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Review of surface photovoltage spectra of nano-sized semiconductor and its applications in heterogeneous photocatalysis

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Abstract

Heterogeneous photocatalysis is a promising technique valuable for environmental purification. Nano-sized semiconductors such as ZnO and TiO₂, which is one of the most basic functional materials, have emerged as effective photocatalyst materials. The surface photovoltage spectra (SPS) can be an effective method for quickly evaluating the photocatalytic activity of semiconductor materials since it can provide a rapid, non-destructive monitor of the semiconductor surface properties such as surface band bending, surface and bulk carrier recombination and surface states, mainly showing the carrier separation and transfer behavior with the aid of light, especially the electric-field-induced surface photovoltage spectra (EFISPS), in which SPS is combined with the electric-field-modified technique. In this review, the basic principles, measurement and applications of the SPS and EFISPS are mainly discussed together with some fundamental aspects like the electric properties of semiconductor surface and the principle of electric field effect. In particular, the applications of SPS to nano-sized semiconductors such as ZnO and TiO₂ in heterogeneous photocatalysis are emphasized, which involve mainly evaluating the photocatalytic activity by analyzing semiconductor surface properties such as the separation efficiency of photoinduced carriers under illumination by the SPS measurement, highlighting our own contributions. The results show that the weaker the surface photovoltage

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signal is, the higher the photocatalytic activity is in the case of nano-sized semiconductor photocatalysts.

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1. Introduction

Nano-sized functional materials of semiconductors promise the prospect of application in many high-technique fields such as photovoltaic conversion and energy storage because of their characteristics of surface structure and surface area with high concentration [1–5].

Heterogeneous photocatalysis is an emerging technique valuable for water and air purification and remediation using semiconductors as environmental photocatalysts. Fundamental and applied research on this subject have been performed extensively during the last 20 years all over the world [6–10]. Illumination of semiconductors such as ZnO and TiO₂ with photons of energies greater than the bandgap energy promotes electrons transitions from the valence band to the conduction band, leaving behind positive holes. The valence band potential is positive enough to generate hydroxyl radicals at the semiconductor surface and the conduction band potential is negative enough to reduce molecular O₂. The hydroxyl radical or hole (h⁺) is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of semiconductor photocatalysts, resulting usually in their complete oxidation to CO₂. The main goal of research and development in this field is the use of the technique for air purification and wastewater treatment. This method offers several advantages of degrading pollutants such as the use of oxygen as the only oxidant, the capability for simultaneous oxidative and reductive reactions, low costs, use of solar and mild condition of reaction, in contrast to conventional techniques such as activated carbon or air stripping that only transfer the contaminants from one phase to another.

One of major limitations in semiconductor photocatalysis is the relatively low value of the overall quantum efficiency mainly because of the high rate of recombination of photoinduced electron–hole pairs at or near the surface. Some success in enhancing the efficiencies of photocatalysts has been achieved by methods such as using nano-sized semiconductor crystallites instead of bulk materials [11,12] and modifying photocatalysts by depositing noble metals like Ag and Pd on their surface [13–16]. These demonstrate that semiconductor particle size and its surface properties are two important factors influencing the performance of photocatalysts in that they can influence the separation efficiency of photo-induced electron–hole pairs, besides the photocatalytic oxidation reactions take place at or near the surface.

The surface photovoltage (SPV) method is a well-established contactless technique for the characterization of semiconductors, which relies on analyzing illumination-induced changes in the surface voltage [17,18]. For five decades, it has been used as

an extensive source of surface and bulk information on various semiconductors and semiconductor interfaces. Many researchers realized that they had invented a powerful tool for semiconductor surface characterization and also coined the term ‘surface photovoltage spectroscopy’ (SPS) [19,20]. Moreover, SPS is more sensitive than X-ray photoelectron or Auger spectroscopy, which makes its scope of applications wider [21].

The SPS technique can provide a rapid, non-destructive monitor of the surface properties of semiconductors [22]. It can offer important information about semiconductor surface, interface and bulk properties, including: surface band bending; surface and bulk carrier recombination; surface state distribution, etc., mainly reflecting the carrier separation and transfer behavior with the aid of light [17,23,24], especially when the SPS technique is combined with the electric-field-modified technique [25]. Hence, the SPS technique is important to semiconductor photocatalysis, that is, SPS measurements can be an effective method for quickly evaluating the photocatalytic activity of semiconductor materials in that it provides a very effective way to study the surface properties involving the charge separation and transfer behavior at the surface or interface as well as the optical characteristics of semiconductor under illumination.

Despite the great body of work about the SPS until now, papers devoted solely to a systematic description of the SPS method have seldom been reported [17]. In this review, the basic principles, measurement and applications of the SPS and Electric-field-induced surface photovoltage spectra (EFISPS) are mainly discussed together with some fundamental aspects like the electric properties of semiconductor surfaces and the principle of the electric field effect. In particular, the applications of SPS to nano-sized semiconductors in heterogeneous photocatalysis are emphasized, highlighting our own contributions, which involve mainly evaluating photocatalytic activity by analyzing semiconductor surface properties such as the separation efficiency of photoinduced carriers under illumination by SPS. Thus, this paper can help us understand the carrier separation and transfer behavior at semiconductor surfaces and its effects on the photocatalytic activity of semiconductors, which is conducive to investigation and preparation of applied semiconductor photocatalysts with high catalytic activity besides this paper is of interest to energy conversion and storage.

2. The principle of the SPS method [26–33]

2.1. Fundamental studies of SPS

In general, a surface is defined as a boundary of media with different physical properties. For example, the surface between a semiconductor and vacuum or gas is referred to as a ‘free surface’. The surface between a semiconductor and another solid is usually referred to as an ‘interface’. However, we usually use the term ‘surface’ to denote any boundary [17].

The interaction between two different materials with different work function can occur because of their different chemical potential. For example, the electrons can transfer from a material with high Fermi level to another a material with low Fermi level when they contact each other. The Fermi level of an n-type semiconductor is higher than that of the metal. Hence, the electrons can transfer from the semiconductor to the metal until thermodynamic equilibrium is established between the two when they contact each other, that is, the Fermi level of the semiconductor and metal at the interface is the same, which results in the formation of an electron depletion region and surface upward-bent band in the semiconductor. On the contrary, the Fermi level of a p-type semiconductor is lower than that of the metal. Thus, the electrons can transfer from the metal to the semiconductor until thermodynamic equilibrium is established between the two when they contact each other, which results in the formation of a hole depletion region and surface downward-bent band in the semiconductor. Fig. 1 shows the formation of semiconductor surface band bending when a semiconductor contacts a metal.

The termination of the periodic structure of a semiconductor at its free surface may form surface-localized electronic states within the semiconductor bandgap because the atomic ambient at or near the surface is different from that in bulk, these states are usually called the “intrinsic surface states”. In addition, “non-intrinsic surface states” can often appear because of adsorbed or impure substances at the surface. The appearance of these surface states induces charge transfer between the bulk and the surface in order to establish thermodynamic equilibrium. The charge transfer results in a non-neutral region (with a non-zero electric field) at the semiconductor surface, usually referred to as the surface space charge region (SCR), along with the electron or hole depletion regions at the surface or interface between a semiconductor and a metal discussed above. In other words, a built-in electric field,

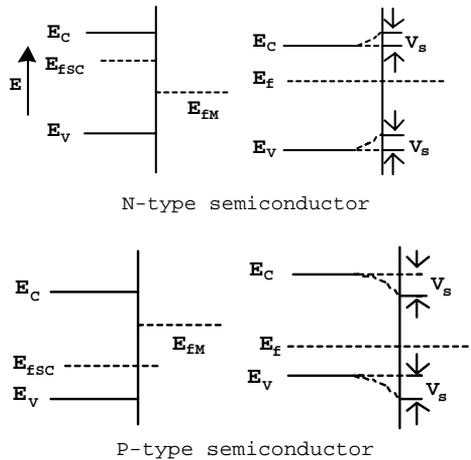


Fig. 1. Plots showing the formation of semiconductor surface band bending when a semiconductor contacts a metal (E_C : the bottom of conduction band; E_V : the top of valence band; E_F : the Fermi energy level; SC: semiconductor; M: metal; V_s : the surface barrier).

denoted as V_S , is produced, which indicates that the electronic energy band in the vicinity of the semiconductor surface gives birth to bending. The thickness of the SCR is usually of the order of $1-10^3$ nm, depending on the carrier density and dielectric constant of the semiconductor [7]. The SCR may usually be found in two different regimes: one is an electron depletion, at which the electron density greatly decreases because the surface state, an acceptor state, can capture electrons near the surface; the other is a hole depletion, at which the hole density greatly decreases because the surface state, donor state, can inject the electrons into the vicinity of the surface. Fig. 2 shows the effect of surface states on the semiconductor surface band bending and the space charge region. By definition, the lower the energy band, the higher the electrical potential, so that a positive V_S corresponds to down-bent bands. The V_S of a p-type semiconductor is positive, while that of n-type semiconductor is negative. Hence, the surface of n-type semiconductor has an upward-bent band, while the surface of p-type semiconductor has a downward-bent band [17].

2.2. The generation of SPV

The V_S , also called surface potential barrier, is measured in a SPV experiment. For a given set of semiconductor bulk and surface properties, the value of V_S is dictated by the charge conservation rule: $Q_{SS} = -Q_{SC}$, where Q_{SS} is the net surface charge and Q_{SC} is the net charge in the SCR (both per unit area). This is because the

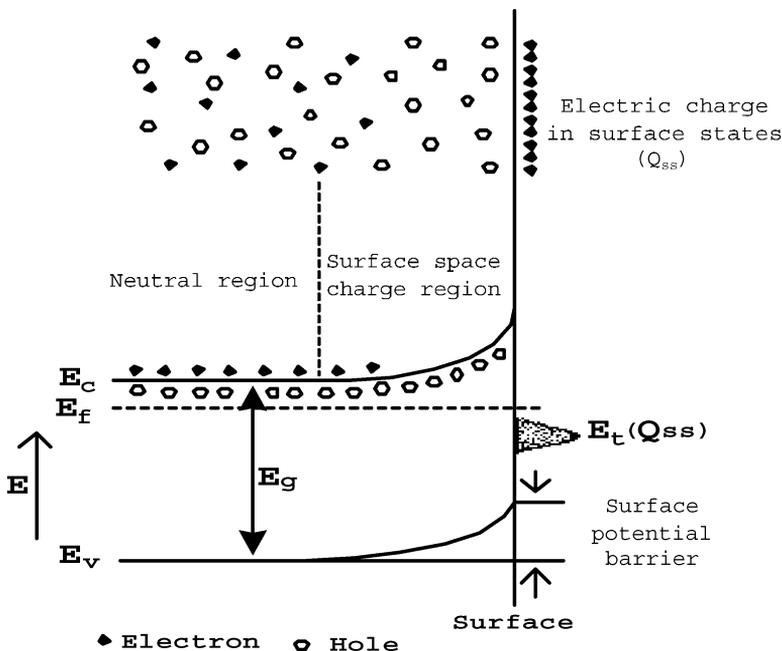


Fig. 2. Plots illustrating the effects of surface states on the semiconductor surface band bending and the space-charge region. (E_i : the energy level of surface state; Q_{SS} : the net surface charge).

semiconductor is the sole supplier of the surface charge. In other words, the V_S is mainly dependent on Q_{SS} or Q_{SC} , which may change, possibly very significantly, upon illumination.

After a semiconductor receives photons of appropriate energy, the absorbed photons induce the formation of free charge carriers by creating electron–hole pairs via band-to-band transitions in the vicinity of the surface and/or by releasing captured charge carriers at the surface states via trap-to-band transitions. Hence, a significant amount of charge may transfer in opposite directions under the built-in electric field (SCR) and/or diffuse from the surface to the bulk or from the bulk to the surface and/or redistribute within the surface or the bulk so that the net surface charge (Q_{SC}) changes. In other words, the surface potential barrier, V_S , changes. The difference (ΔV_S) between the surface potential barrier in the light and that in the dark is defined as the SPS signal.

In addition, an SPS signal may also result from a photochemical reaction, in which the incident illumination changes the surface or the bulk chemically. In particular, it may change the various trap densities at the surface states and hence alter the SPV by means other than by directly exciting charge carriers [34]. But there usually are two kinds of transitions of photo-excited electrons mainly contributing to the SPV, including super-bandgap transitions and sub-bandgap transitions, namely, band-to-band transitions and trap-to-band transitions.

Band-to-band transitions are the transitions by which electron–hole pairs are generated by promoting the electrons from the valence to the conduction if the semiconductor receives photons with energies greater than that of the material's bandgap, E_G . In general, the probability of band-to-band absorption is typically several orders of magnitude larger than that of trap-to-band absorption under super-bandgap illumination in a semiconductor so that the effects of the trap-to-band transitions on the SPS can be neglected [35]. Thus, only the effects of the band-to-band transitions on the SPS can be discussed here. In the case of an n-type semiconductor, the built-in electric field existing across the space charge region drives photo-generated holes toward the surface or interfacial region and electrons toward the interior of material or the bulk. The reverse process takes place at a p-type semiconductor, namely, the built-in electric field existing across the space charge region drives photo-generated electrons toward the surface or interfacial region and holes toward the interior of material or the bulk. Fig. 3 shows the effects of band-to-band transitions on the SPV responses of semiconductors. The transfer and separation processes of the charge carriers result in the redistribution of surface charges under illumination, which makes the net surface charges (Q_{SS}) and the surface band bending decrease, thus the SPV response (SPS) is generated.

Trap-to-band transitions are the transitions of photo-induced electrons that can take place if the semiconductor receives photons with energies lower than that of the material's bandgap, E_G . In principle, the dominant charge generation process here is the exchange of charge carriers between the semiconductor bands and surface states via optical excitation [17]. Although this transition cannot generate electron–hole pairs, it can create free electrons or holes, followed by the redistribution of surface charge so that the net surface charge (Q_{SS}) and the surface electric energy band

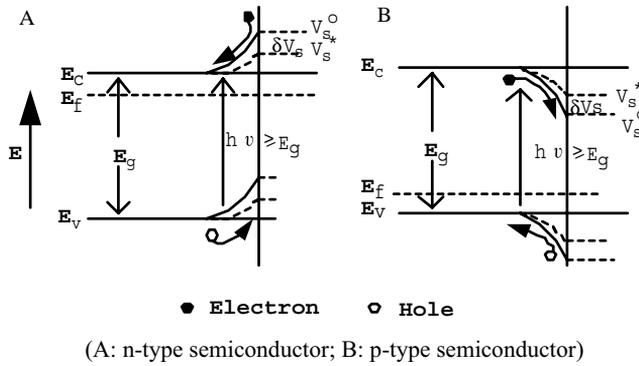


Fig. 3. Plots showing the effects of band-to-band transitions on the surface photovoltage responses of semiconductors. (V_S^0 : the surface barrier before illumination; V_S^* : the surface barrier after illumination).

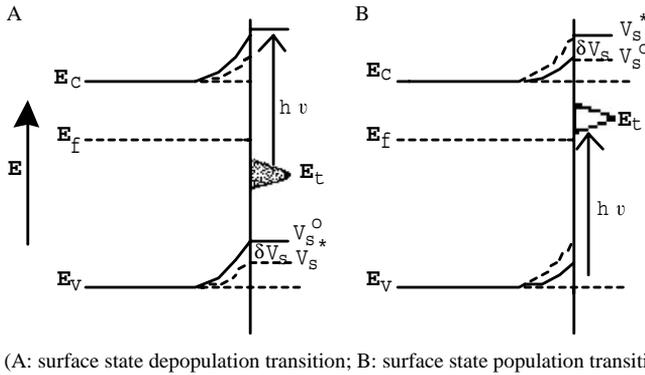


Fig. 4. The basic schematic diagram of the processes demonstrating the effects of the trap-to-band transitions on surface photovoltage responses in an n-type semiconductor. (V_S^0 : the surface barrier before illumination; V_S^* : the surface barrier after illumination).

bending change. Hence, this transition involving both surface states and bulk states may contribute to the SPS signal. Under sub-bandgap illumination, the probability of band-to-band absorption is essentially zero since the photons do not have sufficient energy for inducing such transitions. However, certain mechanisms do allow band-to-band transitions with sub-bandgap photon energies. One notable example is the Franz–Keldysh effect, in which sub-bandgap photons excite band-to-band transition in a sufficiently large electric field via photo-assisted tunneling [36]. The photon energy under such circumstances is typically close to E_G . In fact, this kind of band-to-band transition is usually negligible. Thus, only the effects of the trap-to-band transitions on the SPS are discussed here. For simplicity, it is assumed that the surface state only has one kind of energy level (E_t). In the case of an n-type semiconductor, the basic schematic diagram of the processes demonstrating the effects of trap-to-band transitions on its SPV response is shown in Fig. 4. In a

depleted n-type semiconductor, Q_{SS} is negative and Q_{SC} is positive. Illumination by photons with energy higher than the energy difference between the conduction band (E_C) and a trapped surface state (E_t) may promote electron transitions from the trapped surface state at the energy level E_t into the conduction band (E_C) (Fig. 4(a)), where the excited electrons are quickly swept to the semiconductor bulk under the built-in surface electric field. Thus, Q_{SS} becomes less negative and the surface space-charge region becomes less depleted. Therefore, this trap-to-band transition is also called the transition of surface state depopulation. It is accompanied by a decrease in the (absolute value of) band bending, which can contribute to the SPS signal [37]. Moreover, illumination by photons with energy higher than the energy difference between a trapped surface state (E_t) and the valence band (E_V) may promote electron transitions from the valence band (E_V) into the trapped surface state at the energy level (E_t) (Fig. 4(b)), which is equivalent to hole transitions from the surface state to the valence band. Naturally, this transition requires that the surface state in question be not completely filled prior to excitation. Such transitions can make Q_{SS} become more negative so that the surface barrier increases. Therefore, this trap-to-band transition is also called the transition of the surface state population accompanied by an increase in the (absolute value of) band bending, which can also contribute to the SPS signal. In general, band-to-band transitions usually tend to decrease the surface barrier. Thus, the effect of the transitions of the surface state population is dubbed the “photovoltage inversion” [38]. If the surface state depopulation and population transitions need the same energy, i.e., the energy difference between E_C and E_t is equal to that between E_t and E_V , the surface barrier may not change because of cooperation of the surface state depopulation and population transitions under sub-bandgap illumination. This effect of keeping the surface barrier stable is dubbed “photovoltage quenching” [37]. In fact, the effects of all kinds of trap-to-band transitions on the SPS are more complicated since there may be various surface states with different energy levels between the semiconductor bandgap. In addition, we can also discuss the effects of the trap-to-band transitions on the SPS of a p-type semiconductor by analogy with that of an n-type semiconductor.

3. The principle of the EFISP method

EFISPS is a technique that combines the electric field effect principle with the surface photovoltage spectra (SPS). With the aid of EFISPS, the transfer processes of photoinduced charge carriers can be examined clearly and the semiconductor SPS characteristics can also be interpreted in depth [33].

In general, the effects of an external electric field on a semiconductor mainly involve two conditions: one is that the electric field may influence the separation efficiency of the photoinduced charge carriers; the other is that the electric field may alter the barrier shape of a trap so that the captured charge carriers in the trap are easily released. Here, the effects of an external direct current electric field on the charge carriers and the SCR region of a semiconductor are discussed in detail.

As discussed above in detail, the basic process of semiconductor surface photovoltaic phenomena is that free charge carriers are formed by creating electron-hole pairs via band-to-band transitions and/or by releasing captured charge carriers via trap-to-band transitions after a semiconductor receives the photons of appropriate energy, followed by transfer in opposite directions under the built-in electric field (SCR) and/or diffusion in a certain direction within the surface or the bulk so that the net surface charge (Q_{SS}) changes, indicating that the SPS signal is generated. When an external direct current electric field is applied to the two sides of a semiconductor under illumination, it drives the photoinduced holes to transfer in the same direction as the added electric field because of the work of external force, while the photoinduced electrons are driven to migrate in the opposite direction, indicating that the mobile direction and diffusive distance of photoinduced charge carriers can be varied. However, the external electric field affects free and localized photogenerated carriers in different ways since the localized electric energy level have the ability to bind charges [33]. In addition, a certain amount of charge carriers that might have recombined can separate instead due to the polarization of the external electric field. In other words, the external electric field can promote the separation of the photoinduced charge carriers and hence influence the semiconductor surface photovoltaic effect by influencing the distribution of charge carriers. The effects of the external electric field on the semiconductor SPV can be demonstrated by the schematic diagram shown in Fig. 5. If a positive external electric field is applied to the two sides of a p-type semiconductor, the surface barrier can increase because the external electric field and the built-in electric field (SCR) act in the same direction, which can result in the enhancement of the SPS signal. On the contrary, if the positive external electric field is applied to the two sides of an n-type semiconductor, the surface barrier can decrease because the external electric field and the built-in electric field (SCR) act in the opposite direction, which can result in the decline of the SPS signal.

In the presence of an external electric field, the density of charge carriers in the vicinity of a semiconductor surface may change and deviate from its equilibrium value and result in a SCR. The surface may be in three different conditions: (a) accumulation region, where the majority carrier concentration at the surface is larger than its bulk value; (b) depletion region, where the majority carrier concentration at the surface is smaller than its equilibrium value, but larger than the minority carrier concentration at the surface; and (c) inversion region, where the majority carrier concentration at the surface is smaller than the minority carrier concentration at the surface. For simplicity, an ideal MOS structure with a flat energy band (Fig. 6(a)), consisting of a metal-oxide-semiconductor, is taken as a example for analyzing the effects of the external electric field on the surface space-charge region and surface band bending of a p-type semiconductor, whose schematic diagram is shown in Fig. 6. If a negative external electric field is applied to the metal electrode, it drives the majority carrier holes to migrate from the bulk to the surface so that a positive space charge region is formed, where the electric field exists across the bulk to the surface. Thus, the electric energy band in the vicinity of the semiconductor surface is upward-bent (Fig. 6(b)). In other words, the negative external electric field can result

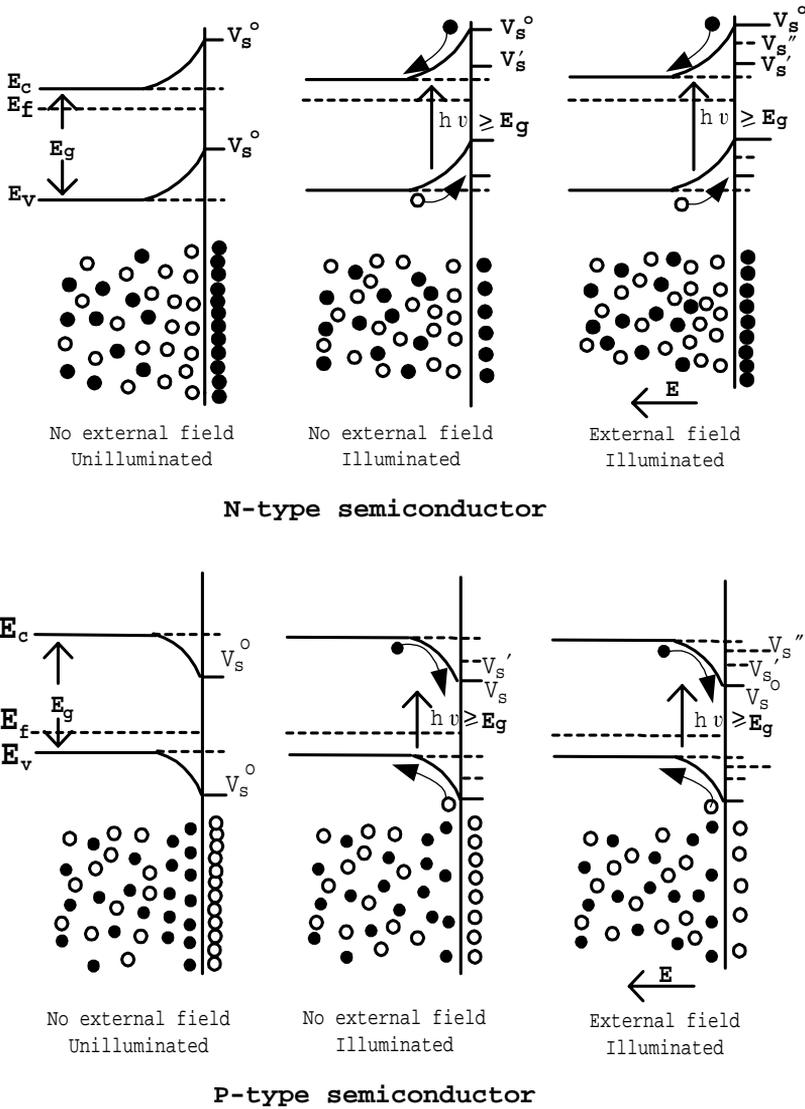


Fig. 5. Plots demonstrating the effects of the external electric field on the photo-induced carriers and SPV response.

in an increase of the concentration or an accumulation of the majority carriers in the vicinity of a p-type semiconductor surface so that an accumulation region is formed. On the contrary, if a positive external electric field is applied to the metal electrode, it drives the majority carrier holes to migrate from the surface to the bulk so that a negative space-charge region is formed, where the electric field exists across the surface to the bulk. Thus, the electric energy band in the vicinity of the surface is

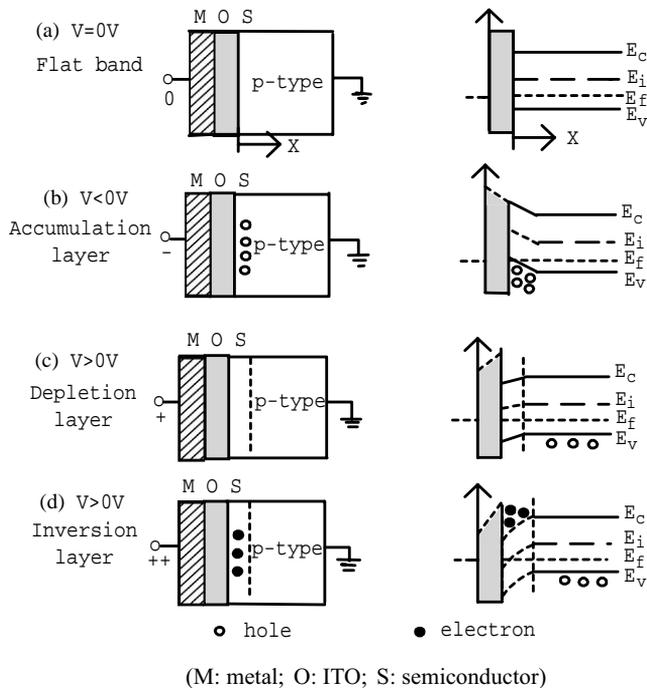


Fig. 6. The schematic diagram showing the effects of the external electric field on the surface space-charge region and surface band bending in a p-type semiconductor.

downward-bent (Fig. 6(c)). In other words, the positive external electric field can result in a decrease of the concentration or depletion of the majority carrier in the vicinity of a p-type semiconductor surface so that a depletion region is formed, where the concentration of the majority carrier at the surface is larger than that of the minority carrier. However, if the applied positive external electric field is large enough to make the concentration of the majority carrier greatly decrease so that the concentration of the majority carrier at the surface is smaller than that of the minority carrier, an inversion region is formed. Similar considerations also apply to n-type semiconductors.

4. The measurement of SPS and EFISPS

The SPS and EFISPS are measured using a photovoltage cell, mainly consisting of two ITO quartz glass electrodes [33, 39]. A schematic diagram of the photovoltage cell is shown in Fig. 7. For a semiconductor powder experiment, the powder sample is sandwiched between two ITO quartz glass electrodes. The difference between the surface potential barrier in the light and that in the dark is the SPS signal according to the principle of surface photovoltage as discussed above. In addition, for EFISPS,

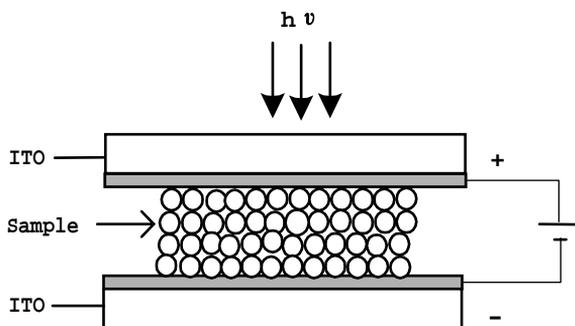


Fig. 7. The schematic diagram of the photovoltage cell structure for the measurement of SPS and EFISPS of powder sample.

an external bias is applied to the two sides of the sample and is regarded as positive when the side under illumination is connected to a positive electrode. When a direct current electric field is applied to the sample, the mobile direction and diffusive distance of photoinduced charge carriers can be varied, and the built-in electric field of the sample surface also changes. Hence, with the aid of an external electric field, the SPS technique can provide more information about the properties of the semiconductor surface.

5. The application of SPS and EFISPS

SPS is easily carried out, and is one of the most sensitive methods to examine the surface properties of a semiconductor. Hence, its application range is wider, mainly involving solar energy conversion and photocatalysis. In particular, SPS is combined with the external electric field to develop EFISPS technique, which can provide a more effective method for characterization of semiconductor properties. These properties mainly include the semiconductor bandgap energy and type and its surface or bulk states. Nano-sized semiconductors have found widespread applications as new functional materials because of their characteristic surface properties, and hence SPS of semiconductor nanoparticles and its application are emphasized, highlighting our work.

5.1. Bandgap energy and semiconductor type and surface states

The first application of SPS is the approximate determination of the semiconductor bandgap. In most semiconductors, there is a large increase in the absorption coefficient near the bandgap, E_G [17]. Therefore, a significant SPS signal increase is to be expected at approximately this energy. Such a simple E_G extraction is nothing more than an emulation of absorption spectroscopy. SPS is also regarded as a kind of spectrum because of its occurrence on the basis of the light absorption

Thus, in the case of semiconductor nanoparticles, their SPS can be used to monitor the well-known quantum size effect, which is explained by quantum mechanical molecular orbital calculations [40], accounting for the well established blue shift in the absorption spectra with decreasing particle size [41]. We recently characterized the ZnO [42] and TiO₂ [12] powder samples with different particle sizes using the technique of SPS. The ZnO SPS is shown in Fig. 8. The sizes of ZnO samples a–d are 12.2, 17.9, 25.3 and 200 nm, respectively. According to the energy band structure of ZnO, the strong SPS response can be attributed to the electron transition from valence band to conduction band of ZnO (O_{2p} Zn_{3d}) [43]. In Fig. 8(d), a clear onset of the SPS signal at the wavelength of 390 nm is found, this onset is in very good agreement with the bandgap of bulk ZnO [44]. It can also be seen that the SPS of the samples a–c show a large deviation from that of the commercial ZnO sample (d). In other words, the SPS of the samples a–c shift to the blue, which demonstrates that the nano-sized ZnO particles present an obvious quantum size effect. Similar results can also be obtained from the SPS of TiO₂ samples [12]. Fig. 9 shows the EFISPS of ZnO nanoparticles (a) described in detail in another paper. The remarkable changes of SPS response of ZnO nanoparticles can be found if an external electric field is applied from Fig. 9, which indicates that the higher the positive external electric field, the weaker the photovoltage. On the contrary, if an opposite external electric field is employed, the response becomes more intense, which are common characteristics of n-type semiconductors. When the experiment is under a negative bias, the SPS response mainly exhibits two obvious features. One is the increase of SPS response, which can be explained that the direction of external electric field added is the same as that of built-in electric field of the ZnO nanoparticles. The other is that the strong SPS response is broadened, which is attributed to the trap-to-band transitions [33]. The electron-trapped surface states may arise from surface oxygen vacancies and hydroxyl [45] since the existence of abundant surface oxygen vacancies and hydroxyl on the surfaces of ZnO nanoparticles has been proved [42,46]. Hence, the SPS response behaviors under different external electric fields suggest that the transport

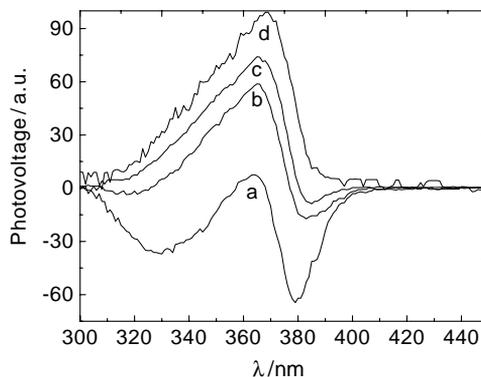


Fig. 8. The SPS responses of a commercial ZnO sample (d:200 nm) and ZnO nanoparticles calcined at 320°C (a:12.2 nm), 430°C (b:17.9 nm) and 550°C (c:25.3 nm).

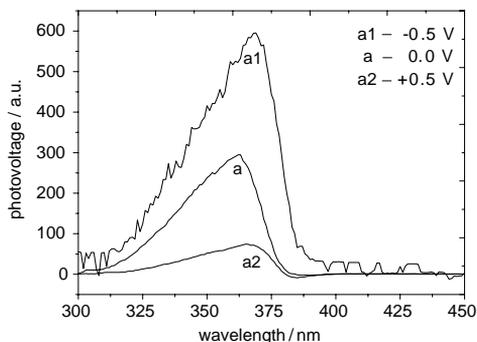


Fig. 9. The EFISPS of ZnO nanoparticle calcined at 320°C(a) (a: 0 V; a1: -0.5 V and a2: 0.5 V external electric field).

directions of carriers can be modified by the external electric field as well as the localized surface states resulting from the existence of surface oxygen deficiencies and hydroxyl.

5.2. Photocatalysis

The SPS technique can be used as an effective method to evaluate the activity of the researched samples in the fields of photocatalysis and photoelectrochemistry since it can provide lots of information about semiconductor surface properties such as the separation and recombination and transport of photoinduced charge carriers under illumination

Compared with the bulk or large particles of a semiconductor, the mechanism of the SPS generation in a nanosized semiconductor is quite different [25]. In conventional photocatalysis or photoelectrochemistry employing single-crystal or polycrystalline materials with larger size, the separation of photoinduced charge carriers is mainly facilitated by the built-in electric field (surface space-charge region). The potential gradient promotes the flow of electrons and holes in the opposite direction so that the surface net charge (Q_{SS}) changes significantly. Hence, the SPS signal of conventional semiconductor particles is strong. For a nanosized semiconductor particle, however, the diameter of individual nanoparticle is too small to permit the space-charge region, and the formed space-charge region can be neglected [47,48]. In other words, the surface band bending at nanoparticle surface is absent or small, as illustrated in Fig. 10. Thus, the charge separation and transport in the nanoparticle do not depend on the built-in electric field, but are mainly determined by carrier diffusion in the same direction so that Q_{SS} does not change by much. Therefore, the SPS signal of a semiconductor nanoparticle is weak. Fig. 8 shows that the smaller its size is, the weaker the SPS signal of ZnO nanoparticles is.

In addition, the transport time for charge carriers to reach the surface from the interior can be estimated by the carrier diffusion equation. For large TiO_2 particle of 1 μm , the electron transport time is 100 ns, while for TiO_2 nanoparticles of 10 nm, the

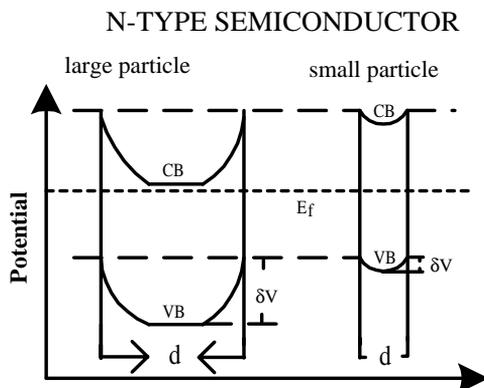


Fig. 10. Plots illustrating the formation of a space-charge region and surface band bending in a large and small semiconductor particle. (d : diameter of semiconductor particle).

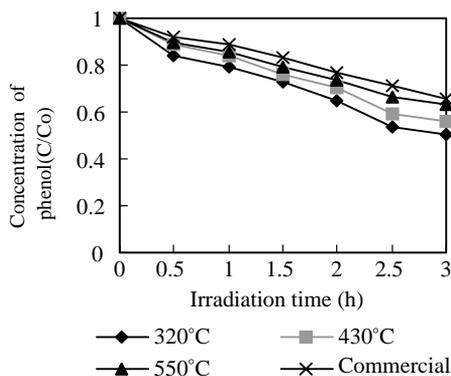


Fig. 11. The curves of photocatalytic degradation of phenol on a commercial ZnO sample (d) and ZnO nanoparticles calcined at 320°C (a), 430°C (b) and 550°C (c).

electron transport time is 10 ps [48,49]. In other words, the smaller the particle size is, the shorter the electron transport time [50]. In general, the recombination time is estimated to be a few nanoseconds [9,51]. Hence, the separation efficiency of photoinduced carriers is very high for semiconductor nanoparticles, so that the activity of semiconductor nanoparticles may be higher than that of conventional semiconductor particle, that is to say, the smaller the size of semiconductor particle is, the higher the photocatalytic activity may be. Fig. 11 shows the photocatalytic activity of ZnO samples in the experiment of photocatalytic degradation of phenol recently described [42]. The activity of ZnO nanoparticles is higher than that of the commercial sample, although the activity decreases with increasing particle size. For TiO₂ samples, the same result can also be obtained [12]. Thus, the results of the SPS

and the photocatalytic activity of ZnO and TiO₂ samples with different size discussed above indicate that they have an intrinsic relationship, i.e., the weaker the SPS signal is, the higher the photocatalytic activity is.

In addition, the rate of O₂ reduction forming O₂⁻ by electron captures in preventing carrier recombination during photocatalytic processes utilizing semiconductor particles is of importance since O₂⁻ formation may be the slowest step in the reaction sequence in the oxidation of organic molecules by OH radicals or directly by positive holes [52]. Cluster deposition of noble metals such as Pt, Pd and Ag on semiconductor surface has been demonstrated to accelerate O₂⁻ formation because the noble metal clusters of appropriate amount or size can effectively trap the photoinduced electrons [13–16]. This is considered as an effective method of semiconductor surface modification to improve the separation efficiency of photoinduced electron and hole pairs.

The SPS response can also be affected by cluster deposition of noble metals in that the clusters can influence the separation efficiency of photoinduced carriers. Fig. 12 shows the SPS spectra of ZnO nanoparticles and Pd/ZnO and Ag/ZnO composite nanoparticles with the noble metal contents of 0.5 and 0.75 wt% described in detail in another paper. It can be found that the SPS response of ZnO nanoparticles becomes much weaker after the noble metal Pd or Ag is deposited on their surfaces, which may result from the noble metal clusters with appropriate amount effectively trapping photoinduced electrons. However, when the amount or size of the noble metal clusters become too large, the advantages of metallic deposition are lost and these sites begin to function as recombination centers [53,54]. For example, the SPS response of Pd/ZnO composite nanoparticles with a Pd content of 0.5 wt% was weaker than that of 0.75 wt%, which may demonstrate the Pd content of 0.75 wt% is excess, while the SPS response of Ag/ZnO composite nanoparticles with the Ag content of 0.5 wt% was stronger than that of 0.75 wt%, which may demonstrate the Ag content of 0.75 wt% is also appropriate. The above discussion indicates that the

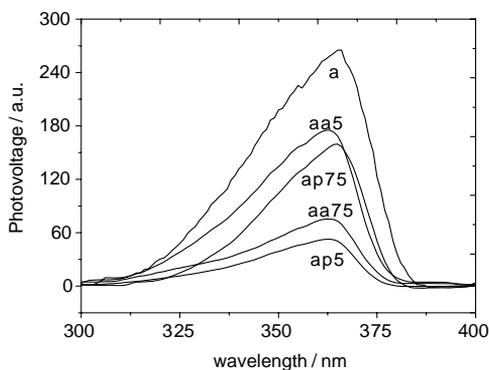


Fig. 12. The SPS responses of ZnO nanoparticle (a) and Pd/ZnO and Ag/ZnO composite nanoparticles with the noble metal contents of 0.5 and 0.75 wt%. (ap5: Pd content of 0.5 wt%; ap75: Pd content of 0.75 wt%; aa5: Ag content of 0.5 wt%; aa75: Ag content of 0.75 wt%).

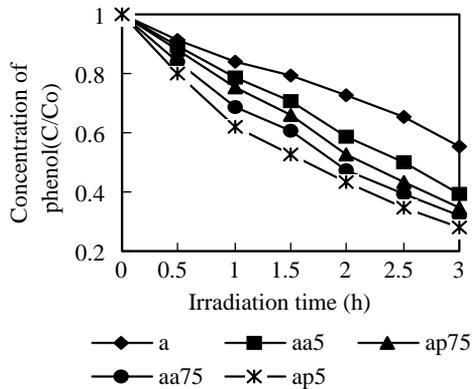


Fig. 13. The curves of photocatalytic degradation of phenol on ZnO nanoparticleS (a) and Pd/ZnO and Ag/ZnO composite nanoparticle S with the noble metal contents of 0.5 and 0.75 wt% (ap5: Pd content of 0.5 wt%; ap75: Pd content of 0.75 wt%; aa5: Ag content of 0.5 wt%; aa75: Ag content of 0.75 wt%).

noble metal can greatly affect the SPS response of ZnO nanoparticles by influencing the separation of photoinduced electron and hole pairs. In other words, the SPS responses can reflect the separation efficiency of photoinduced carriers. The weaker the SPS is, the higher the separation efficiency. Thus, we can also primarily evaluate the photocatalytic activity of noble metal/semiconductor composite nanoparticles by their SPS measurements. Fig 13 shows the photocatalytic activity of Pd/ZnO and Ag/ZnO composite nanoparticles and ZnO nanoparticles in the experiment of photocatalytic degradation of phenol, reflecting the order of their photocatalytic activity as following: Pd (0.5 wt%) > Ag(0.75 wt%) > Pd(0.75 wt%) > Ag (0.5 wt%) > pure ZnO nanoparticles. This order corresponds to the result of SPS characterization.

6. Conclusions

In this review, the basic principles, measurement and applications of SPS and EFISPS are mainly discussed together with some fundamental aspects like the electric properties of semiconductor surfaces and the principle of electric field effect. In particular, the applications of SPS to nano-sized semiconductors such as ZnO and TiO₂ in heterogeneous photocatalysis are emphasized, which involve mainly evaluating the photocatalytic activity by analyzing semiconductor surface properties such as the separation efficiency of photoinduced carriers under illumination by the SPS measurement, highlighting our own contributions. The results show that SPS can be an effective method for quickly evaluating the photocatalytic activity of nanosized semiconductor materials, i.e., the weaker the SPV signal, the higher the photocatalytic activity.

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