Single atom (Pd/Pt) supported on graphitic carbon nitride as efficient photocatalyst for visible-light reduction of carbon dioxide

Guoping Gao[1], Yan Jiao[2], Eric R. Waclawik[1] and Aijun Du[1*]

[1]*School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Garden Point Campus, QLD 4001, Brisbane, Australia*

[2]*School of Chemical Engineering, University of Adelaide, Adelaide, SA 5005, Australia*

Table S1 the adsorption energy for Pt and Pd on different deposition sites of Figure 1a

Binding sites (see Figure 1a)	$E_{binding}$ for Pd/g-C_3N_4(eV)	$E_{binding}$ for Pt/g-C_3N_4(eV)
1	-2.17	-2.95
2	Move to position 1	Move to position 1
3	Move to position 1	Move to position 1
4	-1.36	-2.05
5	Move to position 4	-1.29

The binding energy of metal atom on g-C_3N_4 is calculate by eq(1)

$$E_{binding} = E_{M/g-C_3N_4} - E_M - E_{g-C_3N_4} \quad (1)$$

Where $E_{M/g-C_3N_4}$, E_M,and $E_{g-C_3N_4}$ is the total energies of single metal atom binded on the $g-C_3N_4$, single metal atom, and $g-C_3N_4$, respectively.

Formation of HCOOH

The pathway of formation HCOOH on Pd/g-C_3N_4, Pt/g-C_3N_4 and Cu/g-C_3N_4 are the same. The overall formula of Formation of HCOOH can be written as:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad (2)$$

Which is divided into two element steps:

$$CO_2 + H^+ + e^- \rightarrow HCOO^* \quad (3)$$

$$HCOO^* + H^+ + e^- \rightarrow HCOOH \quad (4)$$

Formation of CH_3OH

The overall formula of formation of CH_3OH can be written

$$CO_2+6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad (5)$$

The pathway of CH_3OH formation on Pd/g-C_3N_4, and Pt/g-C_3N_4 is the same, but different from that on Cu/g-C_3N_4. On the Pd/g-C_3N_4, and Pt/g-C_3N_4, the pathway following these six element steps:

$$CO_2+H^+ + e^- \rightarrow HCOO^* \quad (6)$$

$$HCOO^*+H^+ + e^- \rightarrow HCOOH^* \quad (7)$$

$$HCOOH^*+H^+ + e^- \rightarrow HCO^* + H_2O^* \quad (8)$$

$$HCO^*+H^+ + e^- \rightarrow CH_2O^* \quad (9)$$

$$CH_2O^*+H^+ + e^- \rightarrow CH_2OH^* \quad (10)$$

$$CH_2OH^*+H^+ + e^- \rightarrow CH_3OH^* \quad (1)$$

The details of pathway of CH_3OH on Cu/g-C_3N_4 are:

$$CO_2+H^+ + e^- \rightarrow HCOO^* \quad (2)$$

$$HCOO^*+H^+ + e^- \rightarrow HCOOH^* \quad (3)$$

$$HCOOH^*+H^+ + e^- \rightarrow H_2COOH^* \quad (4)$$

$$H_2COOH^*+H^+ + e^- \rightarrow H_2C(OH)_2{}^* \quad (5)$$

$$H_2C(OH)_2{}^* \rightarrow CH_2O^* + H_2O^* \quad (6)$$

$$CH_2O^*+H^+ + e^- \rightarrow CH_3O^* \quad (7)$$

$$CH_3O^*+H^+ + e^- \rightarrow CH_3OH^* \quad (8)$$

Formation of CH_4

The overall formula of formation of CH_4 can be written as:

$$CO_2+8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (9)$$

Which is only investigated on Pt/g-C_3N_4, and processes through eight element steps:

$$CO_2+H^+ + e^- \rightarrow HCOO^* \quad (20)$$

$$HCOO^*+H^+ + e^- \rightarrow HCOOH^* \quad (10)$$

$$HCOOH^*+H^+ + e^- \rightarrow HCO^* + H_2O^* \quad (11)$$

$$HCO^*+H^+ + e^- \rightarrow CH_2O^* \quad (12)$$

$$CH_2O^{*}+H^{+}+e^{-}\rightarrow CH_2OH^{*} \quad (13)$$

$$CH_2OH^{*}+H^{+}+e^{-}\rightarrow CH_2^{*}+H_2O^{*} \quad (14)$$

$$CH_2^{*}+H^{+}+e^{-}\rightarrow CH_3^{*} \quad (15)$$

$$CH_3^{*}+H^{+}+e^{-}\rightarrow CH_4^{*} \quad (16)$$

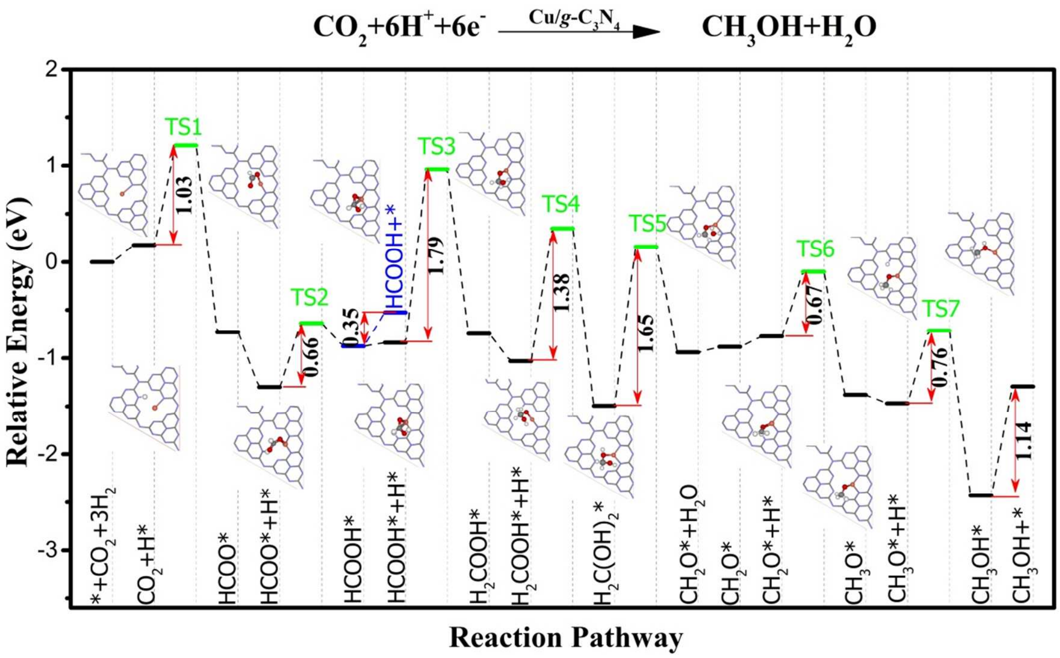

Figure S1 The reaction pathway for CO_2 reduction to HCOOH and CH_3OH on Cu/*g*-C_3N_4. Under standard conditions (pH=0, *p*(H_2)=1 bar, U=0 V_{SHE}), the total energies of $H^{+}(aq)+e^{-}$ and $\frac{1}{2}H_2(g)$ are equal. The reference energy (the total free energy of catalyst, isolated CO_2 and three H_2) is set to zero. The important intermediates and products are shown as well. The substrate is displayed partly in stick model. The colour codes for the catalyst and small molecules: Copper, orange; Carbon, grey; Oxygen, red; and hydrogen, white.