Research paper

Rational design of Si/TiO$_2$ heterojunction photocatalysts: Transfer matrix method

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Xiaolong Yao[a], Lei Chen[a], Mengyin Liu[a], Deqiang Feng[a], Changhong Wang[a], Feng Lu[a], Weihua Wang[a], Xuewei Wang[b], Yahui Cheng[a], Hui Liu[a], Haijun Chen[a,*], Weichao Wang[a,c,*]

[a] Department of Electronics and Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin, 300071, China
[b] School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China
[c] Department of Materials Science & Engineering, the University of Texas at Dallas, Richardson, TX 75252, USA

ABSTRACT

The charge transfer in semiconductor heterojunction photocatalyst is one of the key factors determining its catalytic efficiency and durability in an aqueous environment. The widely used interface model with the simplified rectangular potential barrier fails to precisely predict the carrier transfer process since the band bending and its variation caused by solar energy are both not considered. Here, utilizing transfer matrix method, we take the Si/TiO$_2$ heterojunction as a prototype to shed light on the rational design of the semiconductor heterojunction photocatalyst in terms of its intrinsic characteristics, such as TiO$_2$ thickness and the dopant concentration. We find that the minimum incident energy (MIE) for electrons (holes) tunneling through the Si/TiO$_2$ heterojunction decreases (increases) as the thickness of TiO$_2$ layer increases. Within a moderate condition (TiO$_2$ thickness of 3 nm and dopant concentration of $1 \times 10^{18}\,\mathrm{cm^{-3}}$ ($5 \times 10^{19}\,\mathrm{cm^{-3}}$) in Si (TiO$_2$)), both electrons and holes can transfer through the heterojunction barrier with relatively small incident energy. Furthermore, the photovoltage under illumination is beneficial for reducing MIE for electrons while increasing that for holes. Therefore, our transfer matrix scheme provides insights into rational design of the high efficient photocatalyst.

1. Introduction

The development of semiconductor photocatalysts for water splitting to produce hydrogen using solar energy has undergone considerable research over past decades [1–9]. Constructing semiconductor heterojunctions has been shown to be an effective scheme for improving photocatalytic activity through high efficient photogenerated charge separation and transfer [9–11]. However, a fundamental understanding of the charge transfer in semiconductor heterojunction photocatalysts remains unclear due to the complexity of band structure at heterojunction interface. To date, the extensively adopted interface models for designing and optimizing semiconductor heterojunction photocatalysts are based on the simplified rectangular potential energy barrier, including the Z-scheme [12–16] and the type-II (staggered) heterostructures [17–20]. The fatal weakness of these interface models is the ignorance or only schematically describing band bending at the semiconductor interface that could decisively affect the interfacial charge transfer process [11,21]. Another factor strongly influencing the interfacial potential barrier is the photovoltage emerging under illumination, which is even harder to be considered in above discussed

interface models.

Because of these severe deficiencies, the present interface models cannot accurately predict the photocatalytic activity thus direct the design of semiconductor heterojunction photocatalysts. Here, we utilize the transfer matrix method to quantitatively investigate the dependence of band bending and photovoltage on the charge transfer in a prototype Si/TiO$_2$ heterojunction photocatalyst. This system is widely explored in experiments which in turn validates our predications.

Si has been demonstrated to be efficient for solar hydrogen production [22–24] because of its suitable band gap (1.12 eV) for absorbing sunlight. However, it is challenging to apply Si for photocatalyst directly since it easily corrodes in an aqueous environment [25]. On the other hand, TiO$_2$ is a good passivation material due to its high resistance to photocorrosion, but its conversion efficiency of solar energy to hydrogen is still low because of its large bandgap (E$_g$ = 3.0 ~ 3.2 eV) [6,26–31]. These drawbacks can be overcome by constructing the Si/TiO$_2$ heterojunction photocatalytic system, which provides a higher stability and a larger open circuit voltage [10,11,31–36].

The band bending at semiconductor heterojunction interface is

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determined by the semiconductor material's intrinsic characteristics, for example, the thickness of TiO_2 protective layer and the dopant concentrations of heterojunction components. Therefore, these intrinsic characteristics of semiconductor heterojunction are fundamental factors for the design and optimization of semiconductor heterojunction photocatalysts. When the thickness of TiO_2 protective layer is small enough that the majority carriers (electrons) in TiO_2 layer are completely depleted, the energy band bending in the Si/TiO_2 heterojunction in contact with an electrolyte [37] is quite different from the situation in n-Si/n-TiO_2 heterojunction reported previously where a field-free region may exist inside the TiO_2 layer since the deposition thickness is relatively large [11,37]. On the other hand, in previous work, the complex tunneling potential barriers for charge carriers in heterojunction are simplified as rectangular potential barriers formed by the band edges of the heterojunction components neglecting the band bending in order to characterize the charge transfer process more conveniently [38,39]. Thus, the above-mentioned simplification of tunneling potential cannot accurately describe the realistic charge transfer behavior in semiconductor heterojunction.

In this paper, we apply the transfer matrix method to calculate the transmission coefficients [40–42] of charge carriers tunneling through the Si/TiO_2 heterojunction. We firstly consider the simplified rectangular potential barriers at heterojunction interface. Next, the modification of band structure including band bending and photovoltage is taken into account for revealing the dependence of charge carriers' transmission coefficients on the TiO_2 layer thicknesses and dopant concentrations in heterojunction components. It is found that the MIE for charge carriers tunneling through the Si/TiO_2 heretostructures is closely related to the TiO_2 layer thickness and the dopant concentration. The moderate condition of TiO_2 thickness (3 nm) and the dopant concentration (1×10^{18} cm^{-3} for Si and 5×10^{19} cm^{-3} for TiO_2) is beneficial for electrons and holes tunneling through the heterojunction with relatively low incident energy. Our work reveals that the intrinsic characteristics of Si/TiO_2 heterojunction photocatalysts have decisive influence on their charge transfer and essentially influence the photoactivity without considering the variation of the morphology. These rules can be generalized to design other semiconductor heterojunction photocatalysts.

2. Transfer matrix method

The transfer matrix method can be utilized to study the transport property of charge carriers in heterojunction photocatalysts by quantitatively calculating the transmission coefficients for carriers tunneling through a one-dimensional potential energy barrier with arbitrary shape [40]. In this method, the total potential energy is divided into a series of rectangular potential energy as shown in Fig. 1. This method will be accurate if the total number of rectangular potential energy N is
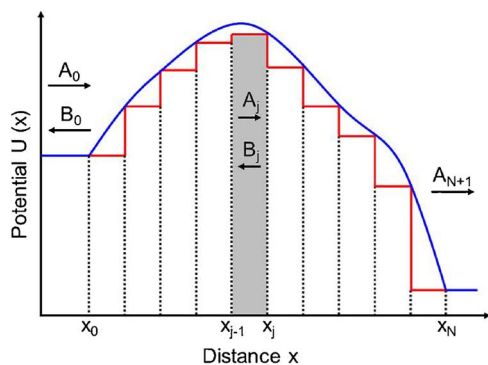

Fig. 1. The one-dimensional potential energy profile with arbitrary shape (blue line) and its approximate potential energy profile (red line) composed by a series of rectangular potential energies (gray rectangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

large enough that the width of each rectangular potential energy is much smaller than the de Broglie wavelength of charge carrier [43].

Consider a particle that approaches an arbitrarily shaped one-dimensional potential barrier from the left with an incident energy E and a mass m^* (Fig. 1). In quantum mechanics, the motion of the particle is described by a complex wave function ψ that is a solution to the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m^*}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x) \tag{1}$$

This wave will be partially transmitted through the barrier and partially reflected when it propagates to the rectangular potential barrier U_j, so the wave functions in intervals (x_{j-1}, x_j) and (x_j, x_{j+1}) are:

$$\psi_j(x) = A_j e^{ik_j x} + B_j e^{-ik_j x} \tag{2}$$

$$\psi_{j+1}(x) = A_{j+1} e^{ik_{j+1}x} + B_{j+1} e^{-ik_{j+1}x} \tag{3}$$

where A_j (B_j) is the amplitude of the transmission (reflection) wave and $k_j = \frac{1}{\hbar}(2m^*(E - U_j))^{\frac{1}{2}}$ is the wave vector within the reduced Planck's constant $\hbar$.

Due to continuity of $\psi_j(x)$ and $\frac{1}{m_j^*}\frac{d\psi_j}{dx}$ at each boundary of the rectangular potential barrier U_j[40], the amplitudes A_j and B_j are correlated with A_{j+1} and B_{j+1} by a 2×2 transfer matrix M_j:

$$\begin{bmatrix} A_j \\ B_j \end{bmatrix} = M_j \begin{bmatrix} A_{j+1} \\ B_{j+1} \end{bmatrix} \tag{4}$$

The transfer matrix M_j in the interval (x_{j-1}, x_j) is given by:

$$M_j = \frac{1}{2}\begin{bmatrix} (1 + S_j)e^{i(k_{j+1}-k_j)x_j} & (1 - S_j)e^{-i(k_{j+1}+k_j)x_j} \\ (1 - S_j)e^{i(k_{j+1}+k_j)x_j} & (1 + S_j)e^{-i(k_{j+1}-k_j)x_j} \end{bmatrix} \tag{5}$$

$$S_j = \frac{m_j^*}{m_{j+1}^*}\frac{k_{j+1}}{k_j} \tag{6}$$

Accordingly, the amplitudes A_0 and B_0 at the left boundary of the arbitrarily shaped potential barrier can be correlated with the amplitudes A_{N+1} and B_{N+1} at the right boundary by the following formula

$$\begin{bmatrix} A_0 \\ B_0 \end{bmatrix} = \prod_{j=0}^{N} M_j \begin{bmatrix} A_{N+1} \\ B_{N+1} \end{bmatrix} = M \begin{bmatrix} A_{N+1} \\ B_{N+1} \end{bmatrix} \tag{7}$$

where

$$M = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \tag{8}$$

By setting $B_{N+1} = 0$ since there is no reflection at right side of the total potential barrier, the transmission coefficient T of particle tunneling the potential barrier can be expressed as follows:

$$T = \frac{m_0^*}{m_{N+1}^*}\frac{k_{N+1}}{k_0}\left(\frac{A_{N+1}}{A_0}\right)^2 = \left(\frac{1}{M_{11}}\right)^2 \tag{9}$$

which indicates the probability of the particle tunneling through the arbitrarily shaped potential barrier. It should be noted here that, for the carriers in semiconductors, their effective masses will change when tunneling through the interface of the semiconductor heterojunction owing to the different periodic potentials of semiconductors [40]. Though, in our work, the effective masses of carriers in all the regions are taken as those values in Si for convenience. As a result, the difference of the semiconductors' periodic potentials is included in the total potential energy of Si/TiO_2 heterojunction.

3. Results and discussion

The band alignment of the Si/TiO_2 heterojunction and the relative position of the redox potentials for water electrolysis are shown in