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s-p orbital hybridization: a strategy for developing efficient photocatalysts with high carrier mobility

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Abstract

Photocatalysis has not only invigorated the field of energy conversion materials, but also is leading to bright prospects for application in the environmental purification field [1]. Akira Fujishima and Kenichi Honda [2] first reported photocatalytic water splitting on a TiO₂ semiconductor electrode under ultraviolet (UV) light in 1972. In semiconductor photocatalysts, electrons are excited from valence band maximum (VBM) to conduction band minimum (CBM) under light irradiation, and then trigger the photocatalytic process [3]. Considering solar-light-driven photocatalysis, semiconductor photocatalysts should possess a narrow band gap and appropriate band positions [4]. It was also found that photoinduced charge generation, separation, and transportation determine activities of semiconductor photocatalysts. High mobility of charge carriers facilitates these processes, which can be achieved in the photocatalysts with highly dispersive bands, because their effective masses of charge carriers are small. Usually, the antibonding hybridization/coupling is predominantly responsible for the band dispersion, especially for oxides. For example, Sn-5s/O-2p anti-bonding coupling in VBM of Sn²⁺ oxides, Cu-3d/O-2p anti-bonding coupling in VBM of Cu⁺ oxides and anti-bonding coupling in CBM of most of semiconductors [5-9]. Especially, s-p orbital hybridization is found to improve the performance of photocatalysts by affecting their band structures [10,11].

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s-p orbital hybridization: a strategy for developing efficient photocatalysts with high carrier mobility

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Photocatalysis has not only invigorated the field of energy conversion materials, but also is leading to bright prospects for application in the environmental purification field [1]. Akira Fujishima and Kenichi Honda [2] first reported photocatalytic water splitting on a TiO₂ semiconductor electrode under ultraviolet (UV) light in 1972. In semiconductor photocatalysts, electrons are excited from valence band maximum (VBM) to conduction band minimum (CBM) under light irradiation, and then trigger the photocatalytic process [3]. Considering solar-light-driven photocatalysis, semiconductor photocatalysts should possess a narrow band gap and appropriate band positions [4]. It was also found that photo-induced charge generation, separation, and transportation determine activities of semiconductor photocatalysts. High mobility of charge carriers facilitates these processes, which can be achieved in the photocatalysts with highly dispersive bands, because their effective masses of charge carriers are small. Usually, the anti-bonding hybridization/coupling is predominantly responsible for the band dispersion, especially for oxides. For example, Sn-5s/O-2p anti-bonding coupling in VBM of Sn²⁺ oxides, Cu-3d/O-2p anti-bonding coupling in VBM of Cu⁺ oxides and anti-bonding coupling in CBM of most of semiconductors [5–9]. Especially, s-p orbital hybridization is found to improve the performance of photocatalysts by affecting their band structures [10,11]. It has been widely recognized that band gaps and band positions can be optimized by adjusting the hybridization of electrons in the band structure by introducing s or p orbitals from the doping elements [12]. Inspired by this, s-p orbital hybridization has attracted great attention recently. It has been reported that the dispersive and broad hybridized In 5s5p orbitals in MIn₂O₄ (M = Ca, Sr), Sr_{0.93}Ba_{0.07}In₂O₄, and AlInO₂ (A = Li, Na) are necessary to induce its high dispersive band structure for photo-excited elec-

tron transfers with small recombination rate [13]. It is also found that O 2p and Ag⁺ s or Zn⁺ s orbitals in photocatalysts can improve the mobility of photo-excited charge carriers because of the greatly dispersed s orbitals [14]. Ag 5s and Ag 5p states of Ag₃PO₄ in the CBM lead to a more dispersive energy band and increase the light absorption ability by narrowing the band gap [15]. It is indeed adopted that the s-p orbital hybridization is an efficient strategy for endowing active photocatalysts with high carrier mobility, yet no investigations on the mechanism behind this phenomenon have been addressed to date. Understanding the roles of s-p orbital hybridization is, therefore, essential for the rational optimization of highly efficient photocatalysts. In this paper, we have studied the origins of dispersive energy bands based on basic quantum mechanics and valence bond theory. Additional evidence for s-p orbital hybridization is explored, with the aim of obtaining smaller effective mass. Finally, three strategies are proposed for designing active photocatalysts with high carrier mobility.

The success of describing high carrier mobility using small effective mass with the dispersive energy band is well known for semiconductors. Effective mass is calculated by the following equation,

$$m^* = \frac{\hbar^2}{\partial^2 E(k) / \partial k^2}, \quad (1)$$

where m^* is the effective mass, \hbar is the reduced Planck constant, and $E(k)$ is the energy of an electron at wave vector k in that particular band. Eq. (1) demonstrates that the effective mass of a semiconductor is obtained by fitting its actual $E(k)$ - k diagram around the CBM or VBM by a parabola [16]. Consequently, a dispersive energy band is desired to provide smaller effective mass, which relates to higher charge carrier mobility in semiconductors [17]. The s-p orbital hybridization, which can produce more dispersive energy band because of their large overlap between orbitals, is investigated here

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in more detail. To investigate whether s-p hybridization can render an explanation for this behavior, the origins of dispersive energy bands are first considered. Then, the reasons for choosing s-p hybridization are addressed. Finally, the strategies for using s-p hybridization in searching for materials with high carrier mobility are proposed.

According to the energy band theory, in the single isolated atom, a single particle orbital has a definite energy which refers to the energy level, as shown at the top of Fig. S1a (online). When two or more isolated atoms are close enough, electrons in the outermost orbital will experience an attractive force causing them to interact with their nearest neighbors, so that these electrons are shared. The energy of shared electrons will change according to Pauli exclusion principle. Ultimately, a continuous energy band is formed as the number of atoms increases, as is exhibited at the bottom of Fig. S1a (online). Whereas, the interaction between inner-shell electrons of nearest-neighbored atoms is much weaker than outermost electrons. Thus, the energy band formed by the outermost electron is broader than those of the inner-shell electrons, as reflected in Fig. S1b (online). In the energy band theory, the band structure of a periodic system is determined by specifying the Bloch functions $\psi(r)$, which are constructed from the electron orbitals based on the reciprocal vector k inside the Brillouin zone (BZ) and the energy eigenvalue $E_n(k)$. The energy eigenvalues of electrons are obtained by solving the Schrödinger equation

$$H \cdot \psi(r) = E_n \cdot \psi(r), \quad (2)$$

$$E_n(k) = E_n^m - A_n - J_n \sum_r e^{ik \cdot r}, \quad (3)$$

where E_n^m is the atomic energy level of a single particle orbital m at ground state, A_n is the change in E_n^m when influenced by the periodic potential field of the crystal structure, which is a minimal value based on the perturbation theory, J_n is the overlap integral of the electron orbital m between atoms, r is the lattice vector, and k is the wave vector of wave function. Differences between maximum and minimum eigenvalue would be confined to the region dominated by J_n , possibly evident as the width of the energy band for the single particle orbitals m . Therefore, the overlap of these orbitals intuitively accommodates widths of energy bands, which is a manifestation of the band dispersion. Consequently, a large overlap between single particle orbitals with same or similar energy of neighboring atoms can create a broad energy band and result in a dispersive band structure.

In general, carrier mobility is degenerate with respect to the value of effective mass in the VBM or CBM. Therefore, valence electrons in the outermost orbitals, whose energy band is located in the vicinity of the Fermi level, are concerned. Here we should mention the origin of band gap, which is analogous to the formation of band broadening. As pictured in Fig. S1c (online), the overlapping of different energy bands introduces a repulsive interaction between them, which produces a band gap in materials by lowering the lower band and raising the higher band. It is worth emphasizing that the band gap reflects the overlapping of different energy bands while band broadening is contributed by the overlapping of particle orbital with same or similar energy. These behaviors are summarized in Fig. S1d (online) [18], taking carbon atoms as the example. Two isolated C atoms display the same two energy levels designated as 2s and 2p (at point I), which broaden into energy bands as the distance between atoms is reduced. The widths of both energy bands originating from 2s and 2p are increased, derived from the larger overlap of the relevant electrons (I-O). In the presence of overlap between the thus-formed energy bands for 2s and 2p, a band gap appears (where point C represents the actual situation in diamond). In order to give an accurate description for the complex real crystal structure, point C is discussed

(Fig. S2 online). Valence electrons of C 2s and C 2p in the unit cell have already overlapped in the diamond lattice. Otherwise, the hybridized s-p orbital will contribute to both the VB and the CB. According to the analysis above, the band width preserved by the valence electrons is determined by s, p, and s-p orbitals, while the band gap is ascribed to the interaction between them.

Since carrier mobility is proportional to dispersion of energy bands, constructing a large overlap of orbitals through rational alignment of valence electrons is then expected to result in high carrier mobility. s-p hybridization, a possible electron configuration for a dispersive energy band, is described here. To understand this, it is instructive to analyze the orbital wave function which gives the distribution of the kinematic states of electrons in real space. The square root of the orbital wave function is the distribution function of electron probability, which is given in Fig. S3a for s, p, and d orbitals [19]. Their relative sizes correspond to the binding ability of orbitals. By setting that value of the s orbital as 1, it is $\sqrt{3}$ and $\sqrt{5}$ for the p orbital and d orbital, respectively [20]. This leads us to conclude that the relative binding ability decreases in the order of s, p, and d orbitals. In addition, s-s and s-p hybridization preferentially yield the strongest type of interaction, σ bonding, which arises from considerable overlap between orbitals (Fig. S3b online). Hence, the strong s-p hybridization is implicitly assumed to be the most favorable configuration for broadening and dispersing the energy band in k space, which is expected to harvest smaller effective mass and higher carrier mobility in semiconductors. Otherwise, the anti-bonding s-p orbital hybridization in CBM (or VBM) is also a good strategy to develop efficient photocatalysts with a high electron (or hole) mobility. Promising candidates for elements of these materials in the periodic table are highlighted with the black frame in Fig. 1a. Cation elements Tl, Pb, Po, and At are not included because of their instability and toxicity. With 9 cation and 16 anion elements selected, there are 144 combinations of elements possible for binary materials.

It has been verified that s-p orbital hybridization is beneficial to energy-band dispersion, which will lower the effective mass and increase the carrier mobility. Motivated by these considerations, we have developed three strategies based on s-p orbital hybridization according to Eq. (3), as shown in the schematic diagram in Fig. 1b. Firstly, E_n^m reflects the intrinsic property of atoms. Elements with rich s and p valence electrons should be selected, such as P-block elements (s^2p^x) or d^{10} metal cations (for example, Ag ($4d^{10}5s^1$) and Zn ($3d^{10}4s^2$)). Secondly, A_n reflects the influence of crystal potential field. The close packed crystal structure, such as the diamond structure, is also helpful to achieve larger overlap between valence electrons. Finally, J_n reflects the interaction between valence electrons of atoms. Larger sizes of atoms are better than smaller one due to their greater opportunity for overlapping with each other. However, the last one should not be overstated because compounds with too large-size atoms may lead to very small band gap which will degrade the performance of photocatalysts.

Some typical s-p hybridization materials are selected to analyze the relationship between band decomposition and effective mass. More insight can be gained by calculating the electron structures of typical photocatalysts that are composed of the candidate elements. Calculation methods are given in the Supplementary data (online). We group them into three categories according to their elements and band composition, as indicated by s-p, s-p-d, and Bi-based species. Summarized orbital compositions of the CBM and VBM (which are depicted in terms of their partial density of states (PDOS) in Fig. S5 online) for these photocatalysts are displayed in Table S1 and Fig. S4 (online). The calculation results imply that the CBM and VBM of these materials are dominated by s-p or p orbitals, except for the s-p-d species. The calculated

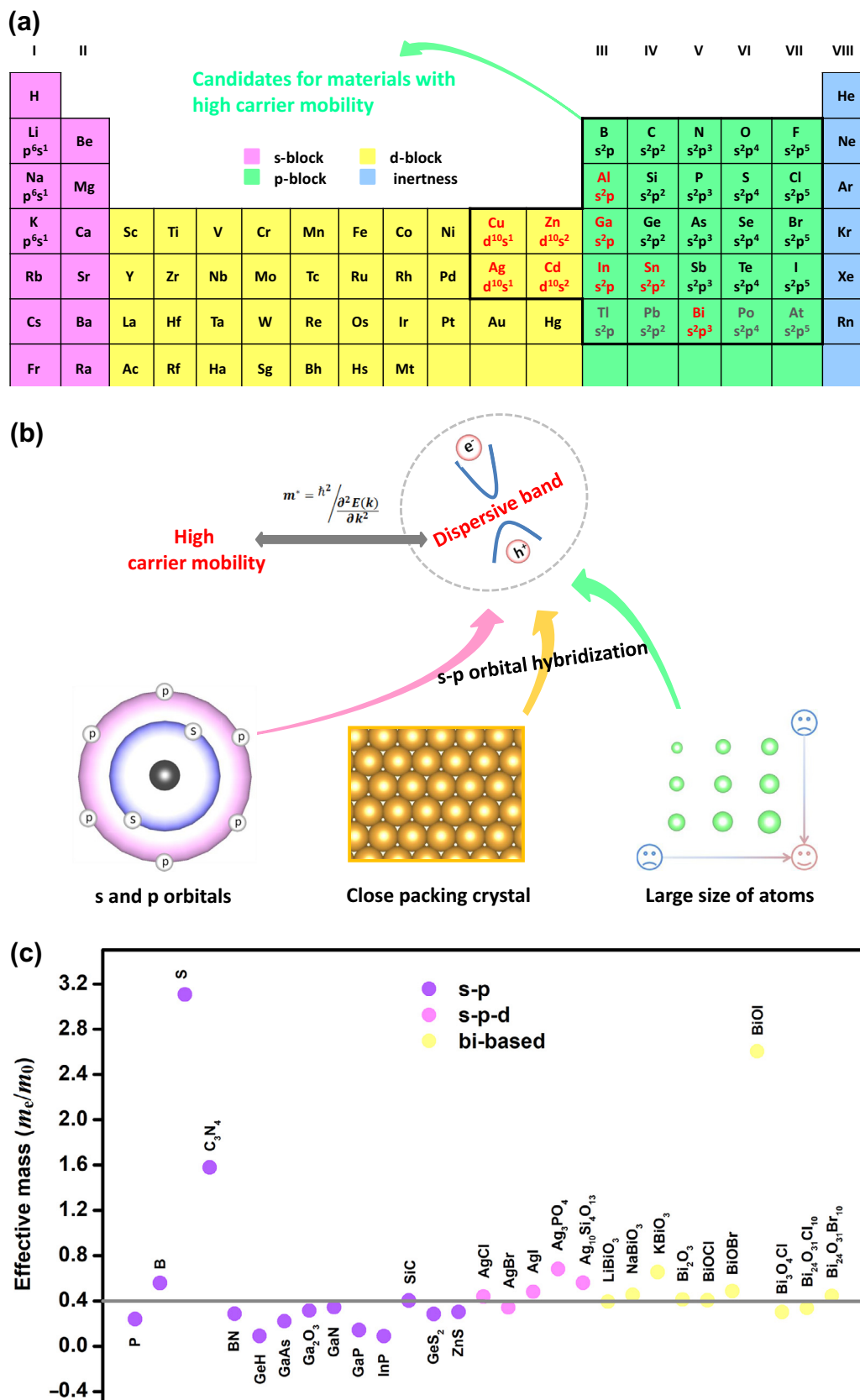


Fig. 1. The s-p orbital hybridization. (a) Candidates for elements of materials with high carrier mobility in the Periodic Table. Red and black elements are possible cations and anions, respectively. Grey ones are not considered. (b) Schematic diagram of principles using to promote s-p hybridization. (c) Effective mass of electrons for selected photocatalysts. Purple, pink, and yellow balls are s-p, s-p-d, and Bi-based species.

band structures are given in Fig. S6 (online) and effective masses of selected photocatalysts are listed in Table S2 (online), elucidating the principles for s-p orbital hybridization by having the smallest effective mass at the CBM (Fig. 1c). The value of effective mass

0.4 m_0 (m_0 is the electron mass) is set as a criterion to identify the electron mobility. The results clearly suggest that effective mass of most of the s-p materials is mostly smaller than those of s-p-d and Bi-based materials. This phenomenon is in good agreement with s-p orbital hybridization strategy that a smaller effective mass results from stronger hybridization between s and p orbitals. As shown in Fig. S4 (online), both the VBM and the CBM of the elements P, B, and S are comprised of s and p orbitals. The VBM and CBM of BN consists of B-p and N-p orbitals, while the CBM of C_3N_4 only originates from C-p and N-p orbitals and the VBM from N-p and N-s orbitals. Other materials in s-p species have similar components, with their CBM coming from s-p orbitals, while hybridized p orbitals are observed in the VBM. Efficient cooperation and hybridization of s and p orbitals may give a good explanation for their higher carrier mobility. In the case of s-p-d species, although d orbitals are observed in the VBM, the participation of p orbitals in the VBM and the existence of s-p hybridization in the CBM support their good photocatalytic activity. In Bi-based materials, the CBM of $MBiO_3$ ($M = Li, Na, K$) compounds consists of s-p orbitals, while p orbitals mainly contribute to the VBM. $BiOX$ ($X = Cl, Br, I$) only has p orbitals in both the CBM and the VBM. Other Bi-based materials all have similar constituents in the CBM (p orbitals) and VBM (s-p orbitals). The lower carrier mobility of Bi-based species may be related to their multiple-element nature and non-compact lattice, which lead to a large effective mass. In all of these selected materials, GeH, GaAs, GaP and InP have the smallest effective masses which are located in the area of s-p species. The small effective mass also has a close relationship to their close packed structures and bigger sizes of atoms, which work together with s-p orbital hybridization for creating a larger overlap between atoms and obtaining smaller effective mass. According to our results, GeH, GaAs, GaP, InP, P, BN, GeS_2 , and ZnS are indicated as the promising candidates for photocatalysts with high carrier mobility.

In conclusion, we have described the origins of dispersive energy bands to determine the decisive factor for high charge carrier mobility. A dispersive energy band indicates a small effective mass in VBM or CBM with expected high carrier mobility. It is estimated that large overlap between valence electrons plays the primary role in large energy band dispersion. s-p orbital hybridization is observed to possibly create larger overlap because of its stronger binding ability. Three strategies, which are helpful for designing active photocatalysts with high carrier mobility, are proposed based on s-p orbital hybridization. Firstly, elements with rich s and p electrons are required to obtain well cooperating s-p orbital hybridization. Secondly, close packed structures are expected to gain stronger overlap between valence electrons. Thirdly, larger sizes of atoms are benefit to achieve smaller effective mass. Based on the results of DOS and effective mass, GeH, GaAs, GaP, InP, P, BN, GeS_2 , and ZnS are indicated as the promising candidates for photocatalysts with high carrier mobility.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.scib.2018.02.020>.

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