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Investigation of Au/Co₃O₄ nanocomposites in glycol oxidation by tailoring Co₃O₄ morphology†

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The interfacial perimeter of nanogold and supports is often deemed as the catalytically active site for multiple reactions while the geometrical configuration of the interfacial perimeter at atomic scale is less studied. Herein, gold nanoparticles (NPs) of ca. 2.0 nm are dispersed on Co₃O₄ support in the shape of nanocubes (dominant Co₃O₄(001) facet) and nanoplates (Co₃O₄(111)), which forms different Au–Co₃O₄ interfaces with respect to the specific facet of the oxide support. A comparison is made on the basis of the interfacial structures and catalytic behavior of ethylene glycol oxidation. STEM analysis identifies that these metallic Au NPs interact with Co₃O₄ with an orientation relationship of Au/Co₃O₄(001) and Au/Co₃O₄(111). XPS and Raman spectroscopy investigations reveal the important variations in the reactivity of surface oxygen, surface O_{ads}/O_L ratio, and evolution of surface oxygen vacancies upon variation of the Co₃O₄ shape. Au/Co₃O₄-P exhibits much better catalytic activity than the Au/Co₃O₄-C counterpart in the aerobic oxidation of ethylene glycol, which is promoted by surface oxygen vacancies and intrinsic defects. It has been revealed that the surface oxygen vacancies participate in activating O₂, thus making Co₃O₄-P a superior support for Au NPs in the catalysis of ethylene glycol oxidation.

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Introduction

Methyl glycolate (MG) is an industrially important chemical, which can be used as solvents, extractants or as food additives. In addition, they are applied in the synthesis of macromolecule polymer material as platform molecules.^{1–3} To date, many strategies have been developed to prepare MG from the different conventional substrates.^{4,5} Moreover, since the heterogeneous Au catalysts were first reported to be active in the oxidation of ethylene glycol to methyl glycolate by Hayashi *et al.*,⁶ a series of studies have shown that Au catalysts supported on various supports are effective in the oxidation of various alcohols.^{7–12}

For analyzing the heterogeneous catalyst, the type of metal (especially Au), particle size and morphology have been extensively explored on the side of anchored metals.¹³ For example, Bianchi *et al.* have substantiated that the decrease in the Au particle diameter of supported catalysts could lead to the increase in catalytic activity in the selective liquid phase

oxidation of glycols.¹⁴ However, Comotti *et al.* revealed that the catalytic activity was inversely proportional to the diameter of Au particles (3–6 nm) in the oxidation of glucose.¹⁵ These findings notably indicate that an Au size effect is apparent in different reactions. Whereas on the side of support, the morphology of oxide supports can mediate the catalytic activity, which is mainly due to their atomic arrangements and electronic structures (*e.g.*, surface defects or surface oxygen vacancies, reconstructions and surface orientations).^{16–18} For instance, the Co₃O₄ morphology of nanotubes,¹⁹ nanosheets,²⁰ nanowires²¹ and nanocubes²² showed distinct shape effect in CO oxidation. Note that the different properties of these Co₃O₄ nanomaterials are strongly associated with exposed crystal planes. Similar to Co₃O₄ nanowires, enclosed by the Co₃O₄(111) facets, show a high CO conversion rate of 161.75 μmol CO g⁻¹ s⁻¹ at 248 °C.²¹ Moreover, the Co₃O₄ nanorods (40% of the Co₃O₄(110) facets) exhibited excellent CO oxidation activity.²³

Although the oxidation of ethylene glycol has been intensively investigated in the field of heterogeneous Au catalysts, identification of active sites and clarification of catalytic mechanism on the supported gold nanoparticles have not yet been fully investigated. Recently, additional studies favour that the reaction should occur at the Au-oxide interfacial perimeter over which the reactants are adsorbed and activated on the gold nanoparticle and the molecular oxygen is active by oxide surfaces (*e.g.* defects).^{24–26} With this respect, both the size of gold particles and the chemical properties of oxide surfaces played critical roles in determining the Au-oxide interfacial

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structures and consequently catalytic activity, which involves electronic and geometric interactions between Au particles and oxide surfaces at their interfaces.

Herein, we have initially prepared the gold NPs of ~ 2 nm supported on Co_3O_4 with different morphology (nanocubes, mainly exposing $\text{Co}_3\text{O}_4\{111\}$ and nanoplate, exposing $\text{Co}_3\text{O}_4\{001\}$) using gold colloids (~ 2 nm Au : PVA particles) as a precursor. Moreover, the size and morphology of Au nanoparticles on the surface of $\text{Co}_3\text{O}_4\text{-C}$ and $\text{Co}_3\text{O}_4\text{-P}$ are similar based on the mathematical statistics, which could simplify the protocols of relationship between Au and oxide support and shed light on the mechanism of oxidation reaction over supported Au NPs. Furthermore, $\text{Au}/\text{Co}_3\text{O}_4\text{-C}$ and $\text{Au}/\text{Co}_3\text{O}_4\text{-P}$ catalysts show a remarkable improvement on the activity than the corresponding plain Co_3O_4 in the glycol oxidation reaction. Furthermore, XPS and Raman spectroscopy results confirmed that the larger number of defects in $\text{Co}_3\text{O}_4\text{-P}$ than in $\text{Co}_3\text{O}_4\text{-C}$ could participate in activating O_2 and in the activation of oxygen species, which demonstrates that $\text{Co}_3\text{O}_4\text{-P}$ is a superior support for Au NPs for catalyzing ethylene glycol oxidation.

Experimental

Synthesis of Co_3O_4 oxides

Co_3O_4 was synthesized by typical procedures reported in the literature.^{27,28} The cubic-like Co_3O_4 ($\text{Co}_3\text{O}_4\text{-C}$ for short) was synthesized by dissolving 10 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 45 mL of ethanol. Then, 10 mL triethylamine (TEA) was dissolved in 25 mL ethanol, which forms a transparent solution. The two solutions were mixed under vigorous stirring for 35 min. After stirring for 30 min, the suspension was transferred into a Teflon-lined stainless steel autoclave and aged at 160°C for 24 h. The solution was filtered and washed by deionized water and ethanol dried at 80°C overnight and then calcined at 350°C for 3 h in air.

For Co_3O_4 nanoplates (abbreviated as $\text{Co}_3\text{O}_4\text{-P}$), 0.9525 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 80 mL of deionized water. Moreover, 2 mL of TEA was added under magnetic stirring. After stirring for 10 min, the solution was transferred into a 100 mL autoclave and reacted at 180°C for 20 h. The precipitate was filtered, washed several times with deionized water and ethanol until free of chloride ions (AgNO_3 test). The solids were dried overnight at 80°C and then calcined at 350°C for 3 h in air. The surfactants in $\text{Co}_3\text{O}_4\text{-P}$ and $\text{Co}_3\text{O}_4\text{-C}$ were completely removed by the calcination and was confirmed by the temperature-programmed oxidation (TPO) measurements (Fig. S1 and S2 in the ESI†).

Preparation of $\text{Au}/\text{Co}_3\text{O}_4$ catalysts

Au : PVA colloids were prepared using a previously reported method.²⁹ Typically, 120 mL of Au sols were deposited on Co_3O_4 support at room temperature and stirred for 3 h at 800 rpm. After stirring, the samples were washed with water and ethanol before being dried overnight at 50°C . The final products were calcined at 300°C for 2 h in the presence of a flow of air to remove all the capping surfactant, which was evidenced by TPO tests (Fig. S3 and S4 in the ESI†). The loading of Au was designed as 1.0 wt%. Moreover, inductively coupled plasma-

atomic emission spectrometer (ICPS-8100, Shimadzu) analysis confirmed that the actual loading of Au was 0.62 wt% for both $\text{Au}/\text{Co}_3\text{O}_4\text{-C}$ and $\text{Au}/\text{Co}_3\text{O}_4\text{-P}$.

Characterization

Scanning transmission electron microscopy (STEM) images were recorded on a F200 microscope operated at 300 kV. The specimen was prepared by ultrasonically dispersing the sample into ethanol, which deposits droplets of the suspensions onto a carbon-enhanced copper grid, and then dries them in air. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 Spirit microscope operated at 120 kV. TPO analysis was measured with an AutoChem II 2920 instrument (Micromeritics) and analyzed using a thermal conductor detector (TCD). Before analysis, 50 mg of samples were pre-treated with a 5 vol% O_2/He mixture (30 mL min^{-1}) at 200°C for 1 h to clean the sample surface. After cooling to room temperature, 5 vol% of O_2/He was used as a feed gas to perform TPO from RT to 600°C . X-ray photoelectron spectra (XPS) were then obtained using an ESCA-LAB MK-II spectrometer with an aluminium anode for $K\alpha$ ($h\nu = 1484.6\text{ eV}$) radiation. The equipment base pressure was 1.7×10^{-10} mbar, and all samples were characterized at room temperature. Detailed spectra were recorded for the region of Co 2p, O 1s and Au 4f photoelectrons with a 0.1 eV step. Analysis was then performed using XPSPEAK41 software and charging effects were corrected by adjusting the binding energy (B.E.) of C 1s to 284.6 eV. The spectra were deconvoluted using the XPSPEAK program by curve fitting with a mixed Gaussian–Lorentzian function. Raman spectra were collected with Renishaw *via* a Raman microscope with a laser wavelength of 785 nm and a laser power of 3 mW and obtained at the same conditions after 60 s of exposure.

Catalytic investigation

The oxidation reactions were conducted in a 10 mL continuous stirred-tank reactor. Typically, the reactions were performed at 90°C under atmosphere of 4 MPa O_2 , stirring at 600 rpm, for 4 h using 2 mL methanol, 500 mg ethylene glycol and 100 mg catalysts. After the reaction, the reactor was cooled to less than 5°C with an ice–water mixture and depressurized. An internal standard of *n*-amyl alcohol was added to liquid products. The conversion of ethylene glycol and selectivity toward the product of methyl glycolate (MG), dimethyl oxalate (DMO), and hydroxyethyl formate (HF) are analyzed by gas chromatography–mass spectrometry method on a GC/MS 7890B-5977A with a capillary column HP-5MS with He as carrier gas. The conversion of ethylene glycol (X_{EG}) and selectivity toward desired product of methyl glycolate (S_{MG}) were calculated using the following equations:

$$X_{\text{EG}}(\%) = \left(1 - \frac{C_{\text{EG}}}{C_{\text{EG,initial}}}\right) \times 100\% \quad (1)$$

$$S_{\text{MG}}(\%) = \frac{C_{\text{MG}}}{C_{\text{DMO}} + C_{\text{HF}} + C_{\text{MG}}} \times 100\% \quad (2)$$

where $C_{\text{EG,initial}}$ represents the initial ethylene glycol concentration, and C_{EG} , C_{MG} , C_{HF} , and C_{DMO} stand for the



concentration of the ethylene glycol, methyl glycolate, dimethyl oxalate, and hydroxyethyl formate after the catalyzed reactions, respectively.

Results and discussion

Characterization of Au/Co₃O₄

TEM images showed that the Co₃O₄-C oxides are monodisperse with a uniform size of ~22 nm (Fig. S5 in the ESI†). Co₃O₄-P with a hexagonal shape was prepared with an average edge length of ~160 nm and thickness of ~25 nm (Fig. S6 in the ESI†). Further, the Au : PVP colloids of 2 nm were adsorbed and deposited onto the surface of the defined Co₃O₄ oxides (Fig. S7 in the ESI†). Au/Co₃O₄ samples primarily kept their initial Co₃O₄ morphologies after the introduction of Au NPs and annealing at 300 °C. HAADF-STEM images showed that the gold particles were dispersed uniformly in space on the oxide-supports (Fig. 1a–f). The gold particles exhibited a mean size of 2.0 ± 0.5 nm and a quasi-truncated octahedron enclosed by Au{111} and {100} facets in the Au/Co₃O₄-C samples. Moreover, Au NPs uniformly anchored on the Co₃O₄(001) facet as the measured inter-planar distance of 0.29 nm corresponds to the (220) crystal plane of cubic Co₃O₄ oxides (Fig. 1b and c).³⁰

For Au/Co₃O₄-P catalysts, lattice fringes with an inter-planar spacing of 0.46 nm can be attributed to the Co₃O₄(111) facets of Co₃O₄-P oxides.^{27,31} Gold particles uniformly loaded onto the Co₃O₄(111) facet and exhibited a quasi-truncated octahedron enclosed by Au{111} and {100} facets, as seen in Fig. 1d and e. Au NPs showed a particle size of 2.0 ± 0.6 nm (Fig. 1d), which is similar with the particle size in the Au/Co₃O₄-C and the parent

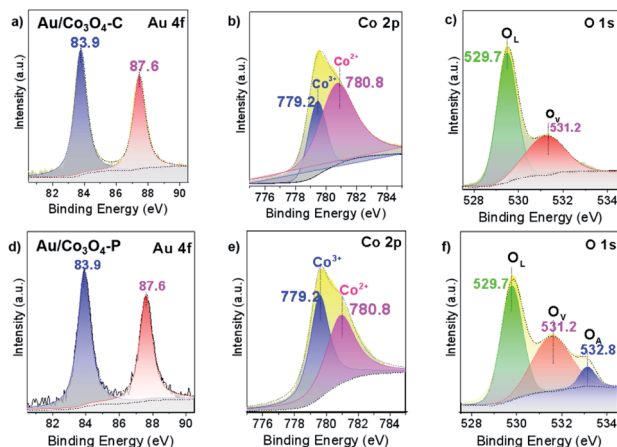


Fig. 2 Au 4f, Co 2p and O1s XPS survey spectra of (a–c) Au/Co₃O₄-C and (d–f) Au/Co₃O₄-P. Note that the Co³⁺, Co²⁺, O_v, O_A and O_{latt} species are fixed at 779.2, 780.8, 531.2, 532.8 and 529.7 eV, respectively.

Au colloids. It demonstrates that the small gold particles exhibited strong interaction with both Co₃O₄(001) and Co₃O₄(111) facets, and the Au NPs should have stronger interaction with Co₃O₄(111) facets with a short lattice spacing of 0.21 nm than the Au NPs on the Co₃O₄(001) plane.

Further, XPS analysis was performed to explore the chemical state of Au/Co₃O₄ catalysts. The spectra of Au 4f, Co 2p and O 1s are compiled in Fig. 2. Au 4f XPS spectra showed two same sets of the Au 4f_{7/2} and Au 4f_{5/2} signals at bonding energies (BEs) of 83.9 and 87.6 eV (Fig. 2a and d), which indicates that the

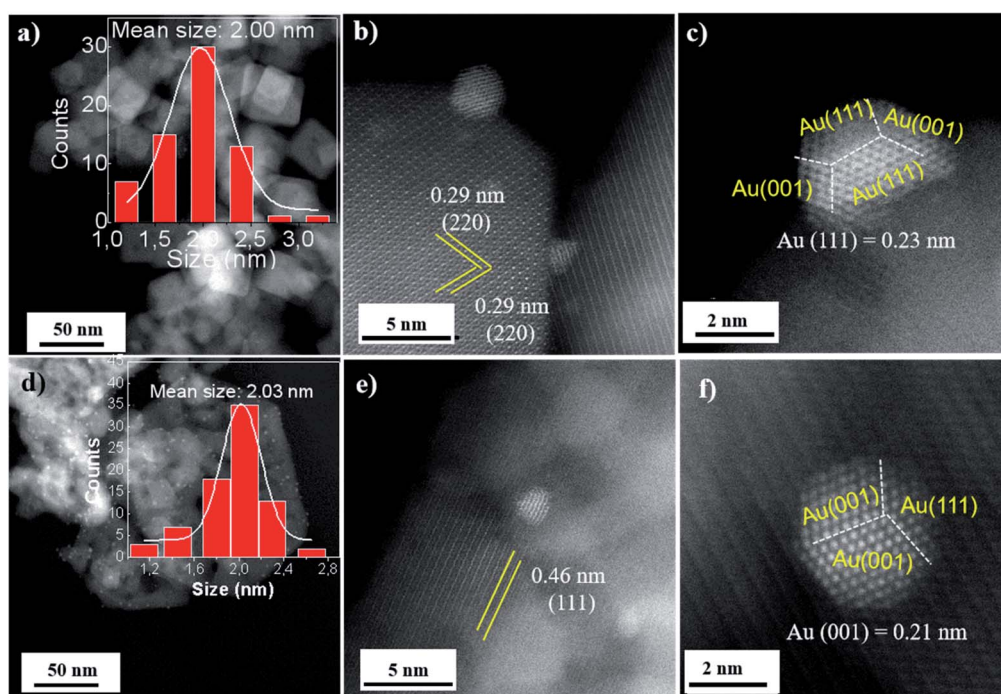


Fig. 1 STEM images of Au particles on the Co₃O₄(001) in the Au/Co₃O₄-C samples (a–c) and Co₃O₄(111) in the Au/Co₃O₄-P (d–f). Insets, in (a) and (c), are the size distribution of the gold nanoparticles.



Table 1 Surface element compositions calculated based on the Fig. 2

Catalysts	Au loading (wt%)	Au mean size (nm)	Co ³⁺ /Co ²⁺ ratio	O _V /O _L ratio
Au/Co ₃ O ₄ -C	0.62	2.00	1.07	0.60
Au/Co ₃ O ₄ -P	0.62	2.03	1.09	0.79

nanogold chemical states are metallic (Au 4f_{7/2} BE of gold foil is ~83.8 eV) in both Au/Co₃O₄-C and Au/Co₃O₄-P samples.³² TEM and XPS results suggest that the chemical property of gold nanoparticles (*e.g.* Au loading, Au mean size, and oxidation state) are similar, which can relieve the factors (*e.g.* size-dependence, charge effects, *etc.*) and focus on the Au-Co₃O₄ interfaces in the aerobic oxidation of ethylene glycol to methyl glycolate (*vide infra*).

In addition, two XPS sets were found at 795.1 and 780.0 eV with an energy difference of ~15.1 eV, which corresponds to Co 2p_{1/2} and Co 2p_{3/2} spin-orbit-split doublet peak of Co₃O₄ spinel.^{33–37} The Co 2p_{3/2} peak of 780.0 eV is fitted and deconvoluted into two peaks of 780.8 and 779.2 eV (Fig. 2b and e), which is attributed to Co²⁺ and Co³⁺ species, respectively. In addition, the surface ratio of Co³⁺/Co²⁺ is similar in the Au/Co₃O₄-P and Au/Co₃O₄-C catalysts (1.07 *vs.* 1.09, Table 1).

Moreover, the O 1s electronic levels were examined. The asymmetric O 1s peaks could be deconvoluted to two components at 531.2 and 529.7 eV for Au/Co₃O₄-C (Fig. 2c). However, the O 1s peaks can be best fitted by three components centred at ~529.7, ~531.2, and ~532.8 eV, which can be ascribed to lattice oxygen atoms (O_L), oxygen vacancies (O_V), and surface oxygen species (O_A), respectively.³⁸ Furthermore, the existence of peak at 532.8 eV (Fig. 2f) for the Au/Co₃O₄-P is assigned to surface chemisorbed or dissociated oxygen.³⁹ The O_V/O_L ratio of Au/Co₃O₄-P (0.79) is much higher than that of Au/Co₃O₄-C (0.60, Table 1). Above all, it is obvious that the XPS strength of surface oxygen species increases for Au/Co₃O₄-P, which indicates the existence of more oxygen vacancy sites on the Au/Co₃O₄-P than that of Au/Co₃O₄-C.

To clearly identify the surface oxygen vacancies of Au/Co₃O₄-C and Au/Co₃O₄-P, Raman analysis was applied. As shown in Fig. 3, the Au/Co₃O₄ catalysts displayed five vibration peaks (A_{1g} + E_g + 3 F_{2g}) in the range of 150–800 cm⁻¹. The peaks at 484, 523 and

622 cm⁻¹ are assigned to the E_g, F_{2g}⁽²⁾ and F_{2g}⁽¹⁾ symmetry, respectively. The Raman peak at 196 cm⁻¹ is attributed to the F_{2g}⁽³⁾ mode of tetrahedral sites (CoO₄) while the peak at 691 cm⁻¹ with A_{1g} symmetry is attributed to the characteristics of octahedral CoO₆ sites, which correspond to the unique characteristics of spinel-type cubic Co₃O₄ phase, which is in great agreement with these reported for Co₃O₄.⁴⁰ The full width at half-maximum (FWHM's) of all peaks in the Au/Co₃O₄-P are higher than that of Au/Co₃O₄-C catalysts, which could account for the high concentration of surface oxygen vacancies and intrinsic defects for Au/Co₃O₄-P.⁴⁰ To summarize, Au/Co₃O₄-P has more defective structures than Au/Co₃O₄-C which can promote the oxidation reactions as these surface defective structures can facilitate adsorption and activation of oxygen species.

Catalytic performance

The aerobic oxidation of ethylene glycol is chosen as a probe reaction to evaluate the catalytic efficiency of Au/Co₃O₄ catalysts and Co₃O₄ catalysts. The aerobic oxidations were carried out in a liquid phase: a 4 MPa O₂ gas at 90 °C for 4 h (details see Experimental section), and the catalytic results are compiled in Fig. 4. Note that both Co₃O₄-C and Co₃O₄-P supports were inactive during the aerobic oxidation of ethylene glycol under such conditions. Clearly, the presence of Au NPs has notably improved the catalytic activity in the EG oxidation reactions. There major products of methyl glycolate (MG), dimethyl oxalate (DMO), and hydroxyethyl formate (HF) were observed by a GC-MS method in the Au/Co₃O₄ catalyzed oxidation reaction of ethylene glycol (EG). Note that DMO can be considered as the further oxidative esterification of MG product and HF is other oxidative esterification of methanol with EG (Scheme S1†).⁴¹ Au/Co₃O₄-P catalysts gave a promising activity in the oxidation of ethylene glycol; a 67% conversion was achieved while a medium EG conversion of ~41% was obtained over the Au/Co₃O₄-C catalysts. Moreover, Au/Co₃O₄-P catalysts gave a higher selectivity (~87%) towards the desired MG product (an important

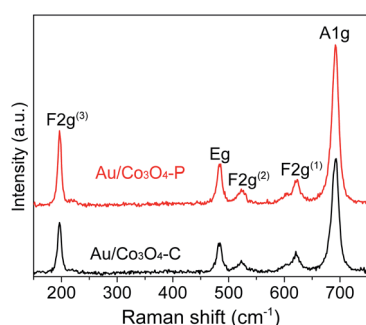


Fig. 3 Raman spectra of the as-prepared Au/Co₃O₄-C and Au/Co₃O₄-P catalysts.

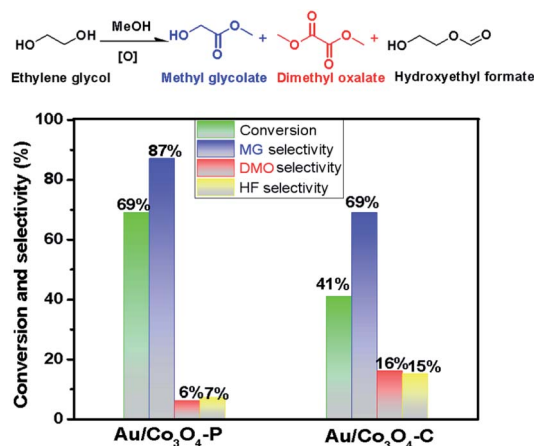


Fig. 4 Catalytic performance of Au/Co₃O₄-P and Au/Co₃O₄-C over oxidation of ethylene glycol. Reaction conditions: 500 mg ethylene glycol and 100 mg catalysts in a 2 mL methanol, 4 MPa O₂, 90 °C, for 4 h.



chemical) than Au/Co₃O₄-C catalysts, as shown in Fig. 4. In all, the Au/Co₃O₄-C catalysts are considered inferior to that of the Au/Co₃O₄-P counterpart.

Previously, Dong *et al.* observed that the correlation between the activity and diameter is consistent with the nature of active exposed atoms.⁴² However, when compared to previous studies, our results show that the interfacial environment between Au and Co₃O₄ support seems to impact the catalytic activity largely, while the Au particles on both Au/Co₃O₄-C and Au/Co₃O₄-P catalysts have similar structure based on our statistical calculation (Table S1 in the ESI†). Indeed, the difference between the activity can be mainly attributable to the change of interfacial environment due to the introduction of Au on the different crystal plane (Co₃O₄{111} for Co₃O₄-P and Co₃O₄{001} for Co₃O₄-C).

Recently, it is widely accepted that the catalytic behavior of supported Au catalyst is strongly associated with Au particles and the nature of the support as well as the Au-support interaction.^{43,44} For liquid oxidation reactions, the situation is more complicated due to the catalyst's surface properties.^{45–47} Herein, the selective oxidation only occurs in the presence of Au, and the Au/Co₃O₄-P shows better activity than that of Au/Co₃O₄-C. Combined with similar Au dispersion in Au/Co₃O₄-P and Au/Co₃O₄-C samples, the oxygen vacancy site rooted in the Au-Co₃O₄ interfacial structure should play a vital role in this glycol oxidation. Nevertheless, we believe that it is justified that the Au/Co₃O₄-P exhibits better catalytic activity than Au/Co₃O₄-C in the oxidation of ethylene glycol, which is promoted by the surface oxygen vacancies and intrinsic defects confirmed by XPS and Raman results.^{48,49}

Conclusions

In summary, gold NPs of *ca.* 2.0 nm immobilized on Co₃O₄ oxides have been synthesized through a simple impregnation of gold colloids and oxides. Au/Co₃O₄-C and Au/Co₃O₄-P catalysts show a remarkable improvement on the activity than the corresponding plain Co₃O₄ oxides in the glycol oxidation reaction. The sensitive factors, *e.g.* size-hierarchy and chemical state of the gold particles, are effectively excluded during the nanogold catalyzed reactions. STEM analyses identified that Au particles with Au{111} and Au{100} exposures interact with Co₃O₄{111} and Co₃O₄{001}. Therefore, Au/Co₃O₄{111} exhibited better catalytic activity and selectivity in the catalyzing glycol oxidation. XPS and Raman spectroscopy analyses confirmed that the surface oxygen vacancies and intrinsic defects on Co₃O₄{111} on the surface of gold NPs are responsible for the high catalytic behavior in catalyzing glycol oxidation.

Conflicts of interest

There are no conflicts to declare.

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