

---

Supporting information for:

Support Effect on the Size and Catalytic Activity  
of Thiolated Au<sub>25</sub> Nanoclusters as Precatalyst

*Jun Fang,<sup>†</sup> Jingguo Li,<sup>†</sup> Bin Zhang,<sup>†</sup> Xun Yuan,<sup>†</sup> Hiroyuki Asakura,<sup>‡</sup> Tsunehiro Tanaka,  
<sup>§,¶</sup> Kentaro Teramura,<sup>§,¶,||</sup> Jianping Xie,<sup>\*,†</sup> and Ning Yan<sup>\*,†</sup>*

<sup>†</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, 4  
Engineering Drive 4, 117585, Singapore.

<sup>‡</sup>Synchrotron Radiation Research Center, Nagoya University, Chikusa-ku, Nagoya 464-8603,  
Japan.

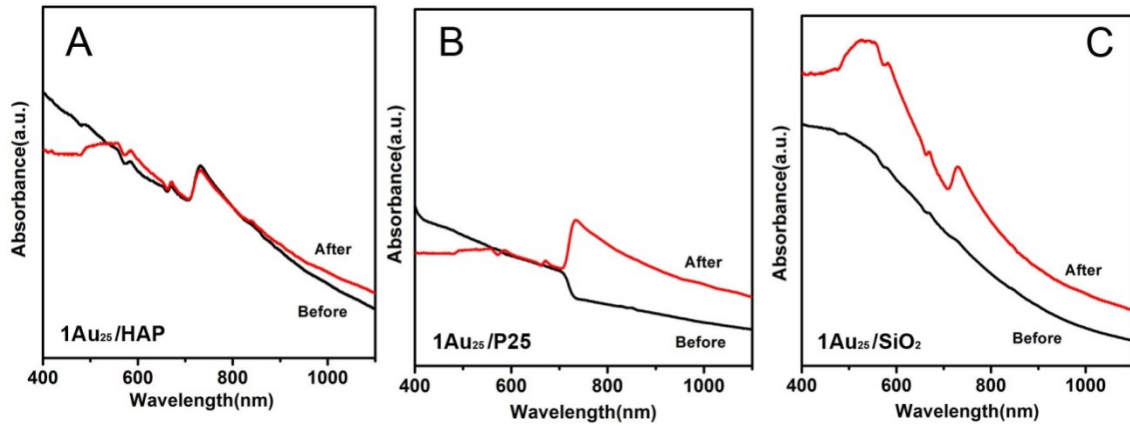
<sup>§</sup>Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,  
Kyoto 615-8510, Japan.

<sup>¶</sup>Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto,  
615-8520, Japan.

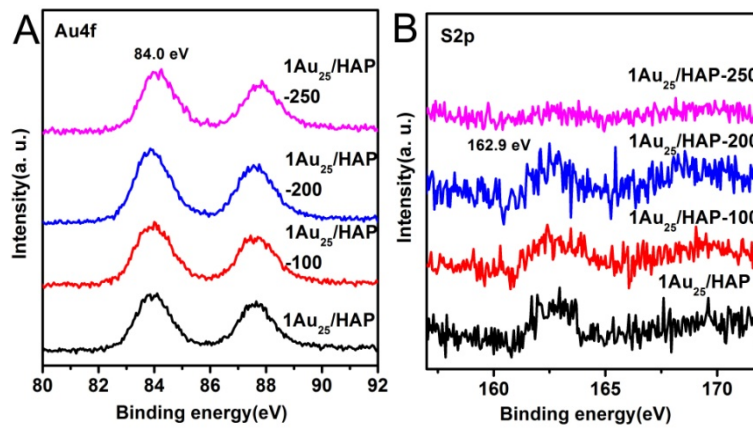
<sup>||</sup>Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and  
Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

\*Corresponding Author. Prof. Dr. Ning Yan E-mail: [ning.yan@nus.edu.sg](mailto:ning.yan@nus.edu.sg)

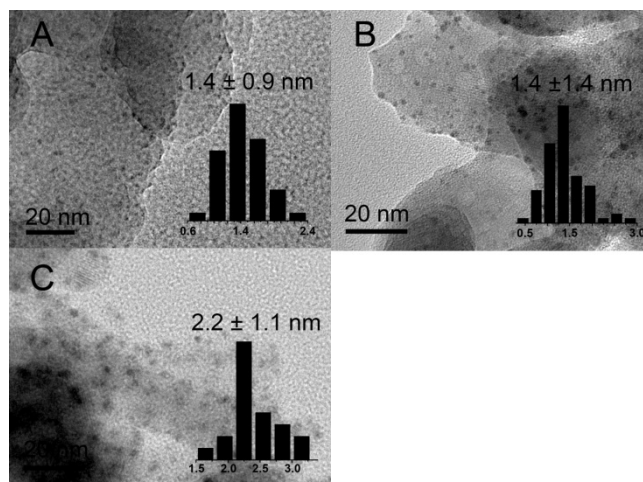
Prof. Dr. Jianping Xie E-mail: [chexiej@nus.edu.sg](mailto:chexiej@nus.edu.sg)



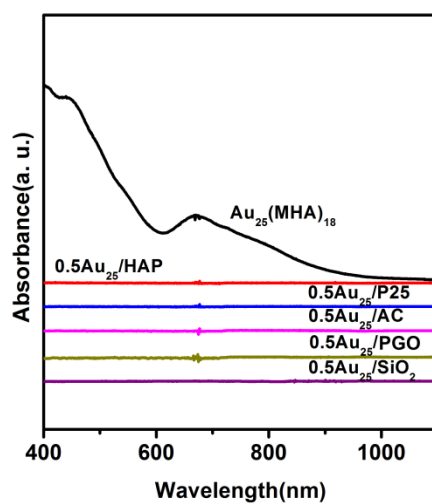
**Figure S1.** UV-Vis diffuse reflectance spectra of 1Au<sub>25</sub>/HAP, 1Au<sub>25</sub>/P25, 1Au<sub>25</sub>/SiO<sub>2</sub> before (black line) and after (red line) calcinations at 300 °C. Note that the peaks with wavelength at 586 nm, 672.5 nm and 732 nm were the noises of the equipment which could be detected in all diffuse reflectance spectra of various samples.



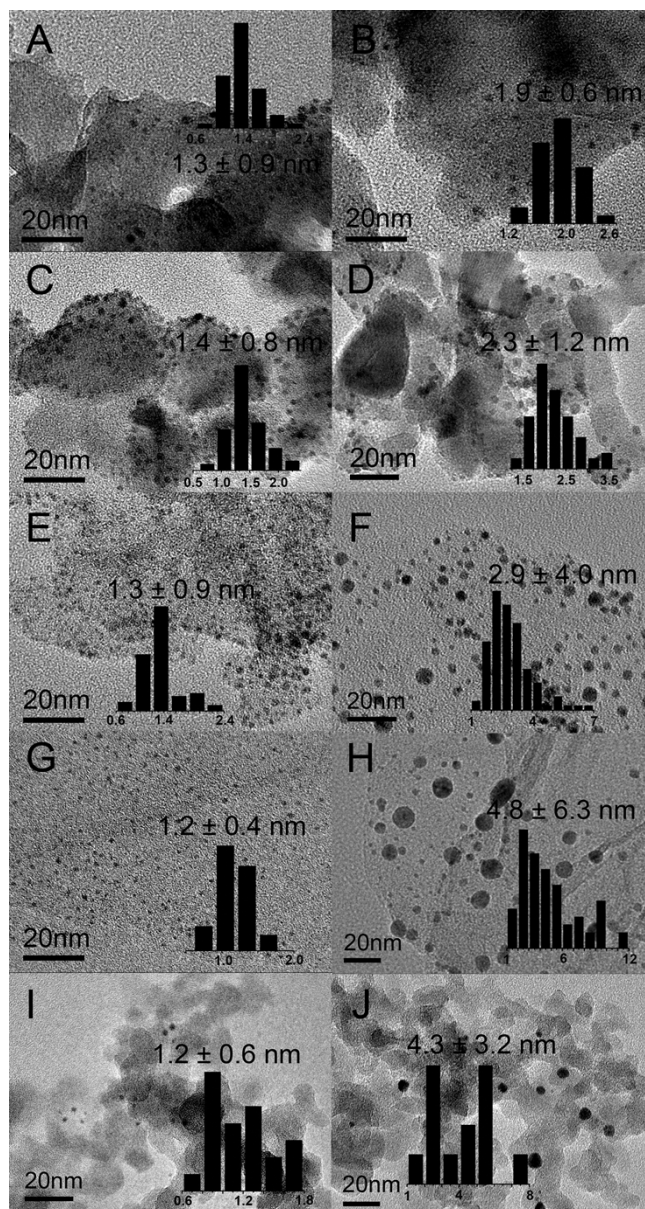
**Figure S2.** XPS spectra of Au<sub>4f</sub> (A) and S<sub>2p</sub> (B) for various 1Au<sub>25</sub>/HAP samples calcined at different temperature.



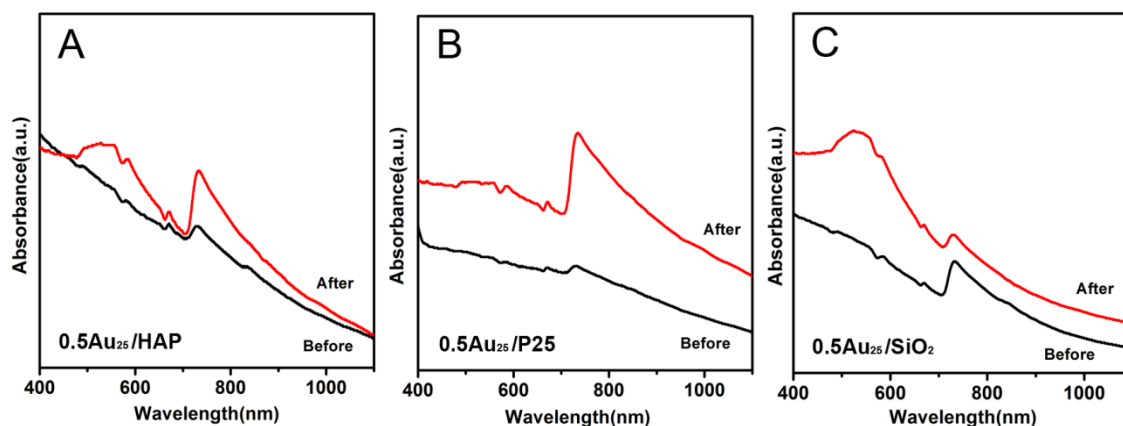
**Figure S3.** TEM images of various  $1\text{Au}_{25}/\text{HAP}$  samples calcined at different temperature: (A) 100 °C, (B) 200 °C, (C) 250 °C.



**Figure S4.** UV-Vis absorption spectra of  $\text{Au}_{25}(\text{MHA})_{18}$  solution before (black line) and after (color lines) the addition of various supports.



**Figure S5.** TEM images and size distribution (inset) of various Au<sub>25</sub>(0.5wt%)/support samples before and after 300 °C calcination. Before calcination: (A) **0.5Au<sub>25</sub>/HAP**, (C) **0.5Au<sub>25</sub>/P25**, (E) **0.5Au<sub>25</sub>/AC**, (G) **0.5Au<sub>25</sub>/PGO**, (I) **0.5Au<sub>25</sub>/SiO<sub>2</sub>**; after calcination: (B) **0.5Au<sub>25</sub>/HAP-300**, (D) **0.5Au<sub>25</sub>/P25-300**, (F) **0.5Au<sub>25</sub>/AC-300**, (H) **0.5Au<sub>25</sub>/PGO-300**, (J) **0.5Au<sub>25</sub>/SiO<sub>2</sub>-300**.

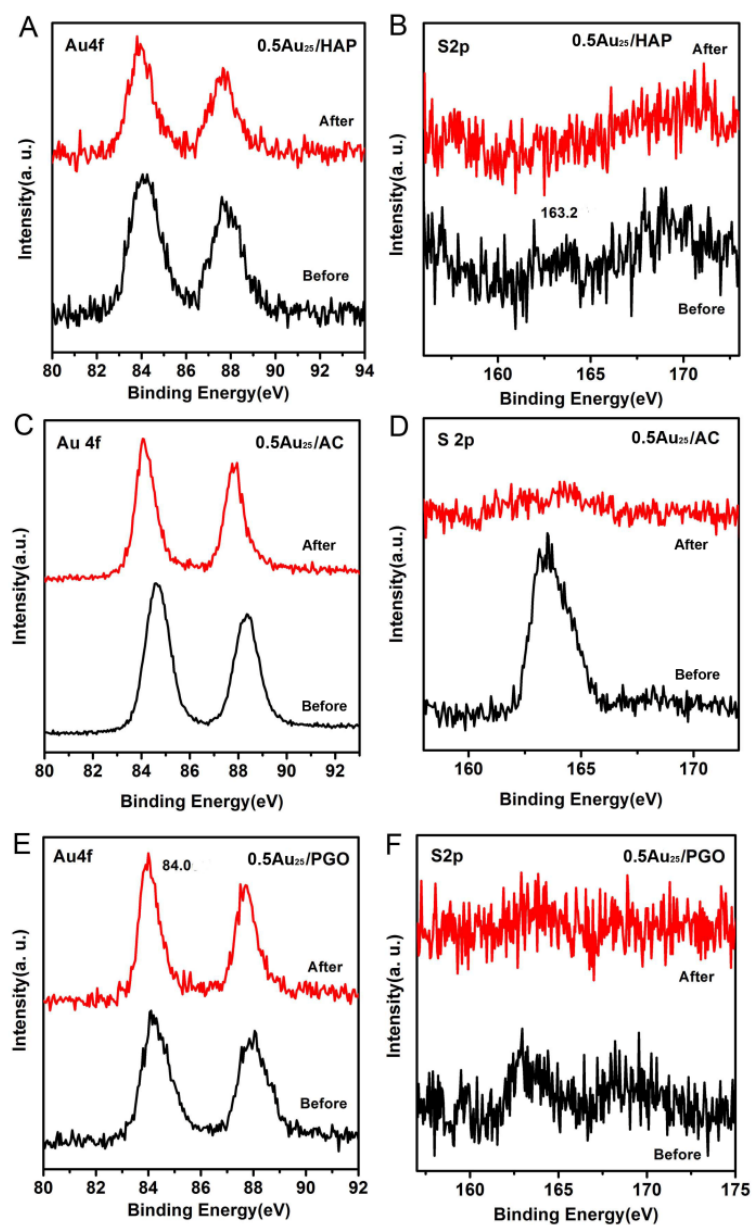


**Figure S6.** UV-Vis diffuse reflectance spectra of  $0.5\text{Au}_{25}/\text{HAP}$ ,  $0.5\text{Au}_{25}/\text{P25}$ ,  $0.5\text{Au}_{25}/\text{SiO}_2$  before (black line) and after (red line) calcination at 300 °C.

**Table S1.** Catalytic activity comparison of styrene oxidation by various supported  $\text{Au}_{25}$  catalysts.

Sample	Conversion (%)	Styrene oxide selectivity
$0.5\text{Au}_{25}/\text{HAP}$	73.9	30.9
$0.5\text{Au}_{25}/\text{HAP-300}$	70.1	33.9
$0.5\text{Au}_{25}/\text{P25}$	63.3	27.9
$0.5\text{Au}_{25}/\text{P25-300}$	51.6	11.7
$0.5\text{Au}_{25}/\text{AC}$	34.4	3.9
$0.5\text{Au}_{25}/\text{AC-300}$	41.7	13.6
$0.5\text{Au}_{25}/\text{PGO}$	42.6	2.4
$0.5\text{Au}_{25}/\text{PGO-300}$	59.4	28.2
$0.5\text{Au}_{25}/\text{SiO}_2$	44.9	28.8
$0.5\text{Au}_{25}/\text{SiO}_2\text{-300}$	55.1	29.2

Reaction conditions: 40 mg styrene, 15 mg 0.5 wt% supported Au catalysts ( $8 \times 10^{-4}$  mmol of metal), 195 mg TBHP, 5 mL toluene (substrate-to-metal molar ratio, 960:1), temperature 80 °C, reaction time 16 h.



**Figure S7.** Au4f and S2p XPS spectra for Au<sub>25</sub> clusters (0.5 wt%) loaded on various supports before and after 300 °C calcination.