wt%	%	wt%	%	
	$M_{Pd}$		$M_{Au}$		
1wt%AuPd/TiO₂(PVP)	0.39	2.5	0.4	2.5	0.98
1wt%AuPd/TiO₂(PVA)	0.37	5%	0.35	9%	1.05

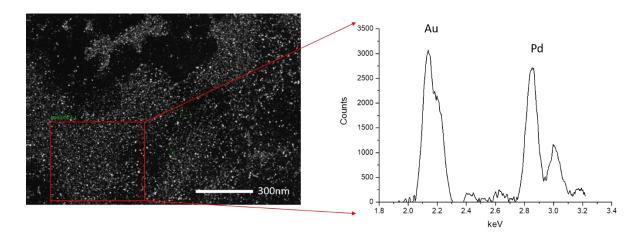
<sup>&</sup>lt;sup>a</sup> The sample for ICP-AES was obtained by digesting the catalysts in *aqua regia*. The solution was then filtered and diluted down to a metal concentration of about 10ppm before being tested.



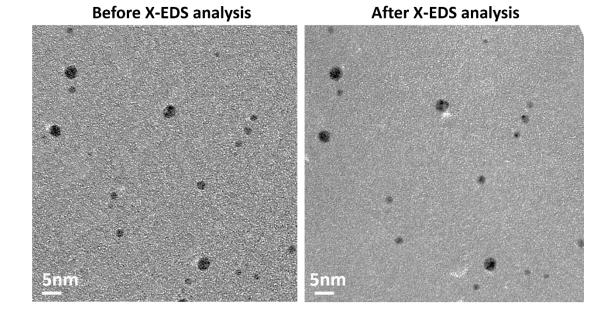
**Figure S1.** (a) A representative BF-TEM image of AuPd colloids; (b) The same image after local threshold filtering using ImageJ; (c) Particle sizes measured by ImageJ with outlines highlighted.



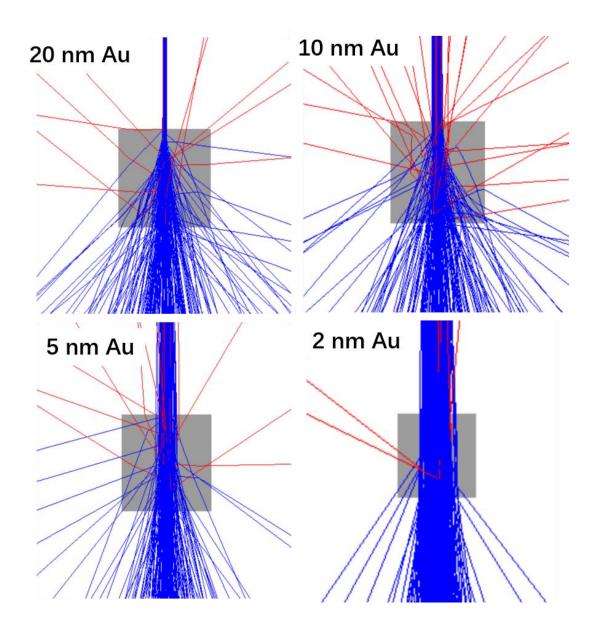
**Figure S2.** The raw X-ED spectrum (black, *top*), after signal smoothing (red, *top*) and after background removal (blue, *bottom*).



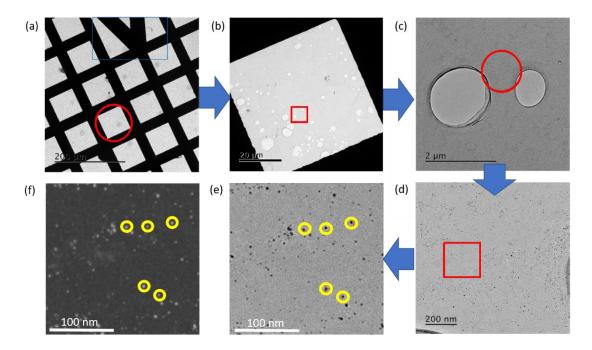
**Figure S3.** SEM image of the area having a high particle density that was used for the 'average' EDS analysis and the corresponding (background subtracted) spectrum acquired from the area highlighted by the red box.



**Figure S4**. BF-TEM images acquired before and after the X-EDS analysis, showing no sign of particle growth provided the particles were reasonably isolated, which is a pre-requirement for the SEM analysis in the first place.



**Figure S5**. Monte Carlo simulation of the interaction between a 20 keV electron probe (1nm) with Au nanocubes with different dimensions (*i.e.*, 20 nm, 10 nm, 5 nm and 2 nm). The blue lines represent individual electron trajectories travelling downwards, while red lines are backscattered electrons.



**Figure S6.** (a-e) A series of BF-TEM images demonstrating how to locate the particles. The arrows indicating the zoom-in sequence from the area of interest (highlighted in red). (f) is the corresponding SEM-BSE image of the same field of view compared to (e). Some isolated particles (such as those highlighted in yellow) can be analysed using EDX using the method described in the paper.