Electronic Supplementary Information

Increased electrode activity during geosmin oxidation provided by Pt nanoparticle-embedded nanocarbon film

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TEM images

Fig. S1 shows TEM images of all the Pt-C films, and the statistical distribution of their embedded PtNP sizes counted from each TEM image. The TEM mage of the Pt-C film (10.6 at.%) is the same as in Fig. 2, but the length of the scale bar is different.

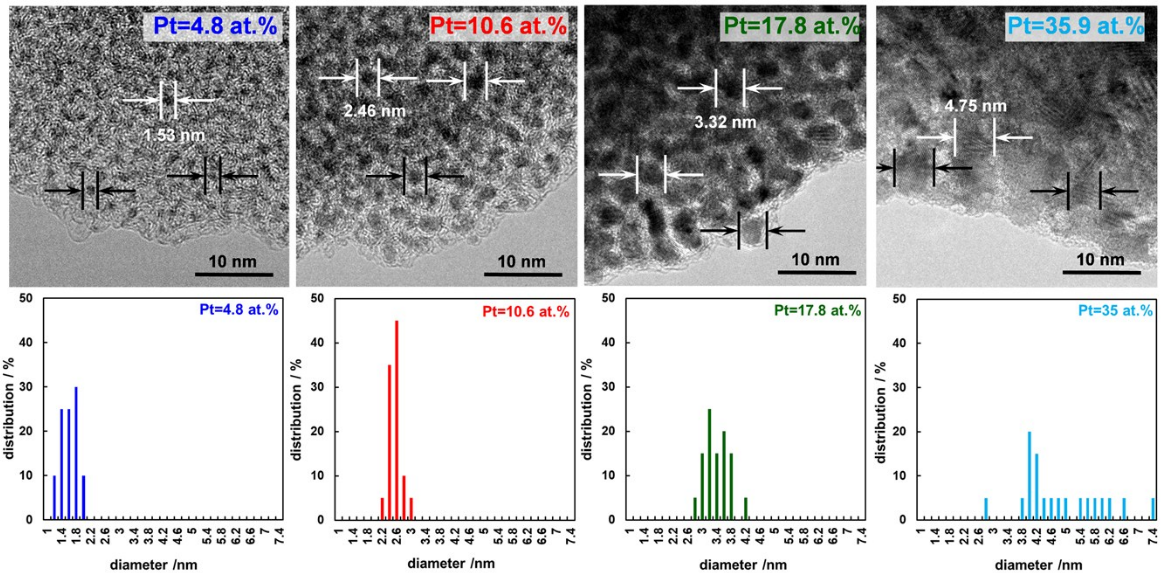


Fig. S1 Plan view of all the Pt-C films observed by TEM (top) and the statistical distribution of their embedded PtNP sizes counted from each TEM image (bottom).

Calculation of actual electrochemical Pt surface area

The actual electrochemical Pt surface area was obtained from the charge consumed during hydrogen adsorption/desorption in the CVs (Fig. 3a). The detail method is as follows. For example, we here explained how to calculate this Pt surface area of the Pt-C (10.6 at.%) film electrode.

The actual electrochemical Pt surface area was calculated as following equation.

$$\text{Area} = Q_H / (210\ \mu\text{C/cm}^2)$$

where Q_H is the charge for hydrogen desorption, and 210 (μC/cm^2) represent the charge required to oxidize a monolayer of H_2 on bright Pt (ref. 47).

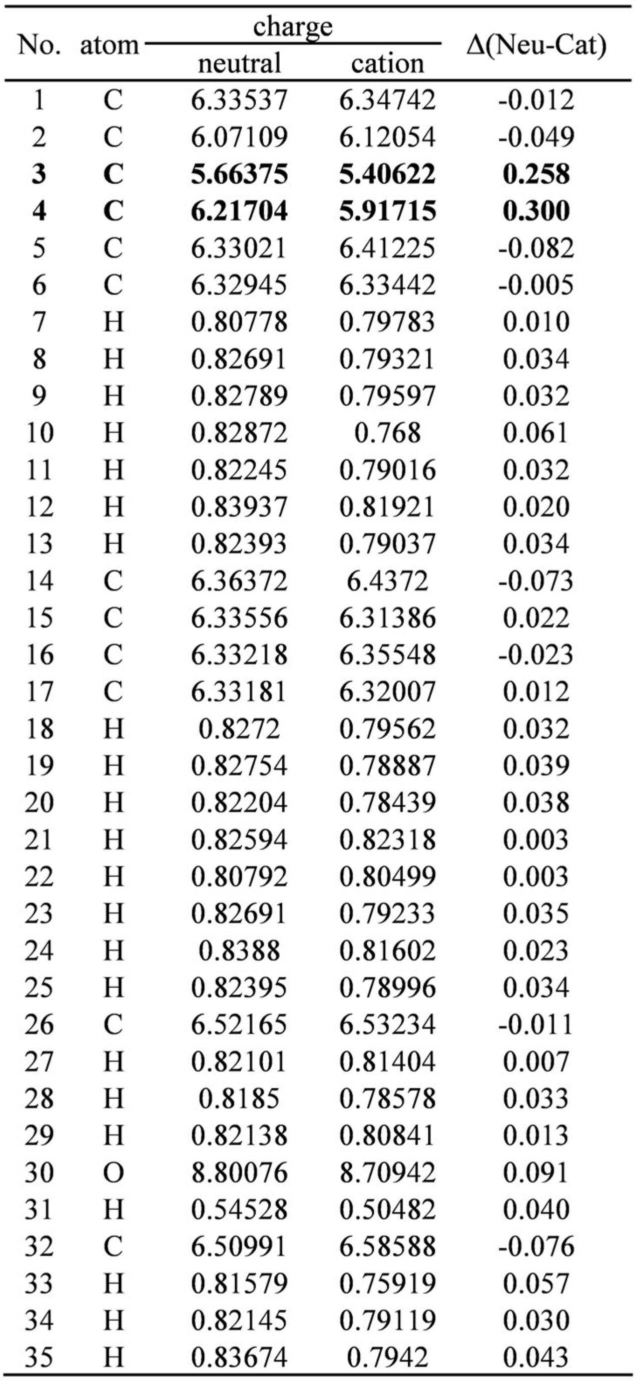
From the result of CV measurement (Fig. 3a), the Q_H value of the Pt-C (10.6 at.%) film electrode is 2.95×10^{-7} C.

$$\begin{aligned}\text{Therefore, area [Pt-C (10.6 at.\%)]} &= (2.95 \times 10^{-7}\ \text{C}) / (210\ \mu\text{C/cm}^2) \\ &= 0.00141\ \text{cm}^2 \\ &= 0.141\ \text{mm}^2\end{aligned}$$

We also calculated the other Pt surface areas (as shown in Fig. 3(b)) in the same manner.

Computational estimation of geosmin oxidation reaction

Table S1 Electronic status of normal geosmin (neutral), - geosmin lacking one electron (cation), and the difference (Δ(Neu-Cat)). The numbers of atoms (1 to 35) correspond to the numbers in Fig. 6(b)



No.	atom	charge		Δ(Neu-Cat)
		neutral	cation	
1	C	6.33537	6.34742	-0.012
2	C	6.07109	6.12054	-0.049
3	**C**	**5.66375**	**5.40622**	**0.258**
4	**C**	**6.21704**	**5.91715**	**0.300**
5	C	6.33021	6.41225	-0.082
6	C	6.32945	6.33442	-0.005
7	H	0.80778	0.79783	0.010
8	H	0.82691	0.79321	0.034
9	H	0.82789	0.79597	0.032
10	H	0.82872	0.768	0.061
11	H	0.82245	0.79016	0.032
12	H	0.83937	0.81921	0.020
13	H	0.82393	0.79037	0.034
14	C	6.36372	6.4372	-0.073
15	C	6.33556	6.31386	0.022
16	C	6.33218	6.35548	-0.023
17	C	6.33181	6.32007	0.012
18	H	0.8272	0.79562	0.032
19	H	0.82754	0.78887	0.039
20	H	0.82204	0.78439	0.038
21	H	0.82594	0.82318	0.003
22	H	0.80792	0.80499	0.003
23	H	0.82691	0.79233	0.035
24	H	0.8388	0.81602	0.023
25	H	0.82395	0.78996	0.034
26	C	6.52165	6.53234	-0.011
27	H	0.82101	0.81404	0.007
28	H	0.8185	0.78578	0.033
29	H	0.82138	0.80841	0.013
30	O	8.80076	8.70942	0.091
31	H	0.54528	0.50482	0.040
32	C	6.50991	6.58588	-0.076
33	H	0.81579	0.75919	0.057
34	H	0.82145	0.79119	0.030
35	H	0.83674	0.7942	0.043

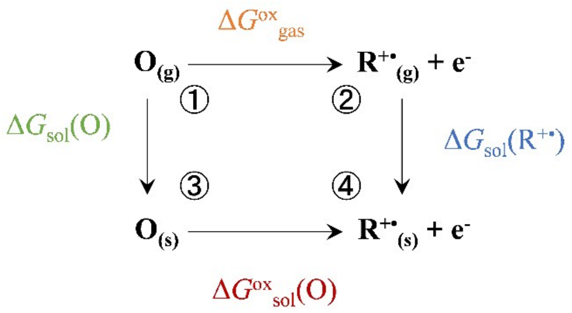
Calculation of theoretical E_{ox} value of geosmin (E_{ox}^{theo})

The theoretical E_{ox} values were calculated by the Nernst equation using the free energy changes in the gas phase (ΔG_{gas}) and solution (ΔG_{sol}) as a previous report (ref. 33). Briefly, the calculation method is as follows;

The electrode oxidation potential is related to the free-energy change ΔG^0 by the Nernst equation

$$E^0 = – G^0/\mathrm{nF} + E_\mathrm{H}$$

where n is the number of electrons transferred (n=1 in this study), F is Faraday's constant (96485.3365 C mol^{-1}), and E_H is the absolute potential of the normal hydrogen electrode (-4.36 V). Therefore, the one-electron oxidation potential can be calculated using the thermodynamic cycle represented in the following Scheme.



The upper part of the cycle represents the gas-phase process, and the lower part corresponds to the solvent phase. According to the cycle, the free energy of oxidation in solution can be calculated as

$$\Delta G^{ox}_{sol}(O) = \Delta G^{ox}_{gas} + \Delta G_{sol}(R^{+\bullet}) – \Delta G_{sol}(O)$$

and includes calculations of free energies of oxidation and free energies of solvation of the neutral ($\Delta G_{sol}(O)$) and oxidized ($\Delta G_{sol}(R^{+\bullet})$) forms.

First of all, we calculated each free-energy from the DFT calculation. Each ΔG was obtained as follows.

$\Delta G^{ox}_{gas} = – 0.291598$ Hartree (au)
$\Delta G_{sol}(R^{+\bullet}) = 0.082009$ Hartree (au)
$\Delta G_{sol}(O) = 0.009005$ Hartree (au)

Therefore, $\Delta G^{ox}_{sol}(O) = \Delta G^{ox}_{gas} + \Delta G_{sol}(R^{+\bullet}) – \Delta G_{sol}(O)$

$$= – 0.218594 \text{ Hartree (au)}$$
$$= – 0.218594 \times 627.509467 \text{ (kcal mol}^{-1}) \times 4.184 \text{ (J cal}^{-1}) \times 1000$$
$$= – 573918.4617 \text{ (J mol}^{-1})$$

From Nernst equation,

$$E^0 = -\Delta G^0/\mathrm{nF} + E_\mathrm{H}$$
$$= -[-573918.4617\ (\mathrm{J\ mol^{-1}})]/[1 \times 96485.3365\ (\mathrm{C\ mol^{-1}})] - 4.36\ (\mathrm{V})$$
$$= 1.588\ (\mathrm{V})$$

This E^0 (E_{ox}) value (1.588 V vs. a normal hydrogen electrode) was converted by subtracting 0.197 V (vs Ag/AgCl), and we finally obtained theoretical E_{ox} of geosmin is 1.391 V (vs Ag/AgCl) as shown in the main text.

Calculation of the binding free energy (ΔG_{bind}) between geosmin and Pt.

The ΔG_{bind} values between geosmin and Pt were calculated as follows. Here, we explained how to calculate the ΔG_{bind} value between C3 site of geosmin and Pt13 cluster (Fig.6(c), left).

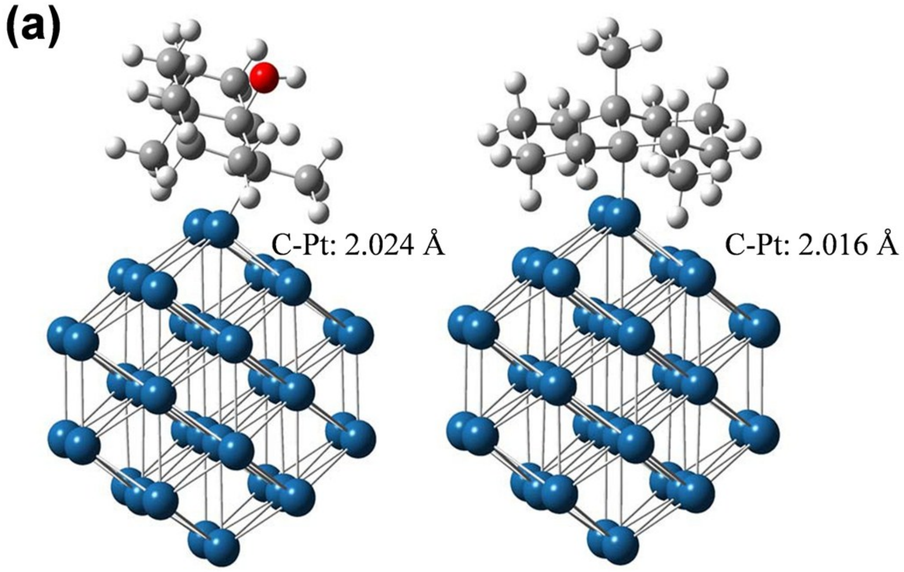
At first, we calculated the ΔG values of each molecule below,

$\Delta G_{\mathrm{geosmin}} = -\ 469.53844$ Hartree (au)
$\Delta G_{\mathrm{Pt13}} = -\ 357.874639$ Hartree (au)
$\Delta G_{\mathrm{geosmin(C3)\text{-}Pt13}} = -\ 827.413079$ Hartree (au)

The ΔG_{bind} values between C3 site of geosmin and Pt13 cluster was calculated as following equation.

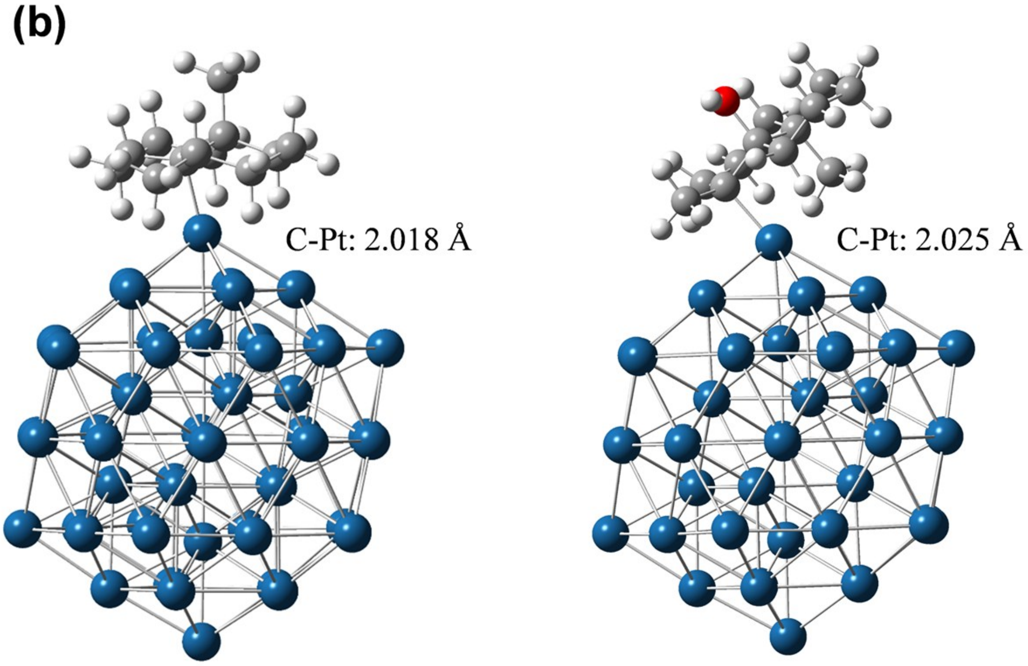
$$\Delta G_{\mathrm{bind}} = (\Delta G_{\mathrm{geosmin(C3)\text{-}Pt13}}) - (\Delta G_{\mathrm{geosmin}} + \Delta G_{\mathrm{Pt13}})$$
$$= 0.089741\ \text{Hartree (au)}$$
$$= 0.089741 \times 627.509467\ (\mathrm{kcal\ mol^{-1}})$$
$$= 56.3\ \mathrm{kcal\ mol^{-1}}$$

We also calculated the other ΔG_{bind} values (as shown in Fig. 6(c and d), Table 2, and Fig.S2) in the same manner.



Pt38 (with C4)
$\Delta G_{\mathrm{bind}} = 48.9$ kcal mol^{-1}

Pt38 (with C3)
$\Delta G_{\mathrm{bind}} = 55.4$ kcal mol^{-1}



Pt55 (with C3)
$\Delta G_{\mathrm{bind}} = 56.3$ kcal mol^{-1}

Pt55 (with C4)
$\Delta G_{\mathrm{bind}} = 48.9$ kcal mol^{-1}

Fig. S2 DFT calculations of the oxidation reaction of geosmin with PtNPs (Pt38) (a) and Pt55 (b).

HPLC-ECD set up using the Pt-C film or Pt film electrode

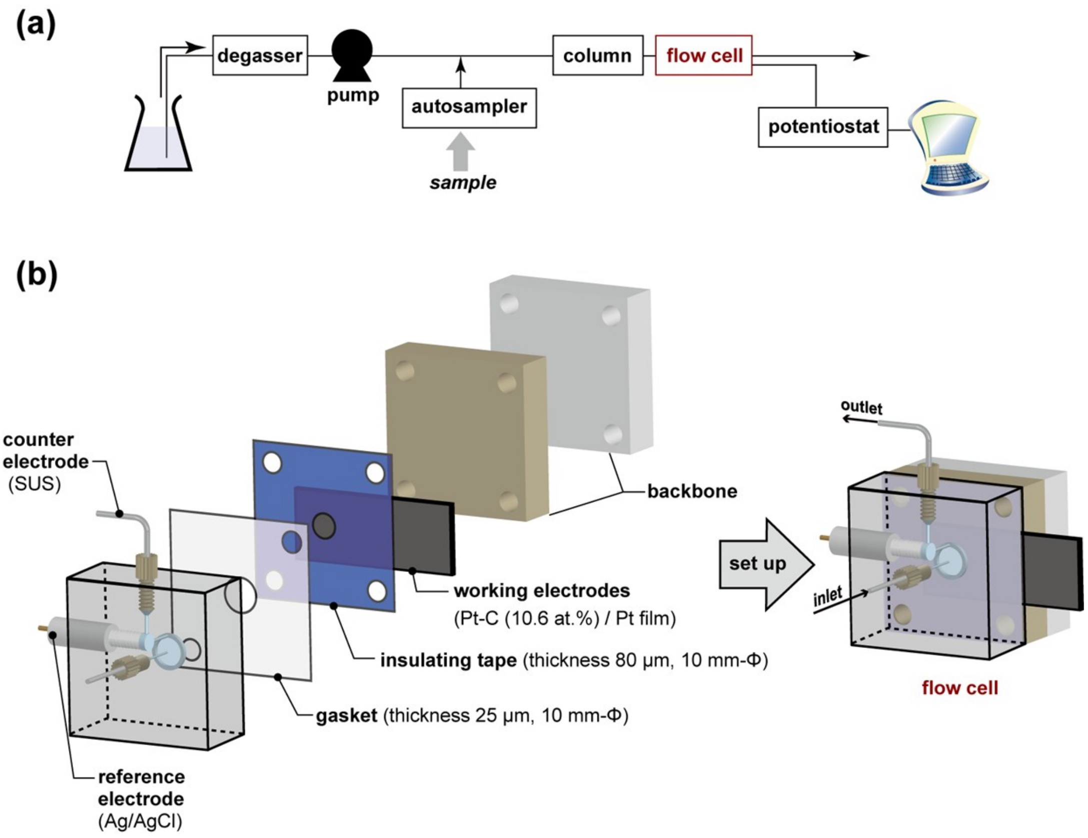


Fig. S3 (a) HPLC-ECD set up using the Pt-C film or Pt film electrode. (b) a flow cell.

HPLC chart

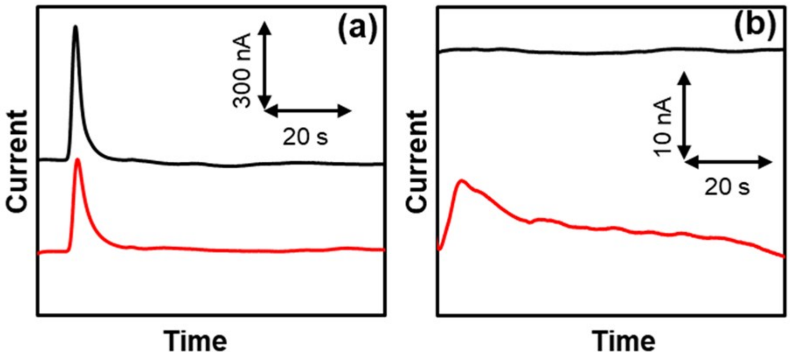


Fig. S4 Typical chromatograms of geosmin (100 µg L^{-1} (a), 100 ng L^{-1} (b)) at the Pt-C film (Pt=10.6 at.%, red) and Pt film (black) electrodes obtained by HPLC-ECD. Conditions: 20 µL injection; mobile phase, 50 mM PB (pH 7.0)/AN (90/10, v/v); flow rate, 200 µL min^{-1}; temperature, 25 °C; detection potential, 1.5 V vs. Ag/AgCl.