Electronic Supplementary Information

Carbon Monoxide Mediated Chemical Deposition of Pt or Pd Quasi-Monolayer on Au Surfaces with Superior Electrocatalysis of Ethanol Oxidation in Alkaline Media

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1. Experimental details

The Au disk or 50-nm thick film electrode was first electrochemically cleaned in 0.5 M $HClO_4$ followed by being bubbled with CO for 10 min at 1 atm. Then a certain volume of 23 mM K_2PtCl_4 was added to reach 0.1 mM K_2PtCl_4 in 0.5 M $HClO_4$. The solution was bubbled with CO for another 10 min to ensure the growth of a quasi-monolayer (q-ML) of Pt on Au (denoted as the Au/Pt electrode). This Au/Pt electrode having a shiny Au appearance was rinsed with ultrapure Milli-Q water (>18 MΩ cm).

1 mg of Au/C (~5nm, 30 wt. %, TKK) was suspended in 1 mL of ultrapure water under sonication for 1 min, and then the suspension was transferred into a CO-saturated 6 mL solution with 0.1 mM K_2PtCl_4, 0.1 mM Na_2PdCl_4 or (0.033 mM K_2PtCl_4 + 0.066 mM Na_2PdCl_4) for the synthesis of Au@Pt/C, Au@Pd/C or Au@(Pd+Pt)/C, respectively. The above mixture was ultrasonicated for 10 min at room temperature. To cover one ML of platinum group metal (PGM) atoms on a 5-nm Au cuboctahedral nanoparticle requires an Au:PGM atomic ratio of ca. 1:0.3 by estimation,[1] in practice, the atomic ratio of Au to the PGM in the precursor solution is controlled to be 1:0.4. The as-formed Au@PGM/C was washed and separated in ultrapure water through centrifugation at 5000 rpm and dried in a vacuum oven at 60 °C. This chemical deposition process can be scaled up.

Au@Pt/C was characterized by XRD, TEM and EDS. The XRD measurement was performed with a D8 ADVANCE (Bruker). High resolution TEM imaging and elemental mapping were accomplished on a JEM-2100F (JEOL) equipped with a built-in EDS.

To prepare the catalyst ink, 1 mg of the as-synthesized Au@PGM/C was suspended in 550 uL of mixed (v/v =10:1) H_2O and Nafion solution (5 wt.%) under ultrasonication for 10 min. 7 μL of the ink was casted on a freshly polished glassy carbon disk electrode (ϕ=3 mm) via a pipette and dried with nitrogen flow. The catalyst-coated GC electrodes were used for electrocatalytic evaluation in 1 M KOH + 1 M CH_3CH_2OH.

The ca. 10-nm thick Pt was galvanostatically electrodeposited on a 50-nm-thick Au film or a Au bulk electrode at 0.3 mA cm^{-2} for 200 s in 4 mM H_2PtCl_6 + 0.7 M Na_2HPO_4 solution, and denoted as the Au/Pt-10 nm electrode. This Au/Pt-10 nm served as the working electrode in spectroelectrochemical measurements.

For all spectroelectrochemical measurements, a Au foil served as the counter electrode, and a Hg/Hg_2SO_4 (saturated Na_2SO_4) (or a Hg/HgO (1 M KOH)) electrode as the reference electrode in acidic (or alkaline) solution. However, all potentials in this work are referred to reversible hydrogen electrode (RHE). High-purity Ar (99.999%) was used for deaeration. Pt/C (50 wt.%, TKK) and Pd/C (40 wt.%, BASF) were taken as the reference samples. A CHI 605B electrochemistry workstation was used for potential and current controls. All measurements were carried out at room temperature.

2. Pt/Pd quasi-monolayer formation on Au

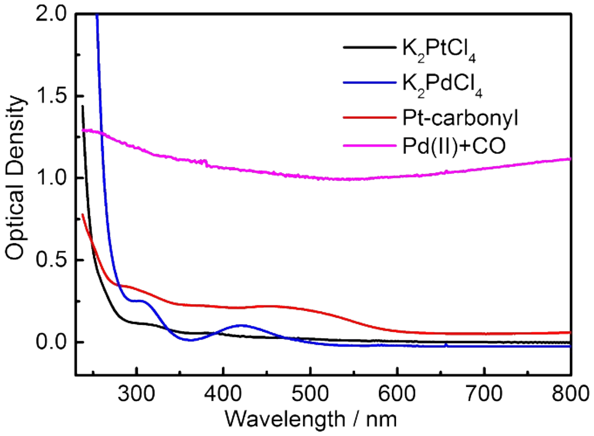
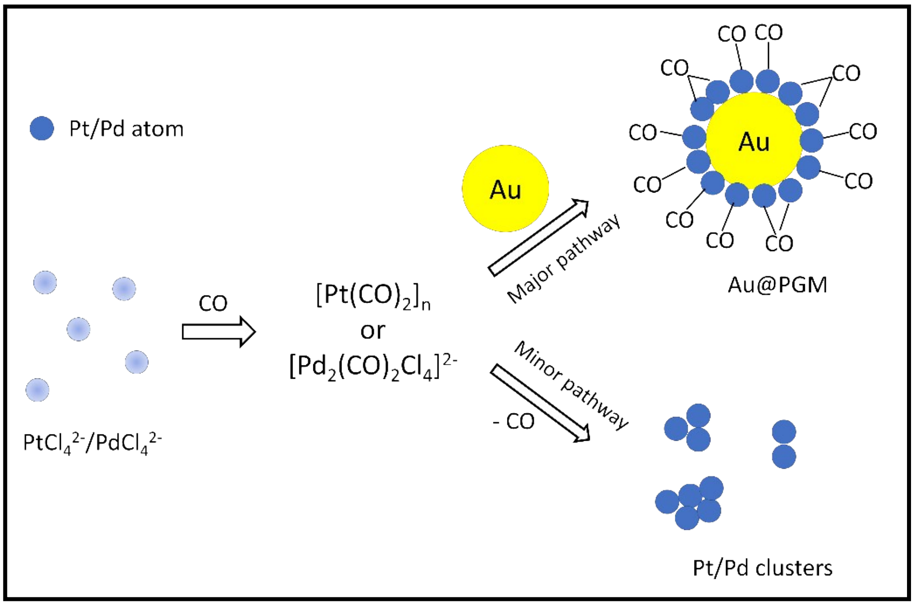


Fig. S1 UV-Vis absorption spectra of 0.5 mM K_2PtCl_4 and 0.5 mM K_2PdCl_4 solution in the absence of CO, and after 10 min bubbling of CO.

In order to understand the role of CO in the formation of Pt q-ML on Au, the structure of Pt carbonyl complex as a result of introducing CO to dilute K_2PtCl_4 was characterized by UV-Vis absorption spectroscopy. Visual inspection indicates a color change from light yellow to cherry red after bubbling CO in the above solution for 10 min. $[PtCl_4]^{2-}$ may react with CO in water to form the Pt-carbonyl complex $[Pt(CO)_2]_n$.[2-4] To facilitate the observation, a higher concentration of K_2PtCl_4 than that for electroless deposition (i.e., 0.5 mM vs. 0.1 mM) was used for UV-Vis absorption spectroscopy measurement. Fig. S1 shows a broad band around 500 nm for the freshly prepared Pt-carbonyl complex solution, suggesting that *n* may be 3, 6 or 9 according to previous studies.[2-4]

The formation of Pt on Au may be illustrated in Scheme S1. Briefly, the above mentioned $[Pt(CO)_2]_n$ is thermo-dynamically unstable and decomposed upon meeting with the Au substrate owing to the strong bimetallic interaction of Au-Pt, forming a Pt shell on Au, and the strong CO adsorption on Pt(shell)-Au(substrate) largely prevents the further 3D growth of Pt. If the Pt-carbonyl complex solution in the absence of Au/C was left in the open air for an extended period of time, the solution gradually turned colorless and a sort of Pt black deposit could be observed, suggesting that a minor parallel pathway to form Pt clusters on carbon black should be minimized in the synthesis of Au@Pt-qML/C by controlling appropriate precursor concentration and deposition time.

The above hypothesis may be extended for the CO-mediated Pd q-ML formation on Au. Compared to Pt carbonyl complex, Pd carbonyl complex is less stable and a strong extinction was observed. According to a previous report,[2] palladium complex may exist in the form of $[Pd_2(CO)_2Cl_4]^{2-}$, which could decompose immediately in the presence of water. Thus, an increasing competition for forming Pd clusters may be envisioned, compared to the case of Pt carbonyl complex, as also evidenced by a small amount of Pd clusters on carbon with EDS elemental mapping.



Scheme S1 Illustration for Pt or Pd shell deposition on Au nanoparticle.

3. CVs for Au/Pt-qML electrodes prepared by different methods

The cyclic voltammogram for the Au/Pt-qML prepared with the CO-mediated electroless deposition method is very close to that for the one prepared either by CO-assisted electrodeposition method or by the Cu-UPD and galvanic redox replacement method, further confirming the feasibility of the CO-mediated electroless deposition method in forming Pt q-ML on Au.

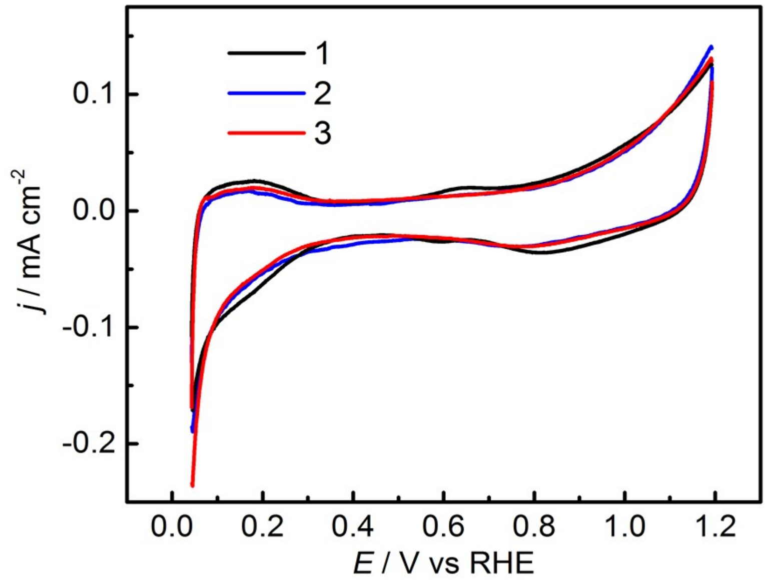


Fig. S2 CVs in 0.5 M $HClO_4$ at 50 mV s^{-1} for Au/Pt bulk electrodes prepared by (1) Cu-UPD on Au from a solution containing 0.1 M H_2SO_4 + 0.05 M $CuSO_4$ at 0.35 V vs RHE with subsequent galvanic redox replacement of Cu by Pt in 0.1 M H_2SO_4 + 3 mM K_2PtCl_4; (2) electrodeposition of Pt q-ML on Au from a CO-saturated Pt(II) solution at 0.3 V vs RHE; (3) CO-mediated electroless deposition as described above.

4. TEM images of Au/C and Au@Pt-qML/C

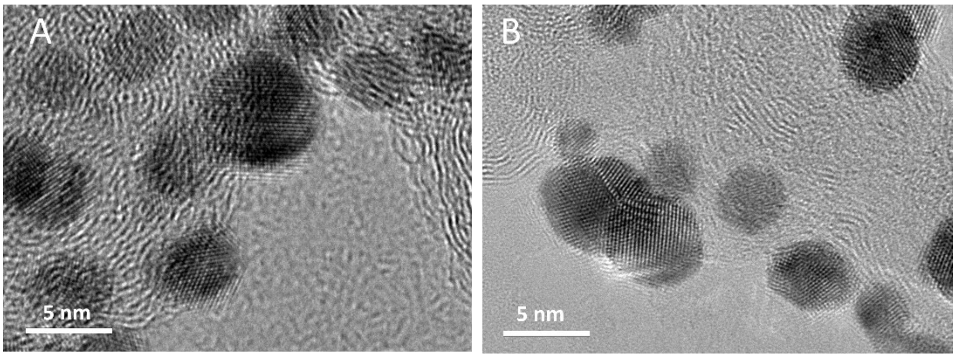


Fig. S3 High resolution TEM images of Au/C (A) and Au@Pt-qML/C (B)

5. XRD measurement on Au/C and Au@PGM-qML/C

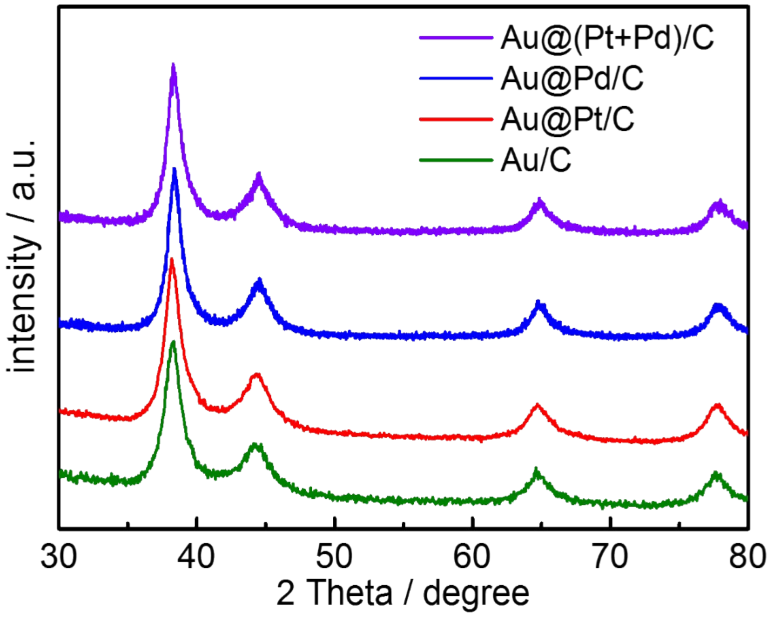


Fig. S4 XRD patterns of Au/C and as-synthesized Au@PGM-qML/C.

6. TEM imaging and EDS mapping on Au@Pd-qML/C

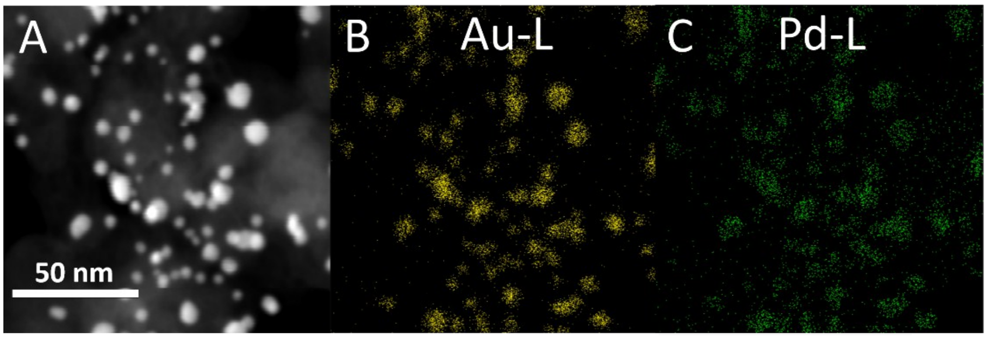


Fig. S5 (A) Dark field-STEM and corresponding EDS-STEM images of Au@Pd-qML/C (B, C).

The elemental mapping of Au@Pd-qML/C clearly showed a preferential deposition of Pd q-ML on Au nanoparticles. A small amount of Pd ultrafine clusters could also be deposited on the carbon substrate which was detected with EDS but remained unseen on dark filed STEM image.

7. Preferential decomposition of Pt carbonyl complex on Au substrate

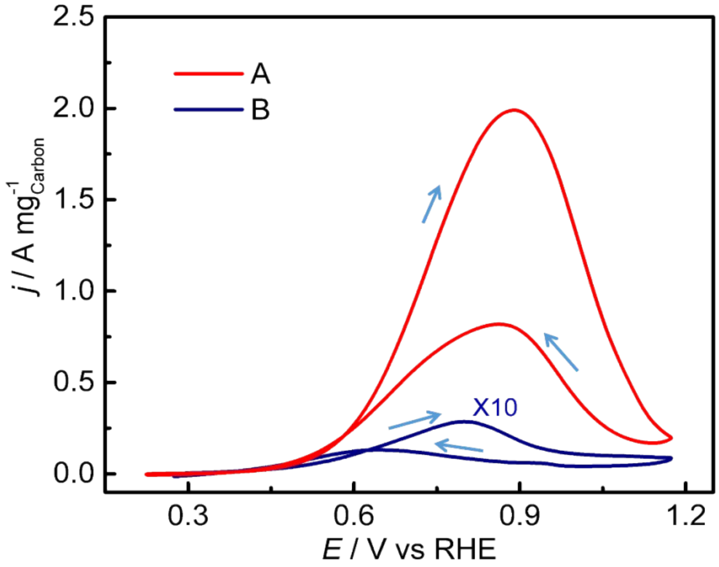


Fig. S6 Comparison of the EOR activities for two carbon black-supported materials in 1 M NaOH + 1 M ethanol at 50 mV s^{-1}. The red curve (A) corresponds to CV for the Au@Pt-qML/C typically prepared by the reported CO-mediated electroless q-ML deposition procedures and the blue curve (B) corresponds to the CV for Vulcan-72 carbon black that is treated in the otherwise same procedures except the absence of Au. Note that the current response of the latter is magnified by a factor of 10.

When carbon black instead of Au/C was treated in the otherwise same procedures as in forming Au@Pt-qML/C, a very small portion of Pt carbonyl complex may decompose to form Pt clusters on the carbon substrate (Pt/C), but the as-obtained Pt/C exhibit an EOR peak current (blue curve with current magnified by 10) only 1/70 times as low as that observed for the Au@Pt-qML/C as prepared at a constant mass of carbon. In addition, a notable hysteresis of the anodic and cathodic peaks was observed in the former. Therefore, Au substrate catalyzes the Pt-carbonyl decomposition to enable the preferential deposition of Pt on Au. In other words, the observed CV response for the former (red curve) comes overwhelmingly from the EOR on Au@Pt-qML nanoparticles rather than on Pt nanoparticles.

8. Comparison of EOR activities on Au/Pt-qML electrode in alkaline and acidic media

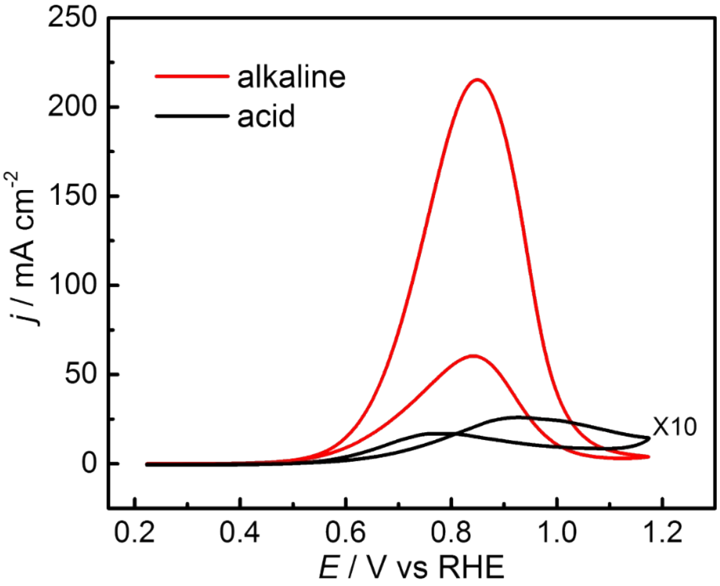


Fig. S7 CVs for the Au/Pt-qML electrode in 0.5 M $HClO_4$ + 1 M CH_3CH_2OH (black curve) and in 1 M NaOH + 1 M CH_3CH_2OH (red curve) at 50 mV s^{-1}

The promoting effect of the underlying Au on EOR at Pt surface was compared in acidic and alkaline solutions. The promoting effect of the underlying Au on EOR at Pt surface is much more pronounced in alkaline media than it is in acidic media with respective enhancement factors of ca. 130 and ca. 3 for the former (Fig. S7) and the latter[5] in term of peak oxidation current. The stronger enhancement of EOR on Au/Pt-qML in alkaline media may be associated with the trapping of OH^-.[6]

9. Effects of deposition time and potential cycling on EOR activity on Au@Pt/C

We have examined the effect of deposition time on electrocatalytic activity towards EOR on the as-formed Au@Pt/C in Fig S8. The deposition time for the powder samples was changed by controlling the sonication time during the synthesis as indicated in the relevant figures. The actual deposition may be a bit longer than the sonication time due to the next step of separation of samples by centrifugation. The CVs of the four as-formed Au@Pt/C in blank 0.5 M $HClO_4$ suggest the coverage of a quasi-monolayer of Pt on Au is largely completed after 10 min's sonication time. For all the tested samples, the EOR peak current in the forward scan increases with potential cycling and then gradually decreases. To remove the effect of surface poisoning species accumulated at open circuit condition, the CVs of the 2nd cycle for tested samples are selected for comparison in this paper (Fig. 4, Fig S7 and Fig S8(B)).

The main contribution of this work is to demonstrate that CO-mediate chemical deposition can be used to deposit a quasi-monolayer of Pt (and/or Pd) on Au. It is always challenging to maintain the stability of a core-shell structure at high potentials, especially when a monolayer of metal is formed. We envision that partial structure disruption of the quasi-monolayer of Pt (Pd) on Au may occur as the potential is repeatedly swept to (hydro)oxide formation potential values. Nevertheless, for the application purpose, given that the amount of Pt on Au is constant, we care more about the durability of the Au@Pt/C samples in EOR. As shown in Fig. S8 (C), 10 min's sonication of Au/C in CO-contained Pt(II) bath yields the Au@Pt-qML/C sample with the best performance for EOR in alkaline media in terms of activity and stability.

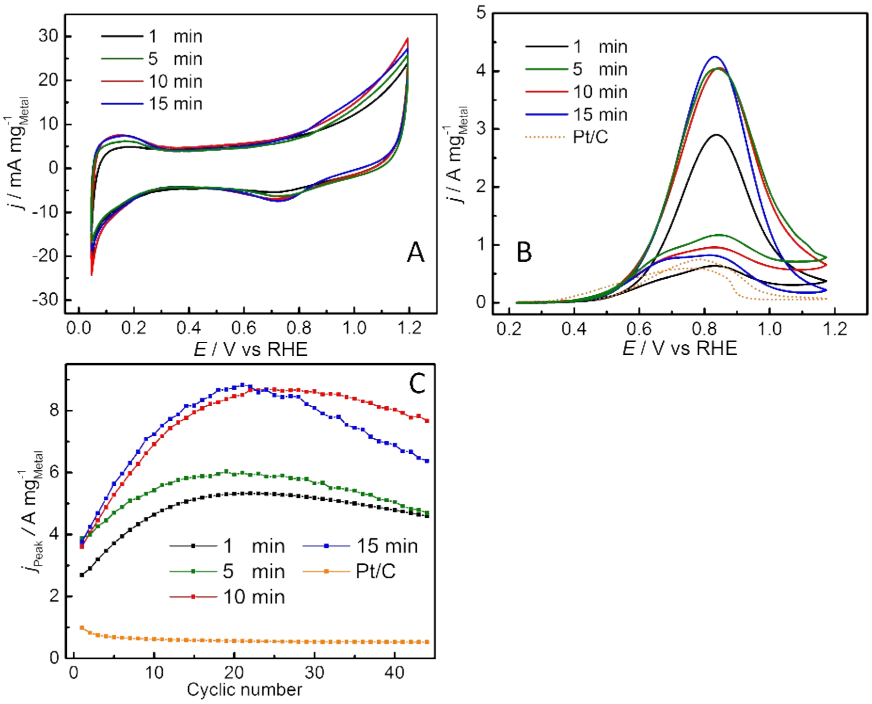


Fig. S8 (A) CVs in 0.5 M $HClO_4$ on Au@Pt/C with different deposition time. (B) CVs of Pt/C and Au@Pt/C with different deposition time in 1 M NaOH + 1 M CH_3CH_2OH. (C) EOR peak current density change with number of cycles on Au@Pt/C and Pt/C. Scan rate: 50 mV s^{-1}.

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