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Supporting Information

Composite semiconductor $H_2WO_4 \cdot H_2O$/AgCl as an efficient and stable photocatalyst under visible light

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Estimation of the VB and CB edges of $H_2WO_4{\cdot}H_2O$

Electronegativity is an intrinsic property, which measures the degree of difficulty for an electron to escape from atomic species. On the basis of density functional theory, Parr and coworkers [1] defined the electronegativity of a neutral atom as the negative of the chemical potential in the ground state:

$$c = -m = -\left(\frac{\partial E}{\partial N}\right)_v . \qquad (1)$$

where E and N are the ground-state electronic energy and the number of electrons, respectively. In terms of energy differences, Eq. 1 can be rewritten as

$$c = -\left(\frac{\partial E}{\partial N}\right)_v = \frac{E(N+1)-E(N)+E(N)-E(N-1)}{2} \approx \frac{I+A}{2} . \qquad (2)$$

where I and A represent the ionization potential (IP) and the electron affinity (EA) of the atom, respectively. Thus, Eq. 1 is equivalent to the Mulliken's definition of electronegativity.[2]

When the atoms are brought together to form a compound, charges will redistribute until the electrochemical potentials of the compound reach the equilibrium. On the basis of bond length arguments, Sanderson postulated that the electronegativity of a compound c_{comp} is given by the geometric mean of the electronegativities of the constituent atoms,[3] that is,

$$c_{comp} = \sqrt[N]{c_1^r c_2^s \cdots c_{n-1}^p c_n^q} . \qquad (3)$$

where c_n, n and N are the electronegativity of the constituent atom, the number of species and the total number of atoms in the compound, respectively. The superscripts r, s, p and q refer to the numbers of the atoms 1, 2, n-1 and n, respectively in the molecule, so that $r + s + \dots + p + q = N$.

The CB edge of a semiconductor at the point of zero charge (E_{CB}^0) is empirically expressed as [4-6]

$$E_{CB}^0 = c_{comp} - 2.303RT \cdot (pH_{ZPC} - pH)/F - E^e - \frac{1}{2}E_g . \qquad (4)$$

where R is the gas constant, T is temperature, and F is the Faraday constant. E_g and E^e are the band gap of the semiconductor and the energy of free electrons on the hydrogen scale (i.e., E^e = ~4.5 eV). Under the reasonable assumption that the solution's pH value at the zero point of charge, pH_{ZPC}, is very close to the solution's pH value, pH, we obtain

$$E_{CB}^0 \approx E_{CB} \approx c_{comp} - E^e - \frac{1}{2}E_g . \qquad (5)$$

From its UV/Vis diffuse reflectance spectrum the band gap of $H_2WO_4{\cdot}H_2O$ is estimated to be 2.92 eV. Thus, from Eq. 5, the CB edge of $H_2WO_4{\cdot}H_2O$ is estimated to be -0.394 eV with respect to the normal hydrogen electrode (NHE), and -4.106 eV with respect to the absolute vacuum scale (AVS). Consequently, on the basis of its band gap (2.92 eV), the VB edge of $H_2WO_4·H_2O$ is determined as 2.506 eV with respect to the NHE, and as -7.026 with respect to the AVS.

According to Morimoto *et al.*,[7] the CB and VB edges of AgCl are -3.3 eV and -6.6 eV, respectively. The VB and CB edges of AgCl and $H_2WO_4·H_2O$ are compared in Figure 1, which shows that the VB and CB edges of $H_2WO_4·H_2O$ lie lower than those of AgCl, respectively, and that $H_2WO_4·H_2O$ has a smaller band gap than does AgCl.

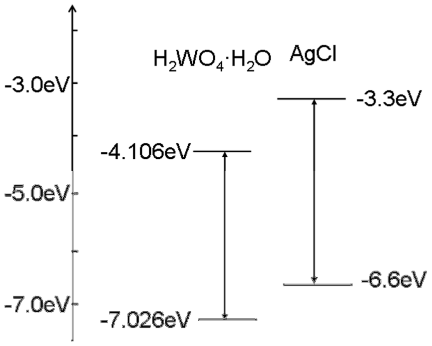

Figure 1. Comparison of the VB and CB edges of $H_2WO_4·H_2O$ and AgCl.

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