

SUPPORTING INFORMATION

SI. Bulk formation energy calculations

SI1. Case of anionic doping

This section gives more details about the thermodynamic equations of the formation energies of the various anionic S-doping configurations and reported in the main text.

For reaction (2), the formation energies per Ti of the various anionic S-doped systems are defined by:

$$E_{form}(2) = \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + 2(p-m)\mu_H + m\cdot\mu_{H_2O} - p\cdot\mu_{H_2S}] \quad (SI1.1)$$

Using $\mu_i = E_i + \Delta\mu_i$, equation (SI1.1) leads to the following expression:

$$E_{form}(2) = \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + (p-m)(E_{H_2} + 2\Delta\mu_H) + m(E_{H_2O} + \Delta\mu_{H_2O}) - p(E_{H_2S} + \Delta\mu_{H_2S})] \quad (SI1.2)$$

$$E_{form}(2) = \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + (p-m)(E_{H_2} + 2\Delta\mu_H) + m(E_{H_2} + \frac{1}{2}E_{O_2} - \Delta E_1 + \Delta\mu_{H_2O}) - p(E_{H_2} + \frac{1}{2}E_{S_2} - \Delta E_2 + \Delta\mu_{H_2S})] \quad (SI1.3)$$

As a consequence, we obtain the following equations given in the main text

$$E_{form}(2) = E_{form}^{0K}(1) + \frac{1}{n} [m(\Delta\mu_{H_2O} - 2\Delta\mu_H - \Delta E_1) - p(\Delta\mu_{H_2S} - 2\Delta\mu_H - \Delta E_2)] \quad (7)$$

with

$$\Delta E_1 = E_{H_2} + \frac{1}{2}E_{O_2} - E_{H_2O} \quad (8)$$

$$\Delta E_2 = \frac{1}{2}E_{S_2} + E_{H_2} - E_{H_2S} \quad (9)$$

$\Delta E_1 = +2.89$ eV and $\Delta E_2 = +1.25$ eV represent the electronic energy variations for the chemical reactions: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ and $H_2S \rightarrow \frac{1}{2}S_2 + H_2$ respectively.

Formally, this equation can be rewritten as follows:

$$E_{form}(2) = E_{form}^{0K}(1) + \frac{1}{n} [m(\Delta\mu_O' - \Delta E_1) - p(\Delta\mu_S' - \Delta E_2)] \quad (10)$$

where

$$\Delta\mu_{H_2S} = \Delta\mu_S' + 2\Delta\mu_H \quad (11)$$

$$\Delta\mu_{H_2O} = \Delta\mu_O' + 2\Delta\mu_H \quad (12)$$

For reaction (3), the formation energies are expressed as follows:

$$E_{form}(3) = \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + p \cdot \mu_{CO(NH_2)_2} - p \cdot \mu_{CS(NH_2)_2} - (p - m)\mu_O] \quad (SI1.4)$$

Using $\mu_i = E_i + \Delta\mu_i$, equation (SI1.4) leads to the following expression:

$$\begin{aligned} E_{form}(3) = & \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + p(E_{CO(NH_2)_2} + \Delta\mu_{CO(NH_2)_2}) - p(E_{CS(NH_2)_2} + \Delta\mu_{CS(NH_2)_2}) \\ & - (p - m)(\frac{1}{2}E_{O_2} + \Delta\mu_O)] \end{aligned} \quad (SI1.5)$$

$$\begin{aligned} E_{form}(3) = & \frac{1}{n} [E_{tot}(doped) - E_{tot}(pure) + p(\Delta E_3 - \frac{1}{2}E_{S_2} + \frac{1}{2}E_{O_2}) + p(\Delta\mu_{CO(NH_2)_2} - \Delta\mu_{CS(NH_2)_2}) \\ & - (p - m)(\frac{1}{2}E_{O_2} + \Delta\mu_O)] \end{aligned} \quad (SI1.6)$$

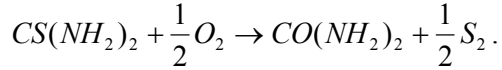
As a consequence, we obtain the following equations given in the main text

$$E_{form}(3) = E_{form}^{0K}(1) + \frac{1}{n} [(m - p)\Delta\mu_O + p(\Delta E_3 + \Delta\mu_{CO(NH_2)_2} - \Delta\mu_{CS(NH_2)_2})] \quad (13)$$

with

$$\Delta E_3 = E_{CO(NH_2)_2} - E_{CS(NH_2)_2} + \frac{1}{2}E_{S_2} - \frac{1}{2}E_{O_2} \quad (14)$$

$\Delta E_3 = -1.89$ eV represents the electronic energy variation for the chemical reaction:



SI2. Case of anionic doping

We give in this section more details about the thermodynamic equations of the formation energies of the various cationic S-doping configurations and reported in the main text.

For reaction (15), the formation energies per Ti are calculated through the following expression:

$$E_{form}(15) = -\frac{1}{n} E_{tot}(pure) + \frac{1}{(n-k)} [E_{tot}(doped) - kE_{O_2} - \frac{p}{2} E_{S_2} - 2k.\Delta\mu_O - p.\Delta\mu_S] \quad (SI2.1)$$

As a consequence, we obtain the following equations given in the main text:

$$E_{form}(15) = E_{form}^{0K}(15) - \frac{1}{(n-k)} [2k.\Delta\mu_O + p.\Delta\mu_S] \quad (18)$$

where

$$E_{form}^{0K}(15) = -\frac{1}{n} E_{tot}(pure) + \frac{1}{(n-k)} [E_{tot}(doped) - kE_{O_2} - \frac{p}{2} E_{S_2}]$$

For reaction (16), the formation energies per Ti are defined by:

$$E_{form}(16) = -\frac{1}{n} E_{tot}(pure) + \frac{1}{(n-k)} [E_{tot}(doped) + pE_{H_2} - kE_{O_2} - pE_{H_2S} + 2p.\Delta\mu_H - 2k.\Delta\mu_O - p.\Delta\mu_{H_2S}] \quad (SI2.2)$$

As a consequence, we obtain the following equation also given in the main text:

$$E_{form}(16) = E_{form}^{0K}(15) - \frac{1}{(n-k)} [2k.\Delta\mu_O + p(\Delta\mu_S' - \Delta E_2)] \quad (19)$$

For reaction (17), the formation energies per Ti are expressed as follows:

$$E_{form}(17) = -\frac{1}{n}E_{tot}(pure) + \frac{1}{(n-k)}[E_{tot}(doped) + pE_{CO(NH_2)_2} - pE_{CS(NH_2)_2} - \frac{(2k+p)}{2}E_{O_2} + p\Delta\mu_{CO(NH_2)_2} - p\Delta\mu_{CS(NH_2)_2} - (2k+p)\Delta\mu_O]$$

(SI2.3)

As a consequence, we obtain the following equation also given in the main text:

$$E_{form}(17) = E_{form}^{0K}(15) - \frac{1}{(n-k)}[(2k+p)\Delta\mu_O - p(\Delta E_3 + \Delta\mu_{CO(NH_2)_2} - \Delta\mu_{CS(NH_2)_2})] \quad (20)$$