

Supporting Information

Study of interface electric field affecting the photocatalysis of ZnO

Zhibing Zhan¹, Yonghao Wang¹, Zhang Lin², Jiye Zhang^{1,*}, Feng Huang^{1,*}

¹Key Laboratory of Optoelectronic Materials Chemistry and Physics, ²State Key Laboratory of Structural Chemistry; Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences Fuzhou, Fujian, 350002, China.

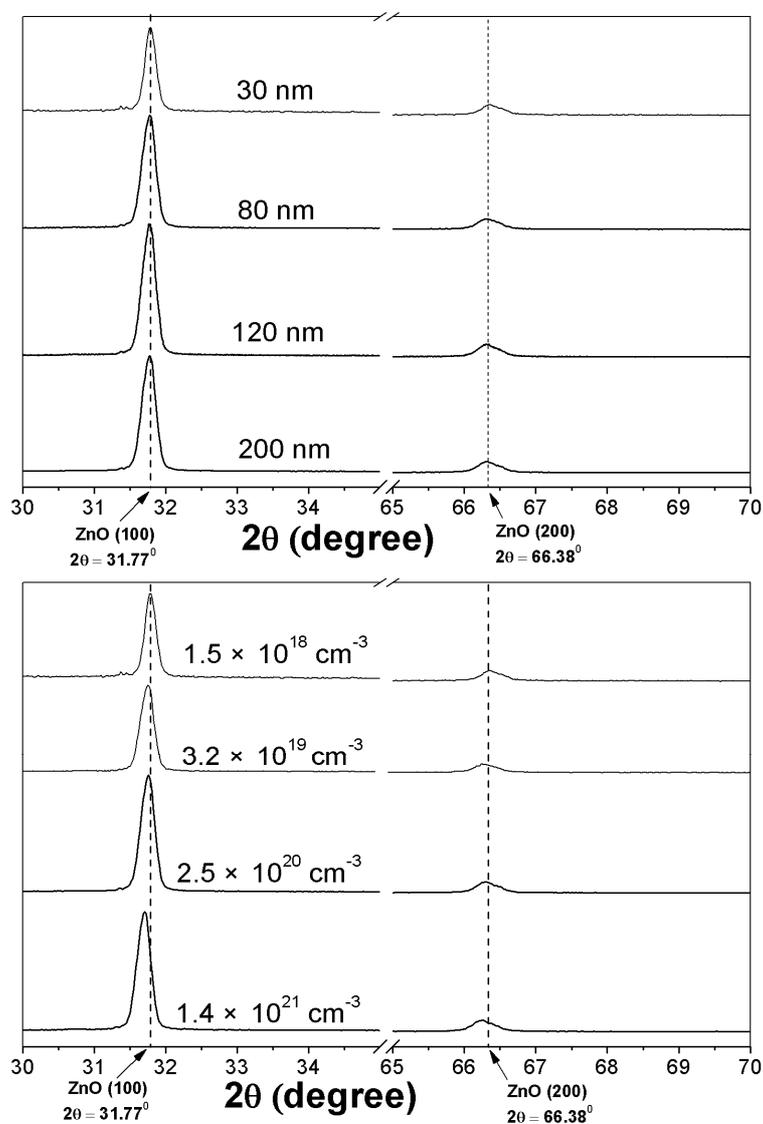


Fig. S1. XRD profiles of AZO TFs deposited on m-plane of ZnO SC with different thickness and different carrier concentration.

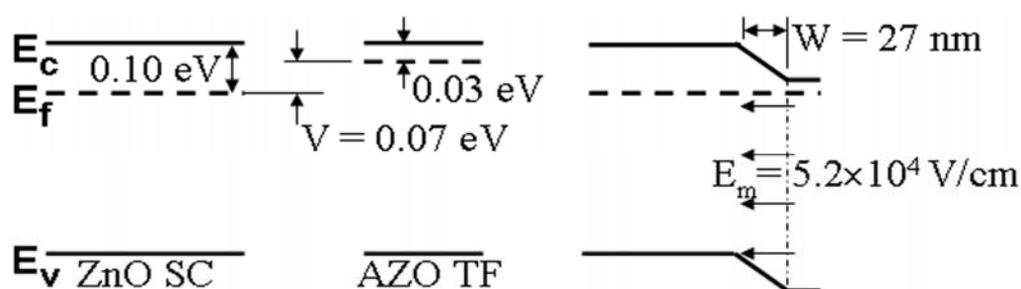


Fig. S2 The schematic energy band diagram of ZnO SC and AZO TF, as well as the calculated IEF between them.

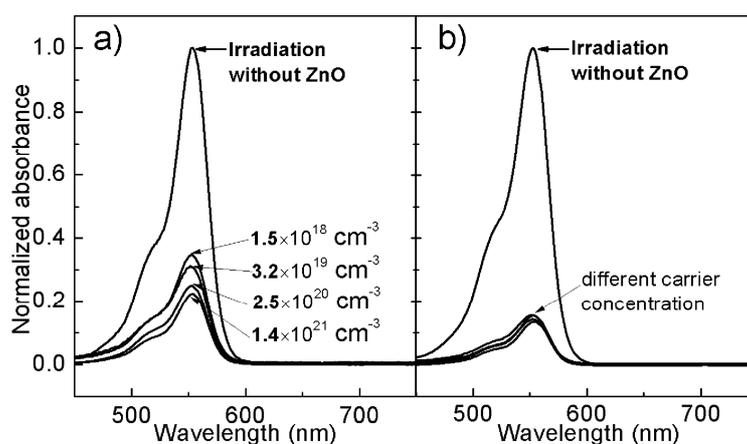


Fig. S3. Degradation of RhB with the concentration of a) 25 μM and b) 5 μM , in the presence of AZO TFs with different carrier concentration deposited on ZnO SCs.

Experimental Section

ZnO SCs: ZnO SCs were obtained from our hydrothermal growth method.¹ After determined the m-plane, it was cut to the size of $5.0 \times 5.0 \times 0.7$ mm. The m-plane was measured by XRD (PANalytical X' Pert Pro diffractometer with Ni-filtered and Cu $K\alpha$ ($\lambda = 0.15406$ nm) source), AFM imaging (Autopre CP-VEECO) and room temperature Hall-effect (Van der Pauw method with a magnetic field strength of 5 kGs) after cleaning and polishing, in order to obtain their structure, morphology and electron concentration values.

AZO TFs Preparation: AZO TFs have been deposited on the m-plane of ZnO SC by magnetron sputtering. The targets were ZnO and Al_2O_3 ceramic disks (5.0 cm diameter by 0.3 cm thickness, 99.99 % purity), respectively. The power of the two targets can be adjusted from 0 to 200 W, according to the Al doping content. The working gas Ar (99.99%) was well regulated at 20 SCCM (standard cubic centimeter

per min) by mass flow controllers (BÜkert Werke GmbH & Co. KG). The working pressure and substrate temperature were maintained at 0.1 Pa and 300 °C, respectively. The distance from the target to the substrate was about 9.0 cm. During the film deposition, the substrate kept in rotation at 9 rounds per min. The deposition time was controlled based on the thickness of the thin film. The vacuum chamber was evacuated to a base pressure of 10^{-4} Pa. Before deposition of a film, targets were pre-sputtered for 15 min with a shutter covering the substrate in order to remove any contaminant on the surface of the targets, and then the shutter was subsequently removed to commence growth.

Photodegradation test: Immersed ZnO SCs deposited or undeposited AZO TFs in 2 ml dye aqueous solution (Rhodamine B and Methylene blue) in the dark for 2h to establish absorption equilibrium, and then the solution was irradiated by UV light (high pressure mercury lamp with 360 nm main wavelength and power of 125 W) for 3 h. As a reference, the same dye solution without ZnO SC was also irradiated under the same condition. The degraded solution was analyzed by UV-vis spectrophotometer (UV-2501PC/2550 SHIMADZU).

Interface electric field (IEF) calculation: ²

To prove the existence of the IEF, we have carried out I-V measurements on our ZnO SC/ AZO TF systems. A typical I-V curve is shown in Fig. S3. As shown in Fig. S3, the rectification effect can be seen obviously, which confirmed that IEF was constructed successfully. The intensity, distribution and direction of IEF can be determined according to the relative magnitude of carrier concentrations at both sides of the interface.

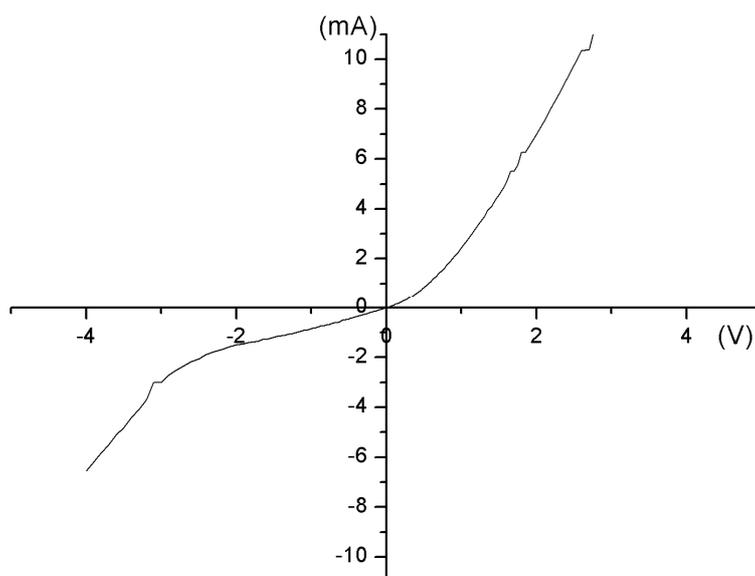


Fig. S4 Typical I-V curve of ZnO SC/ 200 nm AZO TF system

According to semiconductor physics, the carrier concentration N can be expressed as:

$$N = N_c \exp\left(-\frac{E_c - E_f}{kT}\right) \quad (1)$$

Here E_c and E_f are the conduction band and Fermi energy level, respectively. N_c is the effective density of states in the conduction band, which is given by

$$N_c = 2\left(\frac{2\pi m_n m_0 kT}{h^2}\right)^{3/2},$$

where the electron rest mass $m_0 = 9.10 \times 10^{-31}$ Kg, Boltzmann constant $k = 1.38 \times 10^{-23}$ J/K, Planck constant $h = 6.63 \times 10^{-34}$ J·s. For ZnO, the effective mass of electron $m_n = 0.3$,³ when $T = 300$ K, $N_c = 4.1 \times 10^{18}$ cm⁻³. From Eq.1, the difference between the conduction band and Fermi energy level can be expressed as:

$$E_c - E_f = kT \ln\left(\frac{N_c}{N}\right) \quad (2)$$

Thus, from the measured carrier concentration N , the Fermi energy level of ZnO SC and AZO TF can be determined, respectively. The difference between the Fermi energy level of ZnO SC and AZO TF is the built-in potential V .

The width (W) and maximal intensity (E_m) of the IEF can be determined by equations (3) and (4), respectively.²

$$W(\text{cm}) = \left(\frac{2\varepsilon_0\varepsilon_r V}{qn}\right)^{\frac{1}{2}} \quad (3)$$

$$E_m (\text{V / cm}) = \frac{qnW}{\epsilon_0 \epsilon_r} \quad (4)$$

Where vacuum dielectric constant $\epsilon_0 = 8.85 \times 10^{-14}$ F/cm, the relative dielectric constant of ZnO $\epsilon_r = 8.12$,³ electron charge $q = 1.6 \times 10^{-19}$ C, and n is the carrier concentration of the region distributing IEF.

It should be noted that the effect of doped Al on the band gap of AZO TFs has not been considered in above calculation process. In fact, the band gap of AZO FT can be influenced by the content of doped Al. When the content of doped Al is low (carrier concentration is less than 10^{20} cm^{-3}), the effect of doping on the band gap can be neglected.⁴ However, when the content of doped Al is high (carrier concentration is larger than 10^{20} cm^{-3}), the band gap will have small widening. This phenomenon is the result of the competition between the Burstein-Moss shift,⁵ an energy band widening (blue shift) effect resulting from the entering of the Fermi level into the conduction band for degenerate semiconductors, and band gap narrowing effect which is ascribed to the emerging of the impurity band formed by the overlapped impurity states.² According to the optical transmittance spectrum of thin film, the highest widening in our system is about 0.1 eV (for the thin film with carrier concentration of $1.4 \times 10^{21} \text{ cm}^{-3}$). Even if this value is totally counted in build-in potential V , the intensity and width of electric field will only increase about 15 %. Because the widening of the band gap only strengthens the electric field and its influence is limited, we think this do not affect our result that the strengthened electric field will bring about better photodegradation efficiency.

Transit time (T) calculation:

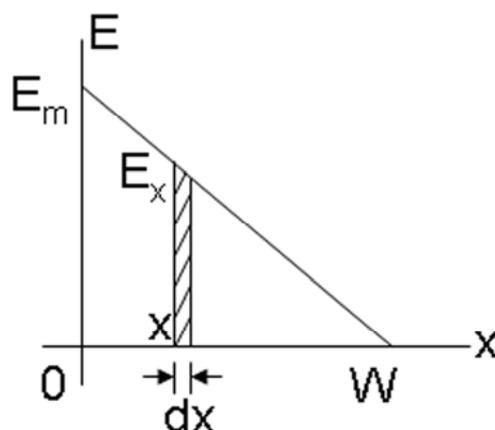


Fig. S5 The distribution of the IEF.

According to semiconductor physics, the intensity of the IEF can be considered as

a linear distribution at the electric field region.² As shown in Fig. S4, at the interface ($x = 0$) and edge ($x = W$), the intensity are E_m and 0, respectively. Electron will make varying acceleration motion under the action of the varying IEF. Let E_x and V_x be value of the intensity of IEF and the velocity of the electron, at the position with the distance of x from the interface ($x = 0$), respectively. Then

$$E_x = E_m \left(1 - \frac{x}{W}\right) \quad (5)$$

$$V_x = \frac{dx}{dt} \quad (6)$$

From the interface ($x = 0$) to the position x , the power of the IEF force converts to the kinetic energy of the electron. So

$$\frac{1}{2} m V_x^2 = \int_0^x q E_y dy = \int_0^x q E_m \left(1 - \frac{y}{W}\right) dy = q E_m x - \frac{q E_m}{2W} x^2 \quad (7)$$

Where electron charge $q = 1.6 \times 10^{-19}$ C, electron mass $m = 9.10 \times 10^{-31}$ Kg.

Combined Eq (6) and (7), V_x can be expressed as:

$$V_x = \frac{dx}{dt} = \sqrt{\frac{2qE_m}{m} x - \frac{qE_m}{mW} x^2} \quad (8)$$

Thus,

$$dt = \frac{dx}{V_x} = \frac{1}{\sqrt{\frac{2qE_m}{m} x - \frac{qE_m}{mW} x^2}} dx \quad (9)$$

The transit time T (the time required for an electron to cross the IEF zone with the width W under the action of IEF forces) can be calculated from the following definite integration.

$$T = \int_0^W \frac{1}{\sqrt{\frac{2qE_m}{m} x - \frac{qE_m}{mW} x^2}} dx = \frac{1}{\sqrt{\frac{2qE_m}{m}}} \int_0^W \frac{1}{\sqrt{x - \frac{x^2}{2W}}} dx \quad (10)$$

When the width (W) and maximal intensity (E_m) of the IEF is known, the transit time T can be determined.

For example, when $W = 27 \text{ nm} = 2.7 \times 10^{-8} \text{ m}$, $E_m = 5.2 \times 10^4 \text{ V/cm} = 5.2 \times 10^6 \text{ V/m}$. Putting the numerical integration ($W = 2.7 \times 10^{-8} \text{ m}$)

$$\int_0^W \frac{1}{\sqrt{x - \frac{x^2}{2W}}} dx = 0.000365$$

and the value of $E_m = 5.2 \times 10^4 \text{ V/cm} = 5.2 \times 10^6 \text{ V/m}$ into Eq. 10, then $T = 2.7 \times 10^{-13} \text{ s} =$

0.27 ps.

Reference

- [1] W. W. Lin, D. G. Chen, J. Y. Zhang, Z. Lin, J. K. Huang, W. Li, Y. H. Wang, F. Huang, *Cryst. Growth Des.* **2009**, 9, 4378.
- [2] S. M. Sze, in *Semiconductor Devices: Physics and Technology*, 2 nd ed., *John Wiley & Sons, Inc, USA*, **2002**, Chapter 2, 4 and 7.
- [3] D. C. Look, K. D. Leedy, D. H. Tomich, B. Bayraktaroglu, *Appl. Phys. Lett.*, **2010**, 96, 062102.
- [4] K. H. Kim, K. C. Park, D. Y. Ma, *J. Appl. Phys.* **1997**, 81, 7764.
- [5] E. Burstein, *Phys. Rev.* **1954**, 93, 632.