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Tuning Gold Nanoparticles with Chelating Ligands for Highly Efficient Electrocatalytic CO₂ Reduction

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Abstract: We report the capped chelating organic molecules as a design principle for tuning heterogeneous nanoparticles for electrochemical catalysis. Gold nanoparticles (AuNPs) functionalized with a chelating tetradentate porphyrin ligand show a 110-fold enhancement, compared to the oleylamine-coated AuNP, in current density for electrochemical reduction of CO₂ to CO in water at an overpotential of 340 mV with Faradaic efficiencies (FEs) of 93%. These catalysts also show excellent stability without deactivation, <5% productivity loss, within 72 hours of electrolysis. DFT calculation results further confirm the chelation effect in stabilizing molecule/NP interface and tailoring catalytic activity. This general approach is thus anticipated to be complementary to current NP catalyst design approaches.

Electrocatalytic reduction of carbon dioxide (CO2RR) into value-added chemicals has emerged as a promising solution for incremental energy demand.[1-22] Among many electrocatalysts for CO₂RR, metal nanoparticles (NPs) have been extensively studied due to their high conductivity, large surface area and high stability under reductive potentials.[23-34] Metal NPs often possess surfactants with long alkyl chains to stabilize the surfaces. Nevertheless, these surfactants can block the catalytically active sites of metal NPs and lower the catalytic activity. [26-28, 33, 35] In addition, the monodentate nature of these surfactants can result in ligand detachment under the electrochemical operation, causing particle aggregation and consequent activity decay. $^{[25,\ 28,\ 31,\ 33]}$ In this context, simultaneous stabilization of metal surface and maintaining catalytically active sites through rational molecular design of surface capping ligands of NPs is highly desired. We thus seek to explore the use of a tetradendate ligand that can chelate on the surface of Au NPs, thereby tuning the CO₂RR reactivity and improving the catalytic stability. We anticipate that this ligand

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scaffold can maximally maintain the exposed active metal sites by forming nearly "bare" metal surface, significantly different from surface functionalized by traditional alkyl surfactants (Scheme 1).

Porphyrin ligand **P1** was prepared following a reported approach (Scheme 1).^[36] Oleylamine-capped Au NPs (**OAm-AuNP**) were synthesized according to literature methods.^[27, 33] The ligand exchange step for preparing porphyrin-functionalized Au NPs (**P1-AuNP**) was carried out by soaking **OAm-AuNP** in 50 mM dichloromethane solutions of **P1** for 12 h (see SI). **P1-AuNP** was collected by centrifugation, and dried overnight for characterizations. **P1-AuNP** was then re-dispersed in dichloromethane and dropcasted on carbon paper for electrochemistry studies.^[28, 33]



Scheme 1. Synthetic scheme for the preparation of P1-AuNP.

The successful attachment of P1 to the surface of Au NPs was first identified by UV-Vis spectroscopy (Figure 1a). The UV-Vis spectrum of OAm-AuNP displays a characteristic Au NP absorption at *ca.* 525 nm,^[37] whereas **P1** exhibits a strong Soret band at 425 nm. Upon ligand exchange, the characteristic absorption peak position red-shifts to 540 nm, retaining a shoulder peak at 425 nm as the signature of porphyrin Soret band. In addition, the FT-IR spectrum (Figure 1b) of OAm-AuNP contains alkyl C-H stretches originated from the surfacecapped oleylamine ligands.^[28] The significantly reduced signal of C-H stretching upon P1 functionalization and the additional spectral features resembling of the free P1 ligand reveal a closeto-completion ligand exchange. The peak intensity at 1680 cm⁻¹, corresponding to the C=O stretches of the thioacetate terminal group,^[38] drastically decreases upon **P1** functionalization, suggesting the in-situ cleavage of the thioacetate groups and formation of Au-S bonds (Figure 1b). The completion of ligand exchange was further corroborated by high-resolution N1s and S2p X-ray photoelectron spectroscopy (XPS). The N1s peak at 399.5 eV is consistent with previously reported spectra assigned to a surface-capped porphyrin layer, [36, 39] revealing the existence of porphyrin on Au surface (Figure 1c) and the minor peak at ca. 400.3 eV is associated with amide moieties.^[40] The

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S2p peak centered at 162.3 eV matches the thiolate peak,^[39] further supporting the Au-S linkages (Figure 1d). High-resolution transmission electron microscopy studies reveal that **P1–AuNP** (Figure 1f, S1b) possesses almost identical morphology to **OAm-AuNP** (Figure 1e, S1a). The size distribution analysis reveals an average particle size of approximately 7.2 nm for both particles (Figure S2). The crystallinity of the particles is also similar, as evidenced by X-ray diffraction studies (Figure S3). Finally, coordination of **P1** to the Au surface was verified by solid state ¹³C NMR spectroscopy (Figure S4).



Figure 1. (a) UV-vis spectra of P1, OAm-AuNP, and P1-AuNP recorded in chloroform. (b) FT-IR spectra of P1, OAm-AuNP, and P1-AuNP. (c) High resolution XPS spectrum of (c) N1s region and (d) S2p region of P1-AuNP. TEM image of (e) OAm-AuNP and (f) P1-AuNP, scale bar, 50 nm.

The catalytic activity of **P1-AuNP** and **OAm-AuNP** for electrochemical CO₂RR was then studied in a custom-made cell with 0.5 M KHCO₃ as the electrolyte. The current density was normalized to the geometric area of the working electrodes and all potentials reported herein are referenced to the reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) studies (Figure 2a) have shown that **P1-AuNP** exhibits significantly larger total current densities and positively shifted onset potentials relative to **OAm-AuNP** electrode. The onset potential at -0.16 V vs RHE, positively shifted by 290 mV relative to **OAm-AuNP** for CO₂RR in neutral aqueous media.

We then conducted controlled potential electrolysis (CPE) in CO₂-saturated KHCO₃ buffers under different applied potentials between -0.30 V and -0.70 V to quantify the products of CO2 reduction. Analysis of the head-space and electrolyte solutions following CPE experiments identified CO and H₂ as the gaseous products for both P1-AuNP and OAm-AuNP. The calculated CO Faradaic efficiencies (FEs) for both electrodes are shown in Figure 2b. P1-AuNP shows higher FEs for CO production compared to OAm-AuNP at all examined potentials. At potential of -0.45 V, P1-AuNP displays an optimal FE for CO production (FE = 93%) with a moderate overpotential of 340 mV. By contrast, OAm-AuNP shows a FE of only 14% for CO generation under the same applied potential. Moreover, P1-AuNP also features significantly enhanced specific current densities (jco) of all potential range compared to OAm-AuNP. As shown in Figure 2c, at the applied potential of -0.45 V, P1-AuNP exhibits a 110-fold increase in specific CO current density compared to OAm-AuNP. The striking increase of current density with P1 ligation implies the superior catalytic activity of P1-AuNP. As a control, both FEs and jco of naked-AuNP (prepared by removal of the surface oleylamine of OAm-AuNP; details in SI) were also collected and compared under the same conditions. In brief, naked-AuNP outperforms OAm-AuNP in terms of both FE and jco, but is not as robust as P1-AuNP (Figure S5).

To understand how **P1** contributes to the observed improvements of catalytic activity and selectivity, we first investigated the electrochemically active surface area (ECSA) of both **OAm-AuNP** and **P1-AuNP** by a Pb underpotential deposition (UPD) method (Figure 2d).^[28, 33, 41-42] The calculated ECSA of **P1-AuNP** is 3.2-fold larger than that of **OAm-AuNP**, most likely due to more exposed Au sites as anticipated in ligand design. To further confirm this hypothesis, we also acquired the ECSA of **naked-AuNP**. It turns out that **naked-AuNP** and **P1-AuNP** possess comparable ECSA (1.17:1) and similar TEM pattern (Figure S6), suggesting that both catalysts expose similar numbers of Au sites for CO₂RR.

Longer-term CPE experiments at the potential of -0.45 V show that P1-AuNP maintains its catalytic activity and high FE for CO generation for up to 72 h. In contrast, the activity of OAm-AuNP drastically lowers in the first 12 h and meanwhile the FE drops from 62% to ~10% (Figure 2e). As the persistence of the surface capped or ligated ligands is believed to be crucial to the associated durability of P1-AuNP,[19-22] we thus further evaluated the post-electrochemical stability (24 h) of P1-AuNP FT-IR, XPS, UPD, and consecutive voltammetry by characterizations. The FT-IR spectrum contains attenuated C-H stretches at ca. 2900-2700 cm⁻¹, which is likely attributed to reductive desorption of residual oleylamine ligand present on the Au surface. In contrast, the IR signals from the ligated P1 (ca. 1800-800 cm⁻¹) remain almost intact (Figure S7). Both N 1s and S 2p signals are quite consistent with prior features according to the XPS studies (Figure S8). The decreased intensities of signal peaks are likely resultant from the detachment of the noncovalently surface coated porphyrins (either physically adsorbed porphyrins or stacking of the porphyrins via π - π interactions) or blockage of the surface sites by residual electrolyte. Furthermore, the electrochemically accessible Au surface area of P1-AuNP electrode before and after electrolysis is also similar as evidenced by the comparable peak areas of Au (111) and (110) in the UPD studies (Figure S9). Finally, improved durability of the catalytic interface has been confirmed by the consecutive voltammetry study^[43] under CO₂ atmosphere, which showed that

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the CV curves nearly coincide after 10 consecutive cycles (Figure S10).



Figure 2. (a) CV scans of OAm-AuNP and P1-AuNP electrodes under CO2saturated 0.5 M KHCO3 at pH 7.3. (b) FEs of CO produced by OAm-AuNP and P1-AuNP electrodes. (c) Specific current densities of CO generated by OAm-AuNP and P1-AuNP electrodes. (d) Pb-upd profiles of the OAm-AuNP and P1-AuNP electrodes in 0.1 M NaOH solution containing 1mM of Pb(OAc)₂, scan rate 50 mV/s. (e) Controlled potential electrolysis of OAm-AuNP and P1-AuNP electrode at -0.45 V over a 72 h time course. (g) Tafel plots of OAm-AuNP and P1-AuNP electrodes.

We next explored the kinetics of CO2 reduction on OAm-AuNP and P1-AuNP electrodes using Tafel analysis (Figure 2f). The data demonstrates that P1 affects the mechanistic pathways for CO₂ reduction. A Tafel slope of 123 mV/decade is observed for OAm-AuNP, comparable to what is expected for rate-determining single-electron transfer (120 mV/decade) from adsorbed CO2 to generate the surface adsorbed CO2. In contrast, the Tafel slope for P1-AuNP is 69 mV/decade, reflecting the possibility that P1-AuNP may undergo a preequilibrating one-electron transfer followed by a rate-limiting chemical step.[28, 31]

Finally, we utilized density functional theory (DFT) and computational hydrogen electrode calculations on two models of Au(111) and P1-Au(111) (Figure S11) to further probe the effects of porphyrin ligation on the Au surface and its reactivity consequences. We first found that the adsorption of CO2 on these two models is energetically favored, as evidenced by their adsorption energy of -0.29 eV for Au (111) and -0.68 eV for P1-Au(111) (Figure S12). We then calculated the possible pathways of CO₂ reduction into CO on both models. In particular, the total

energy of each surface model was computed and converted to free energy at 25 °C, 1 atm, and -0.11 V, the theoretical equilibrium potential of CO2 reduction into $\text{CO}^{[33,\ 42]}$ (details in Supporting Information). The initial step of CO₂ hydrogenation $(CO_2 + H^* \rightarrow COOH^*)$ to generate COOH*, a key intermediate of CO₂ reduction into CO,^[24] is found to be an endothermic process with a ∆G increase by 0.57 eV on P1-Au(111), compared to 1.12 eV on pure Au(111) surface (Figure 3), suggesting that the formation of intermediate COOH* is more favorable on P1-Au(111) surface. Subsequent CO* formation (COOH* \rightarrow CO*) on both surfaces is exothermic, along with a lowered ΔG of 0.15 eV and 0.62 eV on P1-Au(111) and Au(111), respectively. This clearly reflects that the formation of CO* from COOH* is favored on both P1-Au(111) and Au(111) surfaces. For the elementary step of CO desorption, only a small energy input of 0.08 eV (P1-Au(111)) and 0 eV (Au(111)) is associated, indicating a weak binding of CO on Au surface.^[27] Taken together, the catalytic through predicted pathway theoretical calculations unambiguously confirm that the reduction of CO2 to CO on P1-Au(111) is energetically more favored than Au(111). Overall, we conclude that the enhanced catalytic performance of P1-AuNP can be attributed to not only the enlarged ECSA shown by UPD experiments but also the boosted instrinsic acitivty revealed by DFT calculation. It is worthy to mention that solvation effect is a minor factor to our target problem and therefore it has been neglected in our calculations (Figure S13; details in SI).

Other than the bare Au(111), we were also interested in acquiring free energy diagram of OAm-coated Au(111) and the relevant computation was then conducted on a simplified model of CH₃NH₂-Au(111) (Figure S14a; details in SI). In brief, the reaction path monitored on the CH₃NH₂-Au(111) is also energetically less favored than that on P1-Au(111) (Figure S15) in the CO₂ reduction to CO. Furthermore, to understand influence of possible electronic effect, induced by the Au-S bonding at the interface, on the free energy profile, we have carried out additional control calculations to probe the free energy diagram on a simplified model of CH₃SH-Au(111) (Figure S14b; details in SI), which is an effective representative for monodentate alkylthiol. In short, our results confirm that the influence of aforementioned electronic effect on the CO₂RR path is trivial (Figure S15). Particularly, the ΔG calculated from the simplified models is expected to be slightly larger than the real cases, but the variance is negligible (details in SI).



Figure 3. Free energy diagrams for CO2 reduction to CO on Au(111) and P1-Au(111).

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In summary, we have developed a molecular approach to tuning the surface properties of metal nanoparticles for electrocatalysis. The tetradendate ligand enables the formation of hollow scaffold on gold nanoparticle surface, leaving the exposed gold sites electrochemically accessible. The prepared molecular/material hybrid electrode, P1-AuNP, efficiently catalyzes the reduction of CO2 to CO with a high activity (2 mA/cm^2 at 340 mV over-potential) and selectivity (FE = 93%). Furthermore, the catalytic stability is significantly improved by the chelation effect of the multi-dentate porphyrin ligand, with negligible decay of FE and current over a 72-hour electrolysis. Theoretical calculations demonstrate that the reduction of CO₂ to CO on porphyrin-ligated Au surface is thermodynamically more favored. We envision that tuning heterogeneous nanoparticle surface with molecularly-tunable multidentate ligands will be a powerful strategy for the development of novel catalysts for many sub-fields of heterogeneous catalysis.

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Notes

The authors declare no competing financial interests.

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Tuning Gold Nanoparticles with Chelating Ligands for **Highly Efficient** Electrocatalytic CO₂ Reduction



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Gold nanoparticles functionalized with a chelating tetradentate porphyrin ligand exhibit significantly improved catalytic activity and stability for electrochemical CO₂ reduction. The inherent structural and electronic tunability of these prototype nanoparticles offers an unrivaled degree of control over their reactivity. This approach will be complimentary to current heterogeneous catalyst design and applicable for various catalytic reactions.

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