Supporting information

Conductive two-dimensional $M_3(C_6S_3O_3)_2$ monolayers as efficient electrocatalysts for oxygen reduction reaction

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Table S1 Lattice parameter, pore size and formation energy (E_f) of each $M_3(C_6S_3O_3)_2$ monolayer.

M	Co	Cr	Cu	Fe	Mn	Ni	Pd	Rh	Ru
Lattice (Å)	13.64	14.05	13.77	13.79	13.90	13.60	14.05	14.10	14.22
Dp (Å)	10.57	10.87	10.69	10.70	10.73	10.52	10.96	11.06	11.16
Dm (Å)	6.82	7.03	6.89	6.90	6.95	6.80	7.03	7.05	7.11
E_f (eV)	-14.22	-12.06	-6.11	-12.70	-12.41	-13.47	-8.24	-14.21	-18.20

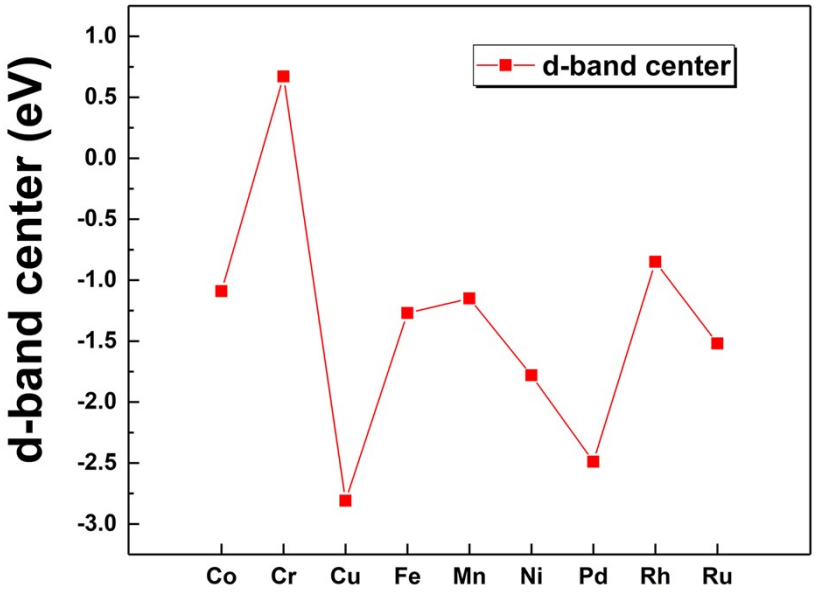

Fig. S1 The value of d-band center (ε_d) of transition metals of different $M_3(C_6S_3O_3)_2$ monolayers.

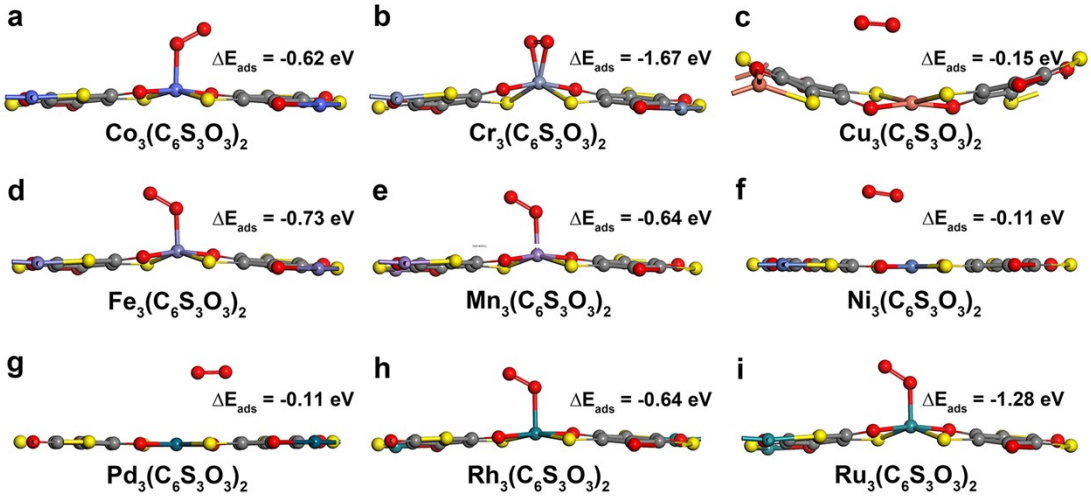

Fig. S2 Schematics of O_2 adsorption on $M_3(C_6S_3O_3)_2$ monolayers.

Table S2 Gibbs free energy change (ΔG) of each elementary step for ORR on $M_3(C_6S_3O_3)_2$ monolayers

M=	Co	Cr	Cu	Fe	Mn	Ni	Pd	Rh	Ru
ΔG_1(eV)	-0.79	-1.66	0.05	-0.94	-1.00	0.09	0.24	-0.81	-1.80
ΔG_2(eV)	-1.78	-3.12	-3.20	-2.23	-2.43	-3.12	-0.76	-1.67	-2.63
ΔG_3(eV)	-1.34	-0.30	-0.58	-1.04	-0.79	-0.62	-2.19	-1.48	-0.46
ΔG_4(eV)	-1.00	-0.16	-1.19	-0.71	-0.70	-1.27	-2.21	-0.96	-0.03

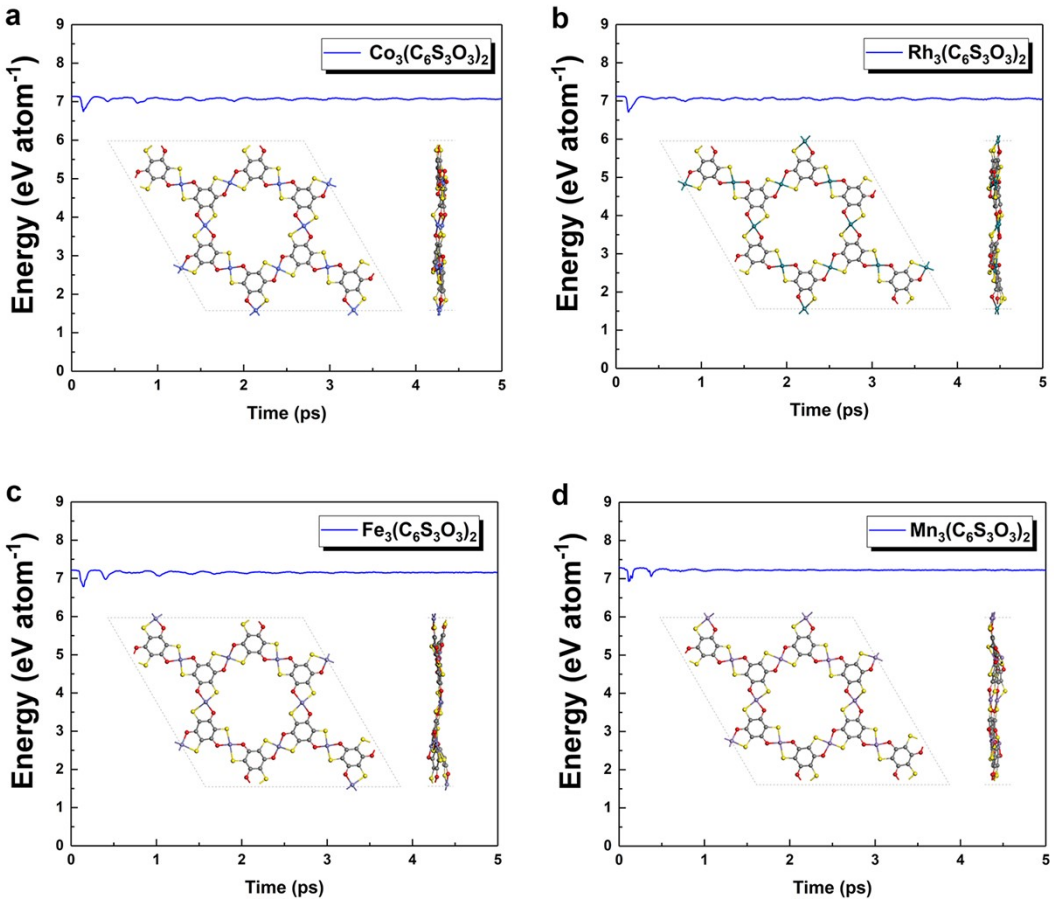

Fig. S3 The change of total energy with time for (a) $Co_3(C_6S_3O_3)_2$, (b) $Rh_3(C_6S_3O_3)_2$, (c) $Fe_3(C_6S_3O_3)_2$, and (d) $Mn_3(C_6S_3O_3)_2$ monolayer by *ab initio* molecular dynamic (AIMD) simulations at 500 K for 5 ps. Inside are top and side views of $Co_3(C_6S_3O_3)_2$, $Rh_3(C_6S_3O_3)_2$, $Fe_3(C_6S_3O_3)_2$, and $Mn_3(C_6S_3O_3)_2$ monolayer at T=500 K after 5 ps.

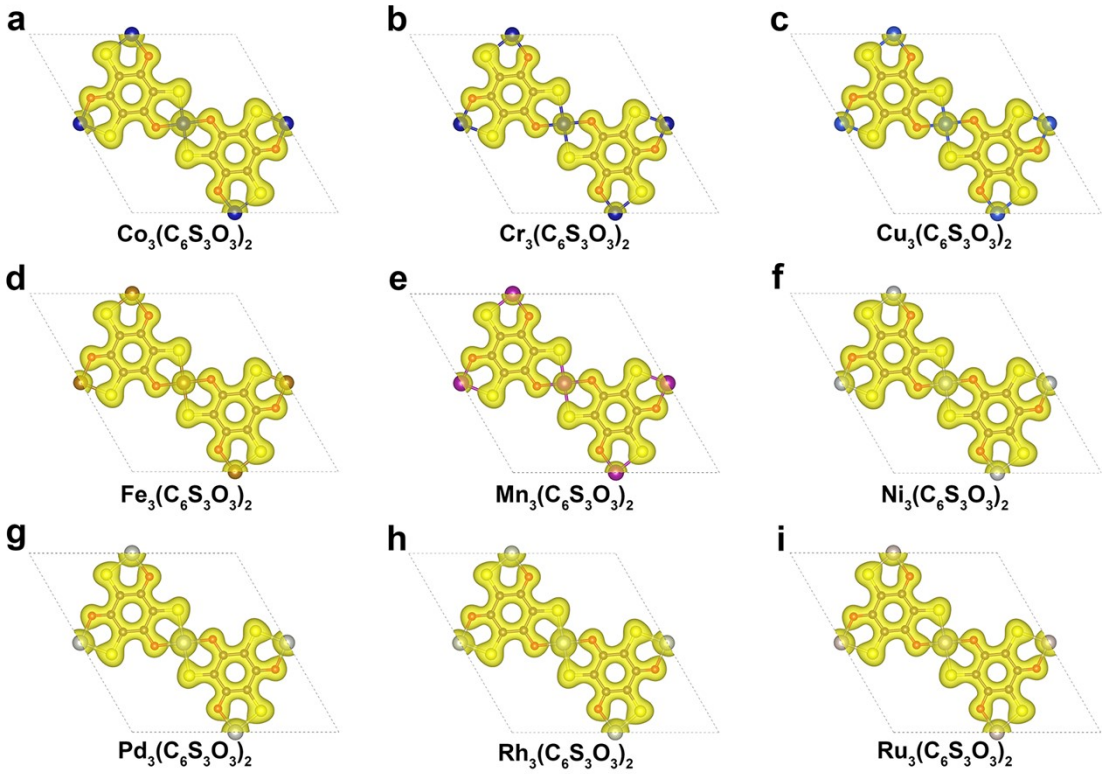

Fig. S4 The charge density distribution of $M_3(C_6S_3O_3)_2$ monolayer. The isosurface value is set to be 0.1 e/Bohr^3.

Table S3 Charge (|e|) transferred between central metal atoms and surrounding oxygen and sulfur atoms of the MS_2O_2 moieties.

	M	O	S
$Co_3(C_6S_3O_3)_2$	-0.86	1.00	-0.04
$Cr_3(C_6S_3O_3)_2$	-1.26	1.04	0.13
$Cu_3(C_6S_3O_3)_2$	-0.81	1.01	-0.04
$Fe_3(C_6S_3O_3)_2$	-1.08	1.01	0.06
$Mn_3(C_6S_3O_3)_2$	-1.28	1.04	0.11
$Ni_3(C_6S_3O_3)_2$	-0.77	0.98	-0.06
$Pd_3(C_6S_3O_3)_2$	-0.63	0.96	-0.10
$Rh_3(C_6S_3O_3)_2$	-0.63	0.96	-0.10
$Ru_3(C_6S_3O_3)_2$	-0.95	0.98	0.02

Details of microkinetics simulations

The polarization curve of the $M_3(C_6S_3O_3)_2$ monolayers was simulated based on a general kinetic model applicable to ORR.[1] The O_2 adsorption (non-electrochemical step) and electrochemical steps are listed below:

$$O_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2\ (dl) \qquad (S1)$$

$$O_2(dl) + * \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_2* \qquad (S2)$$

$$O_2* + H^+ + e^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} OOH* \qquad (S3)$$

$$OOH* + H^+ + e^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} O* + H_2O \qquad (S4)$$

$$O* + H^+ + e^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} OH* \qquad (S5)$$

$$OH* + H^+ + e^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} * + H_2O \qquad (S6)$$

where k_i and k_{-i} denote the forward and reverse reaction rate constant, respectively. O_2(aq) and O_2(dl) refer to the O_2 in the electrolyte and catalyst-electrolyte interfaces, respectively.

According to the above elementary steps, the rate equation for each species can be expressed as:

$$\frac{\partial x_{O_2(dl)}}{\partial t} = k_1 x_{O_2(aq)} - k_{-1} x_{O_2(dl)} - k_2 x_{O_2(dl)} \theta* + k_{-2} \theta_{O_2*} \qquad (S7)$$

$$\frac{\partial x_{O_2*}}{\partial t} = k_2 x_{O_2(dl)} \theta* - k_{-2} x_{O_2*} - k_3 \theta_{O_2*} + k_{-3} \theta_{OOH*} \qquad (S8)$$

$$\frac{\partial x_{OOH*}}{\partial t} = k_3 \theta_{O_2*} - k_{-3} \theta_{OOH*} - k_4 \theta_{OOH*} + k_{-4} \theta_{O*} \qquad (S9)$$

$$\frac{\partial x_{O*}}{\partial t} = k_4 \theta_{OOH*} - k_{-4} \theta_{O*} - k_5 \theta_{O*} + k_{-5} \theta_{OH*} \qquad (S10)$$

$$\frac{\partial x_{OH*}}{\partial t} = k_5 \theta_{O*} - k_{-5} \theta_{OH*} - k_6 \theta_{OH*} + k_{-6} \theta * \qquad (S11)$$

where x, θ and t refer to molar fraction, coverage of the species and time, respectively. x_{H2O} is taken as 1 and x_{O2}(aq) is taken as a value of 2.34×10^{-5}, denoting O_2(g) at equilibrium with O_2(aq) at 1 atm.

For the non-electrochemical step i, the equilibrium constant (K_i) and k_i can be expressed as:

$$K_{\mathrm{i}} = \exp\left(-\frac{\Delta G_i}{k_{\mathrm{B}}\mathrm{T}}\right) \qquad \text{(S12)}$$

$$k_{\mathrm{i}} = \nu_{\mathrm{i}} \exp\left(-\frac{E_{a,i}}{\mathrm{k_B T}}\right) \qquad \text{(S13)}$$

where ΔG_i is the free energy change of step i, ν_{i} is the pre-exponential factor and $E_{a,i}$ is the activation energy. In addition, k_{B} is the Boltzmann constant and T is the temperature taken as 298.15K.

K_{i} and k_{i} for electrochemical step i, which is associated with both the electrode potential(U), can be calculated with the following equations:

$$K_{\mathrm{i}} = \exp\left(-\frac{e\left(U - U_i\right)}{k_{\mathrm{B}}\mathrm{T}}\right) \qquad \text{(S14)}$$

$$k_{\mathrm{i}} = A_{\mathrm{i}} \exp\left(-\frac{E_{\mathrm{a,i}}}{\mathrm{k_B T}}\right)\exp\left(-\frac{e\beta_{\mathrm{i}}\left(U - U_i\right)}{k_{\mathrm{B}}\mathrm{T}}\right) \qquad \text{(S15)}$$

where U_i is the reversible potential of step i derived from $U_i = -\Delta G_i/\mathrm{e}$, A_{i} refers to the effective pre-exponential factor with a value of 1.23×10^9, and β_{i} denotes the symmetric factor taken as 0.5. Since the $E_{\mathrm{a,i}}$ values of electrochemical steps of the ORR are usually small, in the range from 0.10 to 0.26eV,[2] $E_{\mathrm{a,i}}$ = 0.26eV was employed for all the electrochemical steps of the ORR on the $M_3(C_6S_3O_3)_2$ monolayers.

Furthermore, for all the reverse reactions, the rate constants ($k_{-\mathrm{i}}$) can be derived from the following equation:

$$k_{-\mathrm{i}} = \frac{k_{\mathrm{i}}}{K_{\mathrm{i}}} \qquad \text{(S16)}$$

Finally, the current density(j) can be calculated according to the following equation:

$$j = e\rho TOF_{e^-} \qquad \text{(S17)}$$

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1 H. A. Hansen, V. Viswanathan and J. K. Nørskov, *J. Phys. Chem. C*, 2014, **118**, 6706-6718.

2 V. Tripković, E. Skúlason, S. Siahrostami, J. K. Nørskov and J. Rossmeisl, *Electrochim. Acta*, 2010, **55**, 7975-7981.