

Supporting Information

Oxidation of benzylic compounds by gold nanowires at 1 atm O₂

Lei Hu,^a Xueqin Cao,^a Jianhui Yang,^b Min Li,^a Haiyan Hong,^a Qingfeng Xu,^a Jianfeng Ge,^a Lihua Wang,^a Jianmei Lu,^{*a} Liang Chen,^{*b} Hongwei Gu^{*a}

Synthesis of GNWs:

HAuCl₄·4H₂O (0.2 mmol) in 3 mL hexane and 1mL oleylamine was injected into 9 ml oleylamine at room temperature with vigorous stir. The temperature was raised to 80°C to remove hexane and the mixture turned to colorless in 5 minutes. The reaction was kept at 80°C for four hours without stirring. The GNWs were collected by precipitation with 15 ml ethanol and centrifugation at 4500 rmp/min.

Catalyst testing: Catalyst testing was carried out in a sealed glass reactor fitted with a water-cooled reflux head. The same procedure was followed for each run: Au nanowires in reactant was sealed in the reactor and thrice evacuated and flushed with oxygen (99.995%). The reaction took place at a certain temperature under 1 atm. dioxygen. Resulting product mixtures were analyzed by gas chromatography (VARIAN CP-3800 GC, FID detector) using decane (Aldrich) as an internal standard. Conversion of reactant was calculated with reference to products formed. Product identification and gas chromatograph calibration were carried out using both gas chromatography–mass spectroscopy and standard solutions of each product identified. All catalytic tests were repeated three times.

GC analysis of oxidation product of xylene and ethylbenzene:

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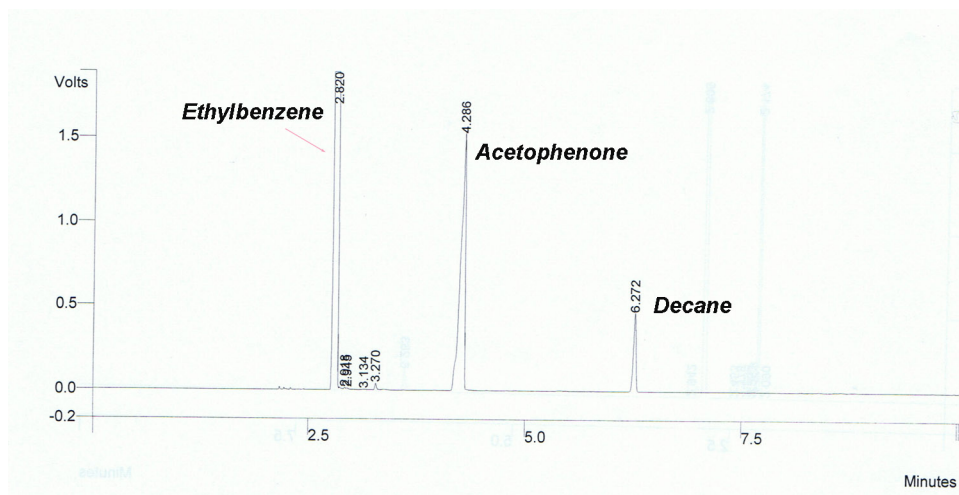
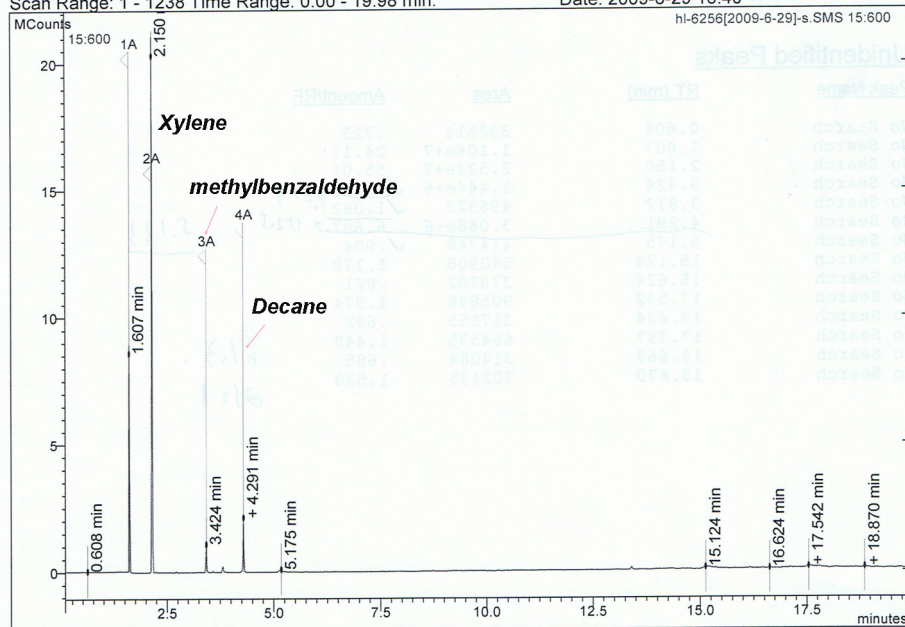
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Sample: hl-6256

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Operator:

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Computational Methods

Spin polarized density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP).¹ The electron exchange and correlation were treated within the generalized gradient approximation (GGA) using the Perdew-Wang (PW91) functional.² The projector-augmented-wave (PAW) method³ was used for the treatment of the core electrons. The cutoff energy was set to 500 eV. All atoms were fully relaxed with the forces converged to less than 0.03 eV/Å. Electron smearing was employed using the Methfessel-Paxton scheme⁴, with a smearing width of $\sigma = 0.1$ eV. The climbing image nudged elastic band (cNEB)⁵ method were used to examine the energy profiles along prescribed reaction pathways. A 30 Å×30 Å×9.57 Å supercell containing one 12-6-1 co-axial gold nanowire (GNW) was constructed in our calculations. The GNW structures were fully relaxed to ensure that it is stable. The Brillouin zone was sampled within a 1×1×3 Monkhorst-Pack mesh.⁶

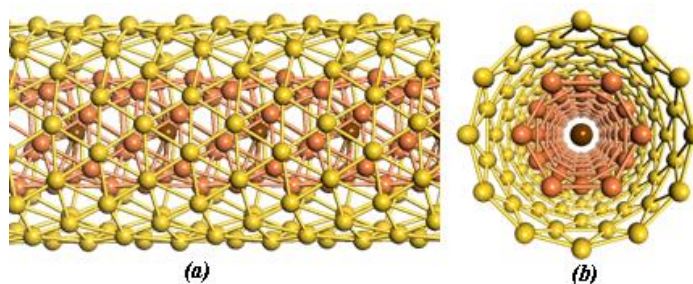


Figure S1. (a) Side view and (b) Top view of the 12-6-1 gold nanowires.

1. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **48**, 13115.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
3. P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.
4. M. Methfessel and A. T. Paxton, *Phys. Rev. B*, 1989, **40**, 3616.
5. G. Henkelman, B. P. Uberuaga and P. Jonsson, *J. Chem. Phys.*, 2000, **113**, 9901.
6. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

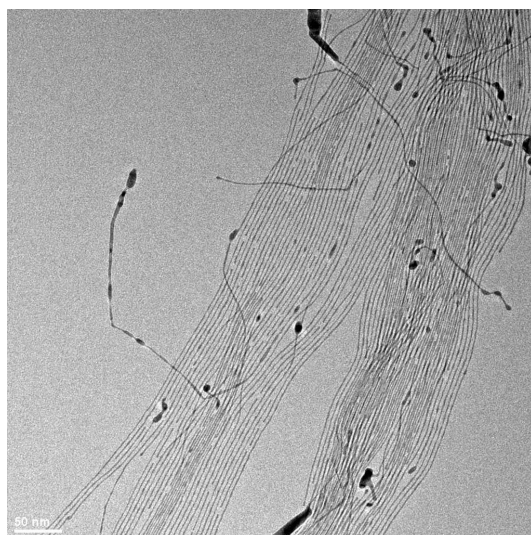


Figure S2. TEM image of 1-mercaptohexadecane capped gold nanowires.

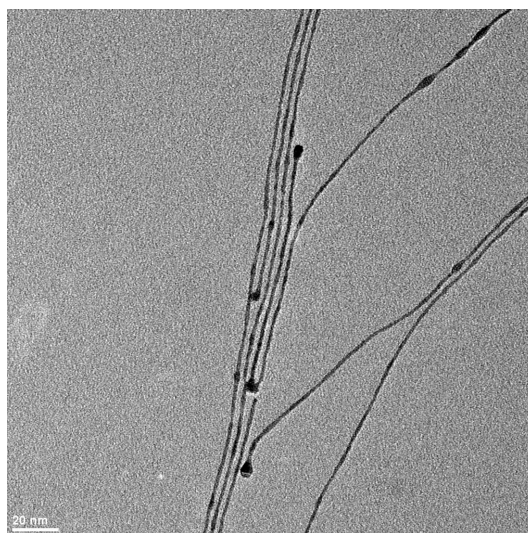


Figure S3. TEM image of gold nanowires after reaction.

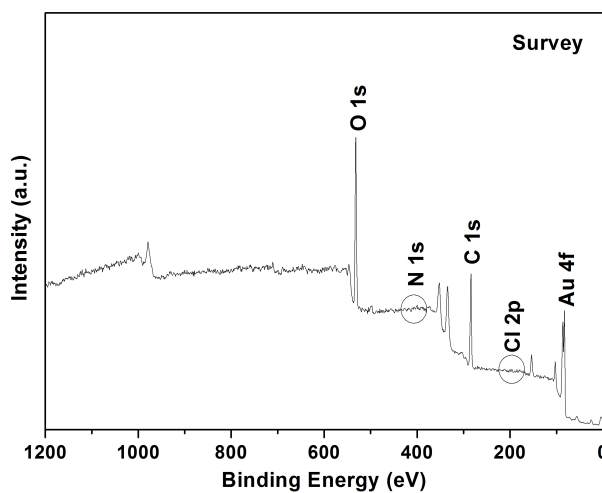


Figure S4. XPS spectra of Au nanowires.

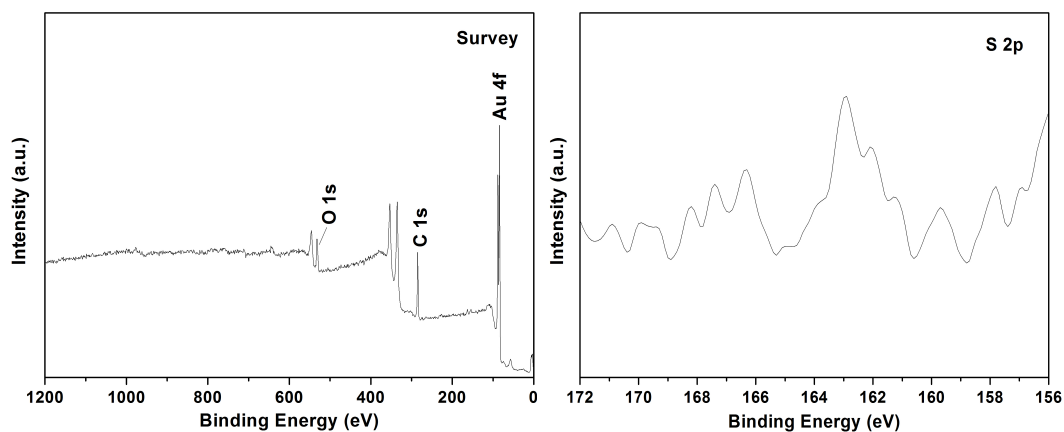


Figure S5. XPS spectra of Au nanowires covered by 1-mercaptohexadecane. 1, survey spectra; 2, S 2p spectra.