Supporting Information

Morphological Effects on the Selectivity of Intramolecular versus Intermolecular Catalytic Reaction on Au Nanoparticles

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Computational detail: All the density functional theory (DFT) calculations were performed with the Vienna Ab Initio Simulation Package¹⁻² (VASP), taking advantage of the Projected Augmented Wave³ (PAW) method to describe ion-electron interactions. The exchange and correlation effects were described by Perdew-Burke-Ernzerhof⁴ (PBE) functional within the generalized gradient approximation (GGA). Throughout this work, a cutoff energy of 500 eV was used for the expansion of the plane-wave basis set. For bulk calculations, the Brillouin zone was sampled using a (12×12×12) Monkhorst-Pack5⁵ mesh. The lattice constant was determined to be 4.15 Å with the above parameters, which is 1.7% larger than the experimental value of 4.08 Å, consistent with the fact that GGA based functional will overestimate the lattice constant of metals.⁶

The two kinds of Au catalysts, Au (111) and Au (211), were modeled by three-layer slabs with a 3×6 supercell, spaced by 25 Å vacuum to avoid the perpendicular interactions between periodic images. During the catalysts building, the two models were optimized by fixing the bottom two layers in their bulk positions and relaxing the very topmost layer until the convergence criterion was reached. The co-adsorption calculations were carried out by using a (3×2×1) Monkhorst-Pack mesh, reciprocally proportional to the lattice parameters. The optimized catalyst slabs were kept fixed in the co-adsorption process in order to improve the calculation speed and the two adsorbates were both allowed to be fully relaxed until the energy barrier between two adjacent ionic steps dropped below 1 meV.

The co-adsorption binding energy (Δ Eco-ads) was defined as

 Δ Eco-ads = E(slab + -S-C₆H₄-NO + -S-C₆H₄-NHOH) + 2E(slab + H) – 3E(slab) – E(HS-C₆H₄-NO) – E(HS-C₆H₄-NHOH) where E(slab + -S-C₆H₄-NO + -S-C₆H₄-NHOH), E(slab + H), E(slab), E(HS-C₆H₄-NO) and E(HS-C₆H₄-NHOH) are the DFT energies of the co-adsorption binding system, the H atom binding system, the clean catalyst slab and the adsorbates in gas phase, respectively. Under this definition, a lower value represents a more stable binding configuration.

The most stable binding site for nitroso molecule on Au(111) and Au(211) was computationally tested. On Au(111) surface, nitroso binding energies on hollow site and top site are calculated to be 0.28 eV and 0.43 eV, respectively. These results strongly indicate that nitroso would bind more tightly on the hollow site of Au(111) surface. Similarly, on Au(211) surface, the value of adsorption energy for nitroso on top bridge site is 0.02 eV, much smaller than the one on top site, which turns out to be 0.41 eV. This gap is even bigger than that on the plain Au(111) surface, implying the thermal advantage of bridge site in capturing nitroso molecule.

The nitroso binding energy is defined as

 $\Delta E_{nitroso} = E(slab + -S-C_6H_4-NO) + E(slab + H) - 2E(slab) - E(HS-C_6H_4-NO)$

where $E(slab + -S-C_6H_4-NO)$, E(slab + H), E(slab), and $E(HS-C_6H_4-NO)$ are the total electronic energies of the nitroso binding system, the H binding system, the clean slab, and the nitroso molecule in gaseous phase, respectively. Under this definition, a smaller value indicates a more stable binding configuration.



Fig. S1 The SEM images of seeds during different synthesis steps. (A) 15 nm, (B) 40 nm, (C) 55 nm, and (D) 65 nm.

Table S1. The Geometric Parameters of the Four Kinds Spinous Au NPs Being Simulated for eachExtinction Spectrum is Shown Below.

	Core diameter	Z span	tip bottom	tip top
Long- SNPs	45 nm	15 nm	15 nm	5 nm
Middle- SNPs	55 nm	10 nm	15 nm	5 nm
Short- SNPs	65 nm	5 nm	15 nm	5 nm
Sphere- NPs	75 nm	0 nm	0 nm	0 nm



Fig. S2 (A) Cross-sectional view of the normalized electric-field intensity distribution profiles for the Long-SNPs (i), Middle-SNPs (ii), Short-SNPs (iii), and Sphere-NPs (iv). (B) UV spectral evolution of four kinds of spinous Au NPs. (C) FDTD calculated extinction spectra showing the spectral evolution of four kinds of spinous Au NPs.



Fig. S3 The time evolution of the ratios between the intensity of the new band at 1590 cm⁻¹ and the O–N–O stretching peak at 1338 cm⁻¹ for four kinds spinous Au NPs.



Fig. S4 (A) HRTEM images taken from one spine of an LSNP Au NPs. (B) The atomic model of a high density of low coordinate atomic steps, such as {211}, {311}, {411}, and {611} steps projected from the [110] zone axis and showing the (100) terraces and (111) steps.



Fig. S5 The HRTEM image of Sphere-NPs. The inset shows the overlarge part of Sphere-NPs surface. The arrow point to Au (111) planes with a lattice spacing of 0.236 nm.

Table S2. The statistical results about the percentages of low coordinated sites on the surface of the four kinds spinous Au NPs.

	Long-SNPs	Middle-SNPs	Short-SNPs	Sphere-NPs
low coordinate sites percentage	≥80%	≥75%	20%	0

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