

Recent advances in solar cells and photo-electrochemical water splitting by scanning electrochemical microscopy

Xiaofan ZHANG (✉)^{1,2}, Man LIU¹, Weiqian KONG¹, Hongbo FAN²

¹ Henan Provincial Key Laboratory of Nanocomposite and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou 450006, China

² School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China

© Higher Education Press and Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract Investigation on the mechanism and kinetics of charge transfer at semiconductor/electrolyte interface is significant for improving the photoelectric conversion efficiency and developing novel and high-efficiency photovoltaic devices. Scanning electrochemical microscopy (SECM), as a powerful analytical technique, has a potential advantage of high spatial and temporal resolution. It has been expanded into a broad range of research fields since the first inception of SECM in 1989 by Bard groups, which includes biological, enzymes, corrosion, energy conversion and storage (such as solar cells, hydrogen and battery). Herein, we review the basic principles and the development of SECM, and chiefly introduce the recent advances of SECM investigation in photoelectrochemical (PEC) cells including solar cells and PEC water splitting. These advances include rapid screening of photocatalysts/photoelectrodes, interfacial reaction kinetics and quantitation of reaction intermediates, which is significant for evaluating the performance, choosing catalysts and developing novel composite photoanodes and high efficiency devices. Finally, we briefly describe the development trends of SECM in energy research.

Keywords scanning electrochemical microscopy (SECM), solar cells, photoelectrochemical (PEC) water splitting, screening, kinetics, intermediates

1 Introduction

Developing of a long-term, sustainable energy economy is one of the most important technical issues facing humanity

[1]. Solar energy is abundant (90 PW), inexhaustible and fairly well distributed over the planet [2]. Solar energy can be converted into usable energy via photoelectrochemical (PEC) cells which can be divided into two categories: regenerative solar cells and photosynthetic cells (e.g., hydrogen) [3]. Regenerative solar cells (e.g., dye-sensitized solar cells (DSSCs), perovskite solar cells (PSCs) and organic solar cells) can convert solar energy to electricity. Photosynthetic cells such as hydrogen can be obtained through PEC water splitting approach, which has been widely investigated since the first demonstration in 1972 by Fujishima and Honda [4]. For these devices, the semiconductor/electrolyte interface (SEI) investigation plays a vital role in improving charge carrier separation, transport and recombination pathways. Up to date, some *in situ* techniques have been developed to probe the dynamics of SEI reactions on the surface of electrodes or solar cells devices, such as photoelectrochemical impedance spectroscopy (PEIS) [5–7], intensity modulated photocurrent or photo-voltage spectroscopy (IMPS/IMVS) [8], transient absorption spectroscopy (TAS) [9,10], scanning-probe measurement (SPM) [11] and synchrotron-based X-ray techniques [12], and so on. Cen et al. reviewed the *in situ* techniques for PEC water splitting and summarized the advantages and limitations of these techniques [13]. Among them, SPM techniques, using a probe to scan the surface of samples, can provide the information of the interactions between the probe and the surface of samples, although they exhibit limited temporal resolution [14]. Thus the SPM techniques such as atomic force microscopy (AFM), scanning tunneling microscopy (STM) can be utilized to characterize different surface properties of the samples [15–18]. And the most popular SPM techniques for *in situ* PEC studies are scanning photocurrent microscopy (SPCM) [19] and scanning electrochemical microscopy (SECM) [20]. Among them, SECM overcomes many typical problems, for example the effects of

Received July 11, 2018; accepted September 20, 2018

E-mail: xiaofanzhang@aliyun.com

Special Issue—Energy Optoelectronics

the resistive potential drop in solution (iR drop), and charging current. SECM is a “non-contact” scanning probe technique, which can provide chemical and/or topographic information about surfaces immersed in a solution. Therefore, SECM cannot only analyze the local chemical and PEC activity of sample surface, but also can be utilized to investigate the surface reaction intermediates and its kinetics as well as screen the active center. Hence, analytical measurements can be performed in the interfacial region. Besides, the researchers have also integrated SECM with alternating current (AC) impedance spectroscopy [21], atomic force microscopy (AFM) [22] and scanning ion-conductance microscope (SICM) [23] to investigate different properties.

In this review, we will describe the basic principle and the development of SECM, and chiefly introduce the recent advances in solar cells and PEC water splitting based on the different operation modes of SECM.

2 Basic principles of scanning electrochemical microscopy (SECM)

2.1 Instrument constitutes

SECM is based on these changes of the faradaic current when the SECM tip is moved across the surface of a sample, which is useful in obtaining topographic and surface reaction kinetic information. Figure 1 shows the typical structure of SECM equipment which includes six components (bipotentiostat, piezoelectric controller or positioning system, probe, electrolytic cell, substrate and computer). Among them, the bipotentiostat is used to precisely measure and control the current and potential of the probe and substrate (or the test samples). A high resolution three-dimensional positioning system is con-

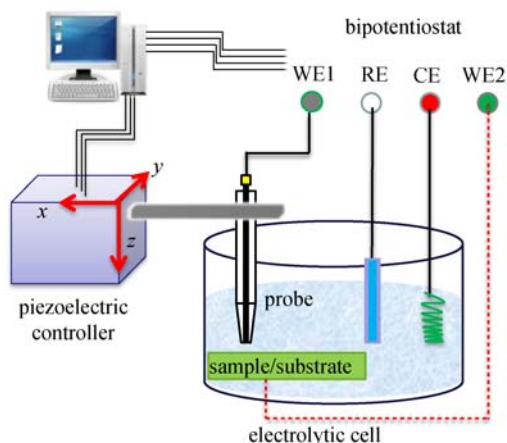


Fig. 1 Simple schematic of a SECM instrument (WE: working electrode, RE: reference electrode, CE: counter electrode)

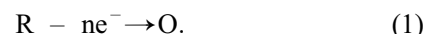
trolled by piezoelectric controller, which allows for accurate movement of the probe and sample using x , y , z stages. Another very important component is the probe or SECM tip (e.g., ultra-microelectrode (UME)), which can offer high mass transport rates, low ohmic effects, low double layer charging [24,25]. UME is optimal for many applications from kinetics measurements to electrochemical imaging. Furthermore, the electrolyte cell provides the reaction site, where the substrate is placed.

2.2 Working modes of scanning electrochemical microscopy (SECM)

SECM measurements can be performed using different working modes. After the first report on SECM in 1989 which introduced feedback and generation/collection (G/C) modes [26,27], a variety of new operation modes have been developed in order to expand its application, such as surface interrogation mode, ion transfer feedback mode, potentiometric detection mode, constant current mode, reverse imaging mode, redox competition mode and direct mode, and so on [28]. Among them, the feedback mode, G/C and surface interrogation (SI) modes are widely used in the fields of PEC cells to study the imaging and interfacial kinetics.

2.2.1 Feedback mode

SECM in feedback mode shows the great advantages in detecting active sites of the surface. In general, the SECM experiment is performed under four-electrode system, in which SECM tip usually serves as one of the dual working electrodes, and the substrate acts as the other one. These electrodes are all immersed in the solution containing redox mediators. The basic principle of the feedback mode is shown in Fig. 2. When the positive potential is applied to the SECM tip, the mediators will take place an oxidation reaction as the following Eq. (1),



Here, R and O represent a reduced and oxidized species in the solution, respectively. On the contrary, a reduction reaction will occur when the negative potential is applied. When the tip is far from the substrate, the steady-state current ($i_{T,\infty}$) can be given from Eq. (2),

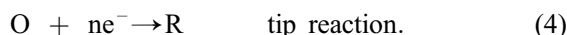
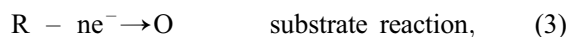
$$i_{T,\infty} = 4nDFca\beta, \quad (2)$$

where n is the number of the electrons of electrode, F is the Faraday constant ($96485 \text{ A}\cdot\text{s}\cdot\text{mol}^{-1}$), D is the diffusion coefficient, c is the concentration of the reactant, a is the radius of the UME tip, and β is a geometric co-efficient [28]. When the tip is close to a conductive substrate or electrochemical active species substrate, the oxidized species formed in reaction (1) diffuse to the substrate and can be reduced back to R (Fig. 2(a)). In this condition, the

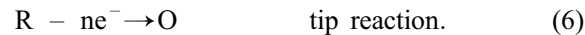
flux of R to the tip is increased, and $i_T > i_{T,\infty}$. This phenomenon is termed “positive feedback” (Fig. 2(c)). On the other hand, if the substrate surface is an insulator, the electron cannot recycle in the redox reaction ($i_T < i_{T,\infty}$, Fig. 2(b)), that is to say, “negative feedback” appears (Fig. 2(d)). If a steady-state is established, the normalized current becomes independent of the ratio of diffusion coefficients and depends only on the tip/substrate distance (d). Moreover, larger i_T is obtained when the d value is smaller. And the approach curve can be presented in form of $i_T/i_{T,\infty}$ vs. L (here $L = d/a$, and d is the distance between the tip and the substrate), which provides information on the kinetics of the process at the substrate.

2.2.2 Generation/collection (G/C) mode

The generation/collection mode includes the substrate generation/tip collection (SG/TC) and tip generation/substrate collection (TG/SC) mode. In these modes, both SECM tip and substrate are working electrodes, and one generates some species which can be collected by the other [28]. In SG/TC mode, the electro-active species are generated at substrate and collected by SECM tip according to the following Eqs. (3) and (4),



However, the reaction occurs in TG/SC mode is counter to SG/TC mode, as exhibited in Eqs. (5) and (6),



Typically, SG/TC mode is used for the measurements of concentration profiles or chemical flux from a substrate. And the TG/SC mode is predominantly used to study reaction kinetics or perform modifications to the substrate.

2.2.3 Surface interrogation (SI) mode

The surface interrogation mode of scanning electrochemical microscopy (SI-SECM) is a new *in situ* electrochemical technique based on SECM operating in a transient feedback mode [29], which is developed by Bard and coworkers [28] and can be used to analyze, detect and quantify the adsorbed surface species on the electrode. The SI-SECM mode consists of a specific application of the feedback mode under transient conditions that allows for the quantification of finite amounts of reacting species on the surface of substrate. Different from the feedback mode, the reactive species (A) are adsorbed at the substrate electrode in SI-SECM mode [28,30]. Figure 3 illustrates the schematic of the mechanism of the surface interrogation mode. First, the substrate is pulsed or scanned to a potential where oxidation occurs and an adsorbed species A is formed. At this time, the tip is kept at open circuit (OC), and the solution only contains the initial mediators in oxidized states (O) (Fig. 3(a)). Figure 3(b) shows the substrate is taken to OC and the tip is pulsed and reduces O to R. Then O can be regenerated via the diffused R reacting

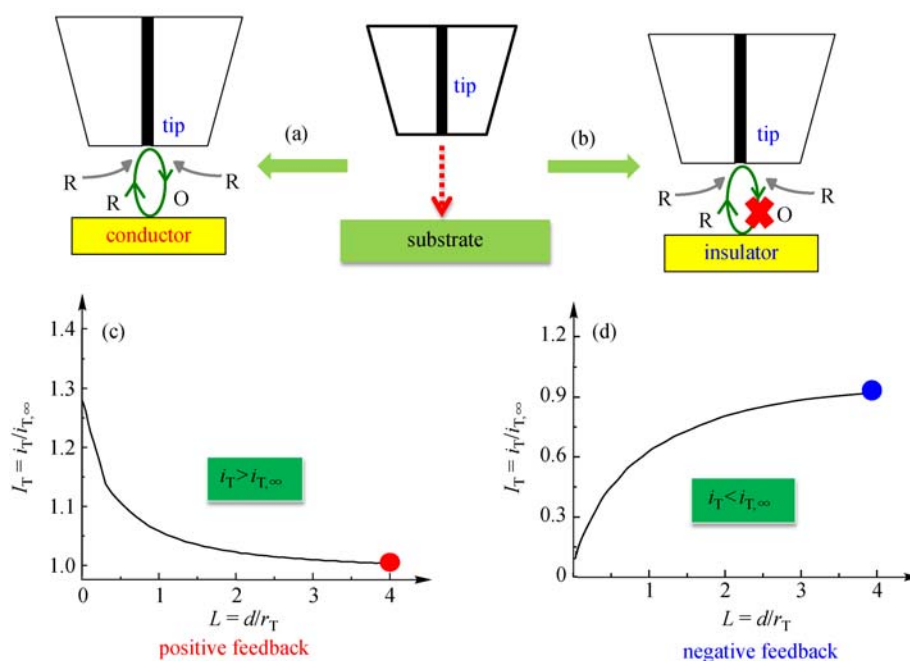


Fig. 2 Basic principle of the feedback mode

with adsorbed species A which is consumed and transferred to final product P. Ideally, regeneration of O should only be obtained through reaction with A. Figure 3(c) exhibits the final state of the system, which shows that all A is depleted and O reacts at the tip at the rate governed by the hindered diffusion into the tip-substrate gap. In summary, the SI mode acts as a transient feedback mode, in which a SECM tip is used to generate a titrant R which can react with A to regenerate O, producing positive feedback. Finally, a negative feedback can be detected as A is depleted from the surface.

Based on these different operation modes, many excellent works have been carried out in various fields such as solar cells, water splitting and battery as listed in Table 1.

3 Application of scanning electrochemical microscopy (SECM)

Since the first introduction in the 1990s, SECM has been widely used to characterize hydrogen oxidation reaction (HER), oxygen evolution reaction (OER), and CO₂ reduction via electrochemical or PEC technologies [50–52]. As the hot topic, application of SECM in solar cells and PEC water splitting has attracted more attention for researchers described as follows.

3.1 Nanostructured solar cells

With the development of PEC technology, more and more new technology is applied to solve relevant scientific

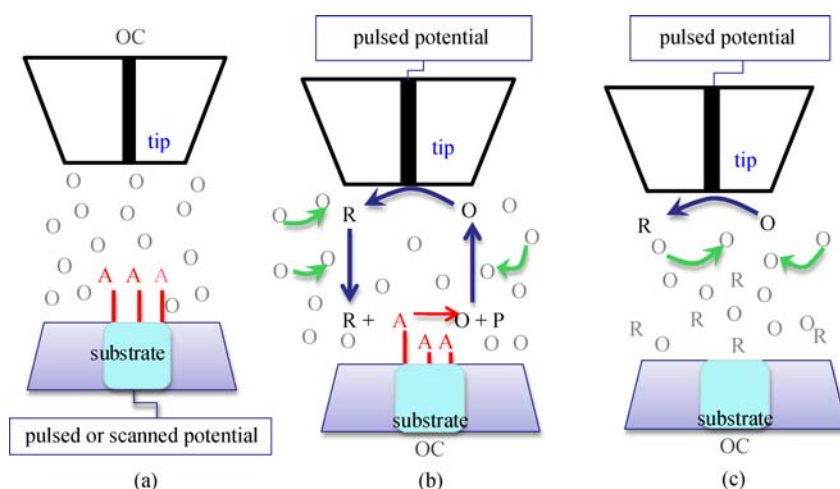


Fig. 3 Schematic diagram of mechanism for the surface interrogation (SI) mode [31,32] (OC is denoted as open circuit)

Table 1 Application of SECM based on the above modes

applications	measurement	mode	Refs.
dye-sensitized solar cells	dye regeneration kinetics	feedback mode	[33–35]
dye-sensitized solar cells	imaging	feedback and SG/TC mode	[36]
perovskite solar cells	kinetics	feedback mode	[37]
oxygen reduction reaction	detect hydrogen peroxide	TG/SC mode	[38]
hydrogen evolution reaction	kinetics	SG/TC mode	[39]
formic acid oxidation	electrocatalytic activity	TG/SC mode	[40]
oxygen reduction reaction	mechanism	SG/TC mode	[41]
Li-ion batteries	Li-ion intercalation	SG/TC mode	[42,43]
supercapacitor	charge transfer kinetics	feedback mode	[44]
corrosion	localized corrosion	TG/SC mode	[45]
photoelectrochemical	kinetics	SI-SECM mode	[46]
photocatalysis	screening	TG/SC mode	[31,47]
electroreduction of CO ₂	CO ₂ reduction	SG/TC mode	[32]
hydrogen evolution reaction	kinetics	feedback mode	[48]
decomposition of formic acid	quantification of adsorbed hydrogen	SI-SECM mode	[49]

problem. Charge transfer process in solar cells is a field worthy of extensive study topic, which includes the regeneration process of the photosensitizers, photoelectric catalyst, and the transfer behavior of photo-generated electron and hole pairs at the interface of photoelectrode/electrolyte. These processes are the necessary steps for generating photocurrent, and play an essential role in improving the photoelectric conversion efficiency of device. Due to the reaction occurring in the PEC interface is a fast charge transfer process, some conventional research methods cannot be able to monitor real time information under working condition. Attributed to the high time and spatial resolution, and sensitivity, SECM is very suitable to detect the trace change of electrochemical active material or chemical group located at the micro-region, which has been proven to be an effective method and plays unique role in studying the interfacial charge transfer kinetics of solar cells.

3.1.1 Dye-sensitized solar cells (DSSCs)

SECM acting as an elegant tool was used to directly determine the mobility of charge carriers and diffusion constant within dye-sensitized nanostructured semiconductors in 2006 [53]. Hence the PEC parameters including conductivity under illumination or heterogeneous kinetics could be obtained by means of SECM. In the field of DSSCs, SECM has been used to investigate the dye regeneration and charge transfer kinetics in the interface of dye/electrode. For example, Wittstock group developed a series of study on dye regeneration kinetics based on the feedback mode of SECM, and distinguished the luminous region using G/C mode, including D149 sensitized ZnO and N719 sensitized TiO₂ solar cells [54–56]. Similarly, Martin group investigated the charge transfer kinetics constants of N719 and N749 sensitized TiO₂ solar cells using SECM [35]. Shen group from Huazhong University of Science and Technology has also developed much valuable research since the first collaboration with Wittstock group [57], in which the charge transfer kinetics between I⁻ and Eosin Y⁺ dye adsorbed on ZnO was first investigated and demonstrated the viability of SECM for understanding DSSCs under working conditions. Later, they extended SECM to investigate the dye-regeneration process based on feedback mode [30,34,58], and dye regeneration process with different mediator concentrations and light intensities. First, they investigated the reaction kinetics of n-type dye sensitized solar cells and studied the influence of redox shuttles [Co(bpy)₃]³⁺/[Co(bpy)₃]²⁺, I₃⁻/I⁻ on the dye regeneration kinetics of C106TBA and LD14. This work interpreted the essential rule for the effects of PEC reaction kinetics on the n-type photovoltaic device properties [48]. Furthermore, they also investigated the reaction kinetics at the photo-cathode/electrolyte interface of p-type devices. They studied the

influence of redox shuttles T₂/T⁻, I₃⁻/I⁻ on the dye regeneration kinetics of P1 [59]. Both these works investigated the back transfer ability of the photo-generated electrons at photo-anode/electrolyte interface with different redox electrolyte, which was very helpful for assessing the interfacial recombination behavior of the photogenerated charges. Taking n-type TiO₂ and p-type CuCrO₂ for an example, Fig. 4 showed the basic principle of SECM and the reaction mechanism of different types DSSCs under short-circuit condition. The photoanodes (for example TiO₂/C 106TBA and TiO₂/LD 14) were placed in the presence of the oxidized species of redox couple and the photocathode (CuCrO₂/P1) with reduced species of redox couple. As shown in Fig. 4(a), under illumination, dye generated hole/electron pairs after absorbed the incident light. Then the holes (D⁺/TiO₂) reacted with redox species Co²⁺ regenerated dye (D/TiO₂) accompanied by the production of Co³⁺ which could be detected by the UME. Finally, Co²⁺ species was regenerated by given potentials relative to Co²⁺/Co³⁺. Therefore, the SECM feedback approach curves can be obtained and fitted, which could relate the tip current to the surface's heterogeneous electron or hole transfer kinetics and eventually obtained the normalized apparent charge-transfer constant (κ). To determine the apparent standard hetero-generous rate constant k^0 , the effective rate constant (k_{eff}) values were plotted in Fig. 4(c) as a function of the corresponding over-potential (η , where $\eta = E_{\text{substrate}} - E_{\text{redox,solution}}^{1/2}$). For p-type (CuCrO₂/P1) DSSCs, the mechanism was similar as illustrated in Fig. 4(b) and the apparent standard hetero-generous rate constant k^0 also could be given from Fig. 4(c). It was observed that k^0 for fluorine-doped tin oxide (FTO)/TiO₂ was slower in electrolyte I₃⁻/I⁻ than that of Co³⁺/Co²⁺, and the hole transfer kinetics constant k^0 for FTO/CuCrO₂ in the case of T₂/T⁻ was slower than that of I₃⁻/I⁻. Further comparison showed the recombination rate constant in p-type DSSCs was much higher than n-type devices, and the interfacial charge recombination kinetics constant were much smaller than the dye-regeneration kinetic constants. This ensures effective charge collection in the DSSC devices. These works may offer some new complementing aspects to establish methods for DSSCs.

3.1.2 Quantum dots sensitized solar cells

Except for DSSCs, inorganic semiconductor quantum dots (QDs) have attracted more interest due to their unique optoelectronic properties derived from the quantum confinement effect. Many narrow band gap QDs (such as CdS, PbS/CdS, CdSe/CdTe and CuInS₂) are suitable for sensitized solar cells (QDSSCs) because they can transfer electrons to large band gap semiconductors in order to further increase the charge separation and transfer efficiencies. Compared to DSSCs, the efficiency of

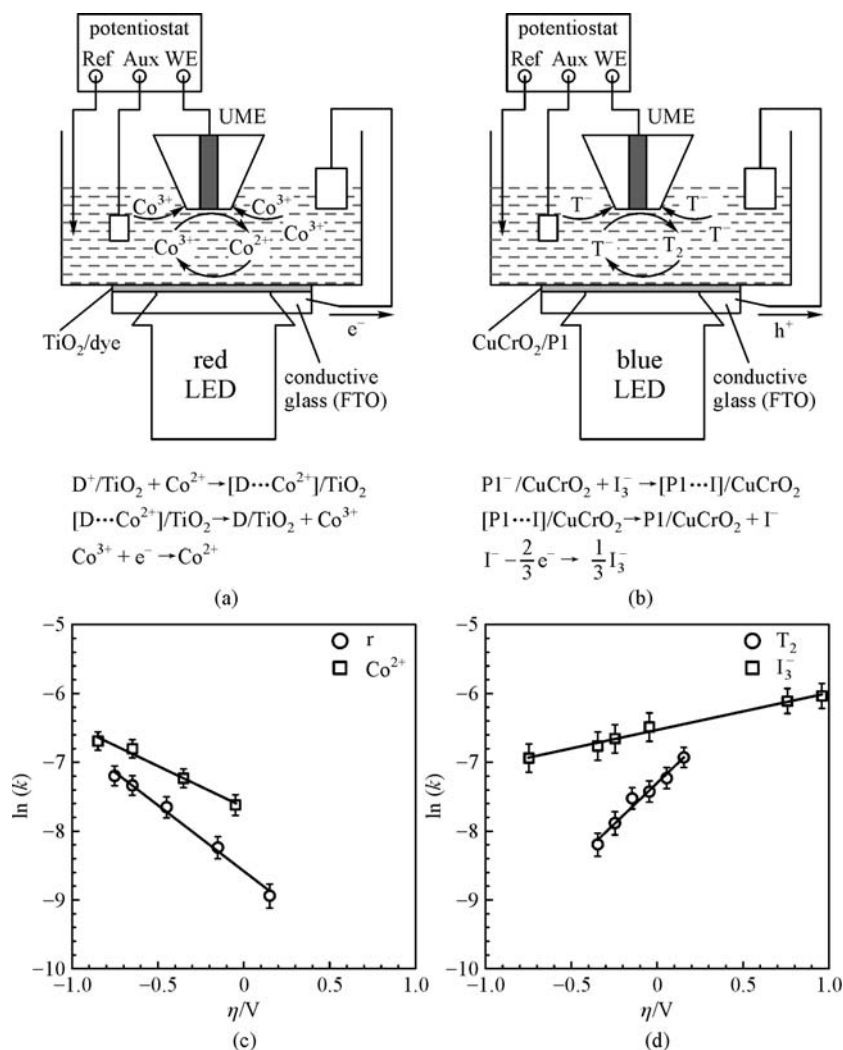


Fig. 4 Basic arrangement for probing the heterogeneous reaction at the (a) n-type dye-sensitized semiconductor (TiO_2) and (b) p-type dye-sensitized semiconductor (CuCrO_2) interface in the feedback mode of SECM under short-circuit conditions. The mediator couple is $\text{Co}^{3+}/\text{Co}^{2+}$ and T_2/T^- , respectively (Ref: reference electrode, Aux: auxiliary electrode, WE-1: working electrode 1, WE-2: working electrode 2). Plot of $\ln(k_{\text{eff}})$ vs. η for (a) FTO/ TiO_2 electrodes in acetonitrile corresponding to the reduction with Γ^- and Co^{2+} and for (b) FTO/ CuCrO_2 electrodes in acetonitrile corresponding to the oxidation with T_2 and I_3^- [59]. Copyright © 2014, John Wiley and Sons

QDSSCs is still very low. Up to now, the main factor restricting the improvement efficiency of QDSSCs is the hole-transfer process namely the regeneration process of QDs sensitizers which depends on the selection of redox electrolytes. Therefore, the investigation of the QDs regeneration process will be significant for improving the efficiency of such devices. Some novel technologies (such as nanosecond laser transient absorption spectroscopy (TAS)) have been used to measure the rate of quantum dots regeneration. In contrast to TAS, SECM is suitable to monitor the fast electron/hole transfer process in devices in working devices. So Shen group employed SECM to scrutinize the influence of redox couples (T_2/T^- , $[\text{Co}(\text{bpy})_3]^{3+}/[\text{Co}(\text{bpy})_3]^{2+}$, I_3^-/I^-) on the quantum dots regeneration rate (CdSe and CdS) [33]. The measurement is also based on monitoring the feedback current, which is

related to the small change in the concentration of the redox shuttle under the active area of UME probe caused by QDs regeneration. The results revealed that the kinetics of QDs regeneration depends on the nature of the QDs and the redox shuttles presented in QDSSCs. This work offers some new complementing aspects to establish the methods for QDSSCs characterization.

3.1.3 Perovskite solar cells

As the new star in the field of photovoltaic, perovskite solar cells, traced back to 2009 [60], has possessed a higher efficiency up to ~23%. However, one of the main restricting factors is the relative poor stability for the environment and optical which are directly related to the interface. To further increase the efficiency of PSCs, it is

crucial to select of interface materials, increase the interfacial charge separation and transportation efficiency except for developing new materials and optimizing of preparation technology. Based on the advantage of SECM, Hsu et al. prepared a variety of $\text{PbI}_2/\text{MAPbI}_3$ perovskites and determined how excess PbI_2 affects its PEC properties via a rapid screening technique using a modified SECM [61]. Subsequently, Wang group investigated the regeneration kinetics at perovskite/oxide interface with SECM [62]. However, the application of SECM in PSCs is only a few and still needs to be explored might due to the instability of PSCs in moist environment or solution.

3.2 Photoelectrochemical water splitting

To efficiently and sustainably split water via PEC technology, several key criteria must be met simultaneously. For instance, (1) the light absorption, the semiconductor should have an adequate band gap (1.8–2.2 eV) so as to absorb a significant portion of the solar spectrum especially the visible light [63,64], (2) the appropriate band edge potentials which must straddle the hydrogen and oxygen redox potentials, (3) efficient charge transfer and separation process, (4) long-term stability in the electrolyte solution and low cost and so on [65]. However, no single semiconductor satisfies all of the above requirements for practical hydrogen production. Therefore, various strategies have been developed in order to improve the PEC activity, such as doping [66–68], constructing hetero-junction [69–71], coupling with co-catalysts [72,73], surface modification [74–77] as well as integrating with solar cells to forming tandem cells [78–80]. Among the factors affecting the PEC performance, the light absorption depends on the band gap of semiconductor, which is its intrinsic property. The application of SECM in

PEC water splitting mainly includes the SECM imaging, kinetics investigation and quantitation of reaction intermediates.

3.2.1 Screening of photocatalysts/photoelectrodes

As we all know, the solar to hydrogen efficiency (STH) of the photoelectrodes is still too low to practical application. Attributed to the varieties of photoelectrode materials, it is still a challenge to rapidly screen photocatalysts in order to economize the evaluation time and cost. Up to dates, many *in situ* technologies have been introduced into PEC field as described in Introduction section. Screening of catalysts for PEC application by SECM has drawn wide attention of many researchers.

Doping has been widely used to extend the light absorption and improve the conductivity of photo-electrodes. However, the essential relation between doping element or content and PEC activity is not investigated in detail. Previously, SECM was used to search for more efficient doped Fe_2O_3 photocatalysts which doped with different elements Sn, Ti, Be, Al [81]. For the screening of single dopants, the array pattern was prepared as shown in Figs. 5(a) and 5(b). Figure 5(c) shows a typical SECM image obtained from a photocatalyst spot array under visible light ($\lambda \geq 420$ nm). The dark brown color (Red dotted box in Fig. 5(c)) implied a largest photocurrent which was obtained from 4% Sn- Fe_2O_3 . Similarly, Fig. 5(d) shows the SECM image obtained from photocatalyst spot arrays consisting of Fe, Sn, and Be under visible light illumination. The highest photocurrent (130 nA) was observed at the composition of the 6% Be–4% Sn-Fe spot. The photocurrent then decreased gradually with further increase of the amount of Be. Lately, Bard group extended SECM to investigate PEC performance by

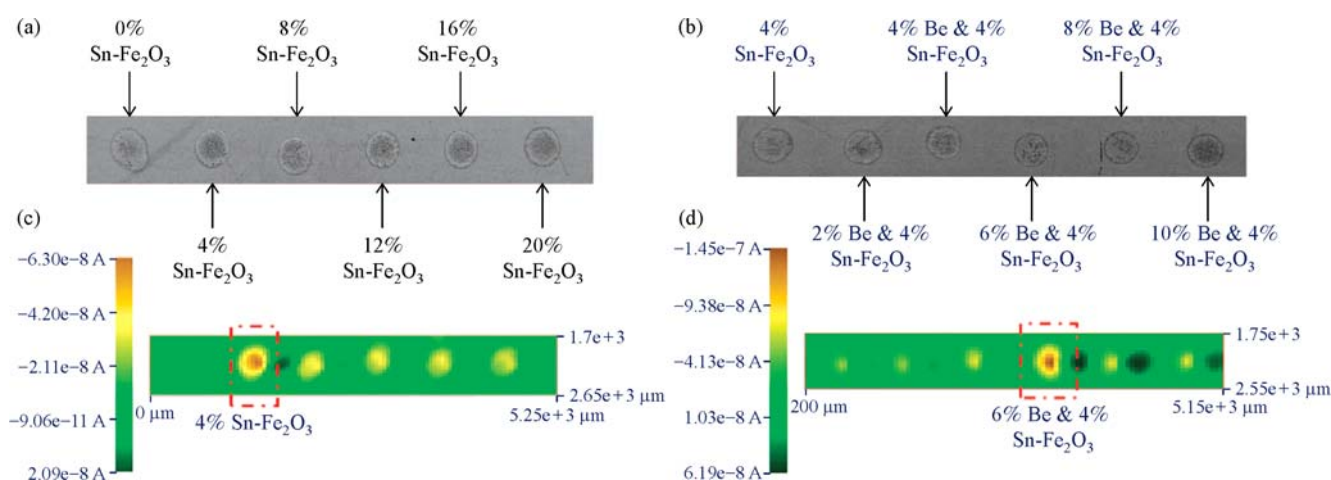


Fig. 5 Dispersed pattern of photocatalyst spot array with different mol % of Sn in Fe_2O_3 (a) and Be in 4% Sn- Fe_2O_3 (b). SECM image of (c) Sn doping Fe_2O_3 and (d) Be doping Sn- Fe_2O_3 measured with spot arrays at 0.2 V vs. Ag/AgCl in 0.2 mol NaOH under visible light irradiation ($\lambda \geq 420$ nm) [81]. Copyright © 2009, American Chemical Society

screening various dopants for BiVO_4 [82]. The results demonstrated the photocurrent of W or Mo doped BiVO_4 was more than 10 times higher than undoped BiVO_4 .

Leonard et al. reported a rapid screening technique based on the SG/TC mode of a modified SECM to study how metal doping affects its PEC properties [83]. As shown in Fig. 6(a), the colors represented the photocurrent for sulfite oxidation at 0.2 V vs. Ag/AgCl in which browns represented higher currents and greens represented lower currents. From the SECM screening, we could see that a maximum photocurrent occurred at a 9% atomic ratio of Zn/W, which was consistent with the LSV results under chopped light (Fig. 6(b)). The results demonstrated SECM can act as a tool to choose the photoelectrodes with better PEC performance.

Except for doping, coupling semiconductor (SC) with electro-catalyst is also a common method to improve photo-catalytic (PC) and PEC performance. However, we cannot randomly couple SC with an excellent electro-catalyst as co-catalyst to expect a higher PC or PEC performance. Ye et al. developed some co-catalysts (IrO_x , Pt, Co_3O_4) dropped onto the W doped BiVO_4 for PEC water oxidation, which was quickly identified the effect of co-catalysts on W doped BiVO_4 by the optical fiber-SECM technique [84]. Fig. 7 shows the principle of SECM and the corresponding image results of the electrocatalyst Ir/Co oxides Co_3O_4 and Pt. The optical fiber-modified SECM technique was used to quickly identify the effect of various electrocatalysts for PEC water oxidation. The experimental results demonstrated Pt and Co_3O_4 were effective on BiVW-O films, while IrO_x was not active, even though IrO_x films showed the highest electrocatalytic activity for water oxidation as electrocatalyst. This work inspired us that the SECM method can be used to optimize electro-

catalysts rapidly, e.g., by investigating different compositions with mixed electro-catalysts and by changing their thickness by dispensing blank solutions or with changing concentration of precursor solutions. Subsequently, Bard group also recently reported a new combinatorial methodology using a modified SECM technique for rapid preparation and screening of semiconductor photo-catalysts [85], which is analogous to the SECM for screening of other electro-catalysts.

Overall, SECM technique is extremely useful in mapping of photoelectrode surface, which can provide valuable spatially resolved information on the process kinetics occurring at the SEI of a PEC system. However, the resolution achieved by this technique is limited by the dimension of the UME. New developments in electrode design will be able to improve the special resolution of this technique.

3.2.2 Investigation on the kinetics of charge transfer at semiconductor (SC)/electrolyte interface (SEI) with scanning electrochemical microscopy (SECM)

Fast charge transfer kinetics at the photoelectrode/electrolyte interface is critical for highly efficient PEC water splitting. SECM is a powerful approach for measuring the kinetics of heterogeneous electron transfer, which can be determined with high lateral resolution while scanning a tip parallel to the surface. Lu group described the electron transfer kinetics at interfaces using SECM in details [86]. Bard group performed surface-selective and time-dependent redox titrations to directly measure the surface OER kinetics of Ni^{IV} and Fe^{IV} in NiOOH , FeOOH , and $\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ ($0 < x < 0.27$), which were popular co-catalyst used in PEC water system [87]. The results

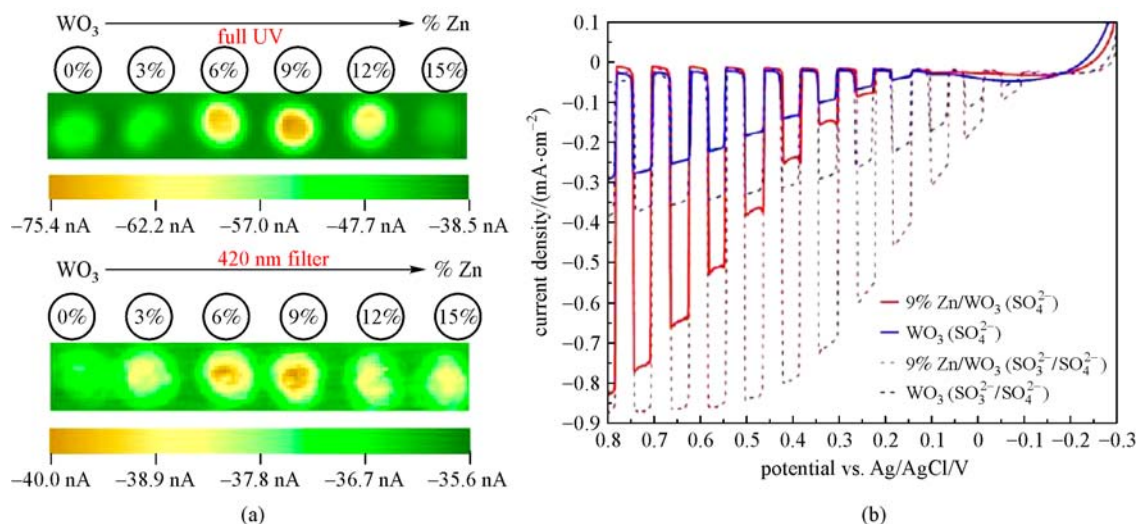


Fig. 6 (a) SECM images for the typical photocurrent response of Zn/ WO_3 composites under full UV irradiation and with a 420 nm long-pass filter. (b) PEC response of electrodes with chopped light under full UV irradiation at 20 mV/s [83]. Copyright © 2013, American Chemical Society

concluded that the remarkable OER activity of $\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ arising from the fast OER kinetics on Fe sites in NiOOH with a rate constant of 1.7 s^{-1} . Currently, we studied the interfacial charge transfer kinetics in PEC

system by SECM based on its feedback mode as show in Fig. 8(a) [88]. For investigating the catalytic reaction kinetics (reaction 1 in Fig. 8(b)) of BiVO_4 at the electrode/electrolyte interface, an extra Pt wire was ultrasonically

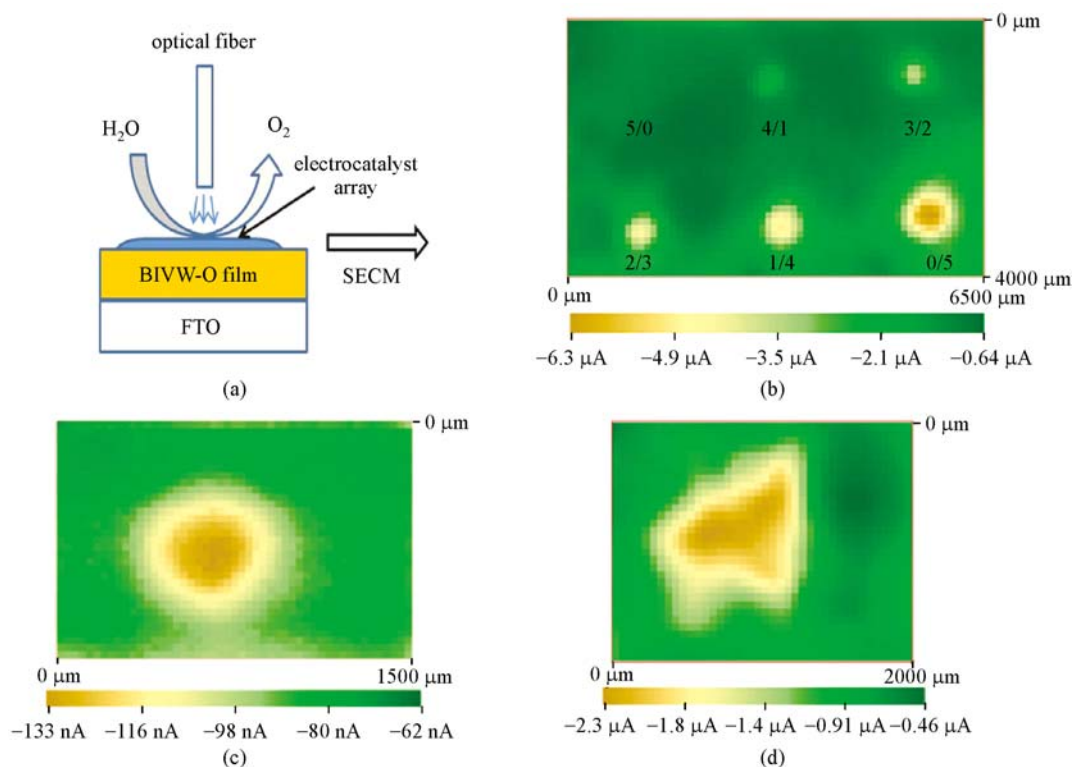


Fig. 7 (a) Operation principle of SECM and the corresponding image results of the electrocatalyst (b) Ir/Co oxide array, (c) photocurrent at Co_3O_4 spot, and (d) photocurrent at Pt spot [84]. Copyright © 2011, American Chemical Society

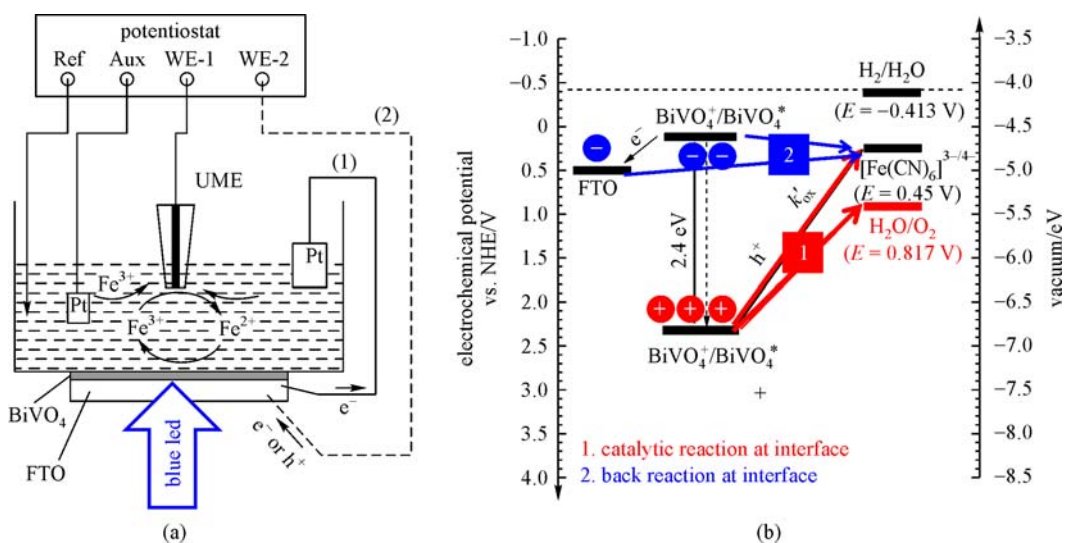


Fig. 8 (a) Basic principles for investigating of interfacial reaction kinetics in PEC water splitting under the feedback mode of SECM (Ref: reference electrode, Aux: auxiliary electrode, WE-1: working electrode 1, WE-2: working electrode 2). The semiconductor photocatalyst is BiVO_4 and the redox probe is $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ (named $\text{Fe}^{3+}/\text{Fe}^{2+}$). (b) Energy scheme of BiVO_4 system on electrochemical and vacuum scale at pH 7.0. Reaction 1 is the catalytic reaction, and reaction 2 is back reaction at interface [88]. Copyright © 2016, American Chemical Society

welded on the substrate electrode FTO with ohmic contact (i.e., FTO/BiVO₄ was named as photoanode) as indicated as connection style 1 in Fig. 8(a). Thus, the PEC cell was operated in short-circuit condition. SECM revealed the surface reaction kinetics constant of BiVO₄ was $9.30 \times 10^7 \text{ mol}^{-1} \cdot \text{cm}^3 \cdot \text{s}^{-1}$. And the ratio of rate constant for hole to electron for Mo:BiVO₄ is ~ 30 times larger than that of BiVO₄. The results reveal that the Mo element can significantly improve the transfer property of the photo-generated holes and suppress the transfer of photo-generated electrons at the photo-anode/electrolyte interface when doped into BiVO₄. This study will provide new ideas for designing and choosing the materials with high performance, and allows us to make a comprehensive analysis of interfacial charge transfer kinetics in PEC system. Subsequently, SECM has also been used for recording the photo-induced charge transfer reactions at BiVO₄ at chemically polarized liquid/liquid (L/L) interfaces [89].

3.2.3 Quantitation of reaction intermediates

Considering the complex process of water oxidation, quantitative of the reaction intermediates (such as H₂O₂, OH·) is very important which is useful for understanding the mechanism. Previously, Ahn and Bard investigated the surface cobalt sites and the intermediates of the electrocatalyst CoPi by surface interrogation scanning electrochemical microscopy (SI-SECM), in which CoPi was a universal co-catalyst for PEC water splitting [90]. Currently, SI-SECM was widely used to detect and quantify the intermediates of photoelectrode during PEC water splitting. For instance, Zigah et al. quantified adsorbed hydroxyl radical OH(ads) generated photoelectrochemically at the surface of a nanostructured TiO₂ substrate electrode [91]. In this study, the geometry of the

simulation space was depicted in Fig. 9(a) and it was adjusted for the experimental conditions, where a tip radius $a = 50 \text{ nm}$ and $RG = 3$, and the substrate was modeled as an active subdomain of radius $b = 150 \text{ nm}$ and depth $d' = 10 \text{ nm}$. The interelectrode distance d was adjusted to 27 nm . Fig. 9(b) described the mode of operation of SI-SECM for the generation and the detection of OH(ads) on the TiO₂ substrate. Finally, the typical ·OH(ads) saturation coverage of $338 \text{ mC} \cdot \text{cm}^{-2}$ was found in nanostructured samples. The decay kinetics of ·OH(ads) by dimerization to produce H₂O₂ were studied through the time dependence of the SI-SECM signal and the surface dimerization rate constant was found to be $\sim k_{\text{OH}} = 2.2 \times 10^3 \text{ mol}^{-1} \cdot \text{m}^2 \cdot \text{s}^{-1}$. Subsequently, this group investigated the reaction kinetics and surface coverage of water oxidation intermediates (H₂O₂) at the W/Mo-BiVO₄ photoanode using SI-SECM [92]. Besides, Cho et al. studied the PEC water oxidation of doping BiVO₄ and detected the oxygen evolution with using optical fiber incorporating a ring electrode via SECM [93].

As a promising narrow semiconductor, the PEC performance of Fe₂O₃ was mainly limited by slow water oxidation and severe recombination in the surface states. Therefore, in order to better understand the pathway of PEC reaction and further improve the PEC performance, it is essential to quantitative analyze of the reaction intermediates of the surface states. Krumov et al. used SI-SECM mode to quantitatively *in situ* probe the reactivity and coverage of reactive surface states in Fe₂O₃ during PEC water oxidation [94]. Besides, they also detected the evolution of H₂O₂ ($1.0 \mu\text{mol} \cdot \text{m}^{-2}$) during the decay process based on the SG/TC mode of SECM, which provided strong evidence for the existence of the ·OH(ads) intermediate on Fe₂O₃ and clearly showed a mechanism for the generation of unwanted products in PEC cells. This study demonstrated how SI-SECM enabled direct observation of multiple adsorbates and

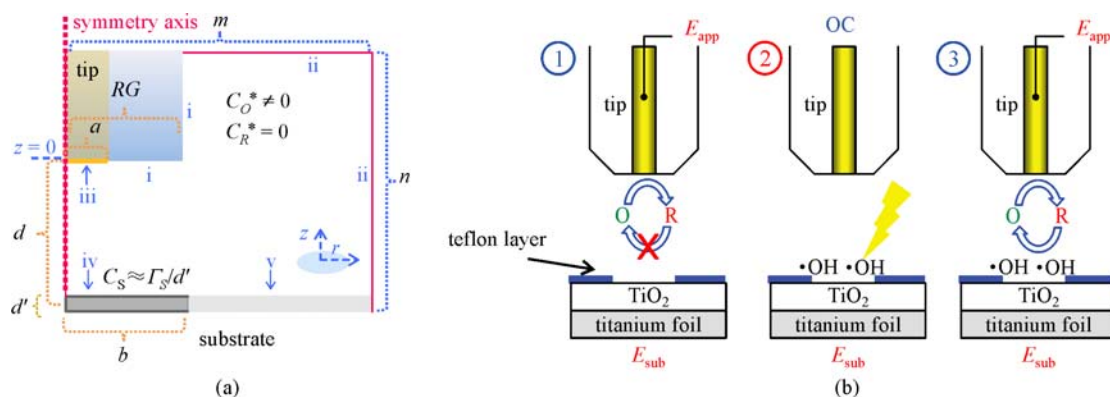


Fig. 9 (a) Description of the general SI-SECM simulation space and conditions. All geometries are in axial 2D and described by z and r were shown. Boundary types: i, insulation; ii, bulk concentration (semi-infinite); iii, flux at the tip; iv, concentration of hydroxyl radical OH at the substrate; v, insulation. (b) Description of the surface interrogation technique for the reduction of ·OH(ads) on TiO₂. ① No ·OH(ads) on TiO₂; ② ·OH(ads) are generated on TiO₂ through surface irradiation. ③ Light is turned off, interrogation of ·OH(ads) takes place by reduced species generated at the tip [91]. Copyright © 2012, Royal Society of Chemistry

reaction pathways on operating photoelectrodes. Bard group also quantified the density of photoactive sites (Fe^{4+} species) on the surface of Fe_2O_3 based on the SI-SECM [95]. In addition, the PEC water oxidation reaction dynamic was elucidated by time-dependent redox titration experiment which was similar to Krumov et al. [94].

4 Conclusions

In summary, we elaborated and summarized the basic principle and application of SECM in PEC fields in recent years. Particularly, discussion is focused on the screening, kinetics and quantitation of reaction intermediates in solar cells and PEC water splitting based on the different modes of SECM. Attributed to its better sensitivity, spatial resolution and more accurate control of the position of the probe, the application of SECM is continuously expanded to various areas up to now. However, it still has some disadvantages such as its spatial resolution is not high enough. So SECM has more and more commonly combined with other instruments, such as AFM and SICM, surface plasma resonance, and so on. And thus it will continue to broaden the scope of the study, and will become a more important electrochemical technique in the future.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 51602120), Natural Science Foundation of Education Department of Henan Province (No. 17A430023), and the opening project of Henan Provincial Key Laboratory of Nanocomposites and Applications (No. hkd20170106).

References

1. Holdren J P. Energy and sustainability. *Science*, 2007, 315(5813): 737
2. Lianos P. Review of recent trends in photoelectrocatalytic conversion of solar energy to electricity and hydrogen. *Applied Catalysis B: Environmental*, 2017, 210: 235–254
3. Li D, Shi J, Li C. Transition-metal-based electrocatalysts as cocatalysts for photoelectrochemical water splitting: a mini review. *Small*, 2018, 14(23): 1704179
4. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238(5358): 37–38
5. Klotz D, Grave D A, Dotan H, Rothschild A. Empirical analysis of the photoelectrochemical impedance response of hematite photoanodes for water photo-oxidation. *Journal of Physical Chemistry Letters*, 2018, 9(6): 1466–1472
6. Wang M, Chen P, Humphry-Baker R, Zakeeruddin S M, Grätzel M. The influence of charge transport and recombination on the performance of dye-sensitized solar cells. *ChemPhysChem*, 2009, 10(1): 290–299
7. Klotz D, Ellis D S, Dotan H, Rothschild A. Empirical in operando analysis of the charge carrier dynamics in hematite photoanodes by PEIS, IMPS and IMVS. *Physical Chemistry Chemical Physics*, 2016, 18(34): 23438–23457
8. Tsyganok A, Klotz D, Malviya K D, Rothschild A, Grave D A. Different roles of $\text{Fe}_{1-x}\text{Ni}_x\text{OOH}$ co-catalyst on hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoanodes with different dopants. *ACS Catalysis*, 2018, 8(4): 2754–2759
9. Berera R, van Grondelle R, Kennis J T. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. *Photosynthesis Research*, 2009, 101(2-3): 105–118
10. Pei G X, Wijten J H J, Weckhuysen B M. Probing the dynamics of photogenerated holes in doped hematite photoanodes for solar water splitting using transient absorption spectroscopy. *Physical Chemistry Chemical Physics*, 2018, 20(15): 9806–9811
11. Wang M, Alemu G, Shen Y. Scanning probe microscopy investigation of metal oxides nanocrystalline. In: *Current Microscopy Contributions to Advances in Science and Technology*, Chapter 3, 2012, 1377–1386
12. Esposito D V, Baxter J B, John J, Lewis N S, Moffat T P, Ogitsu T, O'Neil G D, Pham T A, Talin A A, Velazquez J M, Wood B C. Methods of photoelectrode characterization with high spatial and temporal resolution. *Energy & Environmental Science*, 2015, 8(10): 2863–2885
13. Cen J, Wu Q, Liu M, Orlov A. Developing new understanding of photoelectrochemical water splitting via *in-situ* techniques: a review on recent progress. *Green Energy & Environment*, 2017, 2(2): 100–111
14. Miki T, Yanagi H. Scanning probe microscopic characterization of surface-modified *n*- TiO_2 single-crystal electrodes. *Langmuir*, 1998, 14(12): 3405–3410
15. Wierzbński E, Szklarczyk M. Photoelectrochemical and *in situ* atomic force microscopy studies of films derived from *o*-methoxyaniline solution on gallium arsenide (100) photoelectrode. *Thin Solid Films*, 2003, 424(2): 191–200
16. Toma F M, Cooper J K, Kunzelmann V, McDowell M T, Yu J, Larson D M, Borys N J, Abelyan C, Beeman J W, Yu K M, Yang J, Chen L, Shaner M R, Spurgeon J, Houle F A, Persson K A, Sharp I D. Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes. *Nature Communications*, 2016, 7: 12012
17. Economou N J, Mubeen S, Buratto S K, McFarland E W. Investigation of arrays of photosynthetically active heterostructures using conductive probe atomic force microscopy. *Nano Letters*, 2014, 14(6): 3328–3334
18. Nakamura R, Nakato Y. Primary intermediates of oxygen photoevolution reaction on TiO_2 (Rutile) particles, revealed by *in situ* FTIR absorption and photoluminescence measurements. *Journal of the American Chemical Society*, 2004, 126(4): 1290–1298
19. Zandi O, Hamann T W. Determination of photoelectrochemical water oxidation intermediates on hematite electrode surfaces using operando infrared spectroscopy. *Nature Chemistry*, 2016, 8(8): 778–783
20. McKelvey K, Nadappuram B P, Actis P, Takahashi Y, Korchev Y E, Matsue T, Robinson C, Unwin P R. Fabrication, characterization, and functionalization of dual carbon electrodes as probes for

- scanning electrochemical microscopy (SECM). *Analytical Chemistry*, 2013, 85(15): 7519–7526
21. Zampardi G, Klink S, Kuznetsov V, Erichsen T, Maljusch A, La Mantia F, Schuhmann W, Ventosa E. Combined AFM/SECM investigation of the solid electrolyte interphase in Li-ion batteries. *Chemelectrochem*, 2015, 2(10): 1607–1611
 22. Takahashi Y, Shevchuk A I, Novak P, Murakami Y, Shiku H, Korchev Y E, Matsue T. Simultaneous noncontact topography and electrochemical imaging by SECM/SICM featuring ion current feedback regulation. *Journal of the American Chemical Society*, 2010, 132(29): 10118–10126
 23. Baranski A, Diakowski P. Application of AC impedance techniques to scanning electrochemical microscopy. *Journal of Solid State Electrochemistry*, 2004, 8(10): 683–692
 24. Mirkin M, Fan F, Bard A. Scanning electrochemical microscopy part 13. Evaluation of the tip shapes of nanometer size microelectrodes. *Journal of Electroanalytical Chemistry*, 1992, 328(1-2): 47–62
 25. Bard A, Fan F, Kwak J, Lev O. Scanning electrochemical microscopy: introduction and principles. *Analytical Chemistry*, 1989, 61(3): 132–138
 26. Engstrom R, Pharr C. Scanning electrochemical microscopy. *Analytical Chemistry*, 1989, 61(19): 1099A–1104A
 27. Polcari D, Dauphin-Ducharme P, Mauzeroll J. Scanning electrochemical microscopy: a comprehensive review of experimental parameters from 1989 to 2015. *Chemical Reviews*, 2016, 116(22): 13234–13278
 28. Rodríguez-López J, Alpuche-Aviles M A, Bard A J. Selective insulation with poly(tetrafluoroethylene) of substrate electrodes for electrochemical background reduction in scanning electrochemical microscopy. *Analytical Chemistry*, 2008, 80(5): 1813–1818
 29. Rodríguez-López J. Surface interrogation mode of scanning electrochemical microscopy (SI-SECM): an approach to the study of adsorption and (electro)catalysis at electrodes. *Electroanalytical Chemistry: A Series of Advances*, 2012, 24: 287–341
 30. Zhang B, Xu X, Zhang X, Huang D, Li S, Zhang Y, Zhan F, Deng M, He Y, Chen W, Shen Y, Wang M. Investigation of dye regeneration kinetics in sensitized solar cells by scanning electrochemical microscopy. *ChemPhysChem*, 2014, 15(6): 1182–1189
 31. Weng Y, Hsiao K. Composition optimization of ZnO-based photocatalyst arrays by scanning electrochemical microscopy and the characterization of efficient photocatalysts. *International Journal of Hydrogen Energy*, 2015, 40(8): 3238–3248
 32. Li F, Ciani I, Bertonecello P, Unwin P R, Zhao J J, Bradbury C R, Fermin D J. Scanning electrochemical microscopy of redox-mediated hydrogen evolution catalyzed by two-dimensional assemblies of palladium nanoparticles. *Journal of Physical Chemistry C*, 2008, 112(26): 9686–9694
 33. Zhang B, Yuan H, Zhang X, Huang D, Li S, Wang M, Shen Y. Investigation of regeneration kinetics in quantum-dots-sensitized solar cells with scanning electrochemical microscopy. *ACS Applied Materials & Interfaces*, 2014, 6(23): 20913–20918
 34. Alemu G, Zhang B, Li J, Xu X, Cui J, Shen Y, Wang M. Investigation of dye-regeneration kinetics at dye-sensitized p-type CuCrO₂ film/electrolytes interface with scanning electrochemical microscopy. *Nano*, 2014, 9(5): 1440008
 35. Martin C, Bozic-Weber B, Constable E, Glatzel T, Housecroft C, Wright I. Development of scanning electrochemical microscopy (SECM) techniques for the optimization of dye sensitized solar cells. *Electrochimica Acta*, 2014, 119: 86–91
 36. Schmidt I, Plettenberg I, Kimmich D, Ellis H, Witt J, Dosche C, Wittstock G. Spatially resolved analysis of screen printed photoanodes of dye-sensitized solar cells by scanning electrochemical microscopy. *Electrochimica Acta*, 2016, 222: 735–746
 37. Shen Y, Träuble M, Wittstock G. Detection of hydrogen peroxide produced during electrochemical oxygen reduction using scanning electrochemical microscopy. *Analytical Chemistry*, 2008, 80(3): 750–759
 38. Li H, Du M, Mleczko M J, Koh A L, Nishi Y, Pop E, Bard A J, Zheng X. Kinetic study of hydrogen evolution reaction over strained MoS₂ with sulfur vacancies using scanning electrochemical microscopy. *Journal of the American Chemical Society*, 2016, 138(15): 5123–5129
 39. Jung C, Sánchez-Sánchez C M, Lin C L, Rodríguez-López J, Bard A J. Electrocatalytic activity of Pd-Co bimetallic mixtures for formic acid oxidation studied by scanning electrochemical microscopy. *Analytical Chemistry*, 2009, 81(16): 7003–7008
 40. Sánchez-Sánchez C M, Rodríguez-López J, Bard A J. Scanning electrochemical microscopy. 60. Quantitative calibration of the SECM substrate generation/tip collection mode and its use for the study of the oxygen reduction mechanism. *Analytical Chemistry*, 2008, 80(9): 3254–3260
 41. Ventosa E, Schuhmann W. Scanning electrochemical microscopy of Li-ion batteries. *Physical Chemistry Chemical Physics*, 2015, 17(43): 28441–28450
 42. Xu F, Beak B, Jung C. *In situ* electrochemical studies for Li⁺ ions dissociation from the LiCoO₂ electrode by the substrate-generation/tip-collection mode in SECM. *Journal of Solid State Electrochemistry*, 2012, 16(1): 305–311
 43. Bülter H, Peters F, Schwenzel J, Wittstock G. Spatiotemporal changes of the solid electrolyte interphase in lithium-ion batteries detected by scanning electrochemical microscopy. *Angewandte Chemie*, 2014, 53(39): 10531–10535
 44. Sumboja A, Tefashe U, Wittstock G, Lee P S. Investigation of charge transfer kinetics of polyaniline supercapacitor electrodes by scanning electrochemical microscopy. *Advanced Materials Interfaces*, 2015, 2(1): 1400154
 45. Zhang Q, Ye Z, Zhu Z, Liu X, Zhang J, Cao F. Separation and kinetic study of iron corrosion in acidic solution via a modified tip generation/substrate collection mode by SECM. *Corrosion Science*, 2018, 139: 403–409
 46. Lee J, Ye H, Pan S, Bard A J. Screening of photocatalysts by scanning electrochemical microscopy. *Analytical Chemistry*, 2008, 80(19): 7445–7450
 47. Sreekanth N, Phani K L. Selective reduction of CO₂ to formate through bicarbonate reduction on metal electrodes: new insights gained from SG/TC mode of SECM. *Chemical Communications (Cambridge, England)*, 2014, 50(76): 11143–11146
 48. Rodríguez-López J, Bard A J. Scanning electrochemical microscopy: surface interrogation of adsorbed hydrogen and the open

- circuit catalytic decomposition of formic acid at platinum. *Journal of the American Chemical Society*, 2010, 132(14): 5121–5129
49. Fernández J L, White J M, Sun Y, Tang W, Henkelman G, Bard A J. Characterization and theory of electrocatalysts based on scanning electrochemical microscopy screening methods. *Langmuir*, 2006, 22 (25): 10426–10431
 50. Jantz D, Leonard K. Characterizing electrocatalysts with scanning electrochemical microscopy. *Industrial & Engineering Chemistry Research*, 2018, 57(22): 7431–7440
 51. Li Y, Ning X, Ma Q, Qin D, Lu X. Recent advances in electrochemistry by scanning electrochemical microscopy. *Trends in Analytical Chemistry*, 2016, 80: 242–254
 52. Rincón M E, Trujillo M E, Ávalos J, Casillas N. Photoelectrochemical processes at interfaces of nanostructured TiO₂/carbon black composites studied by scanning photoelectrochemical microscopy. *Journal of Solid State Electrochemistry*, 2007, 11(9): 1287–1294
 53. Bozic B, Figgemeier E. Scanning electrochemical microscopy under illumination: an elegant tool to directly determine the mobility of charge carriers within dye-sensitized nanostructured semiconductors. *Chemical Communications (Cambridge, England)*, 2006, 21 (21): 2268–2270
 54. Tefashe U M, Loewenstein T, Miura H, Schlettwein D, Wittstock G. Scanning electrochemical microscope studies of dye regeneration in indoline (D149)-sensitized ZnO photoelectrochemical cells. *Journal of Electroanalytical Chemistry*, 2010, 650(1): 24–30
 55. Tefashe U M, Rudolph M, Miura H, Schlettwein D, Wittstock G. Photovoltaic characteristics and dye regeneration kinetics in D149-sensitized ZnO with varied dye loading and film thickness. *Physical Chemistry Chemical Physics*, 2012, 14(20): 7533–7542
 56. Tefashe U M, Nonomura K, Vlachopoulos N, Hagfeldt A, Wittstock G. Effect of cationon dye regeneration kinetics of N719-sensitized TiO₂ films in acetonitrile-based and ionic-liquid-based electrolytes investigated by scanning electrochemical microscopy. *Journal of Physical Chemistry C*, 2012, 116(6): 4316–4323
 57. Shen Y, Nonomura K, Schlettwein D, Zhao C, Wittstock G. Photoelectrochemical kinetics of eosin γ -sensitized zinc oxide films investigated by scanning electrochemical microscopy. *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2006, 12(22): 5832–5839
 58. Shen Y, Tefashe U M, Nonomura K, Loewenstein T, Schlettwein D, Wittstock G. Photoelectrochemical kinetics of Eosin Y-sensitized zinc oxide films investigated by scanning electrochemical microscopy under illumination with different LED. *Electrochimica Acta*, 2009, 55(2): 458–464
 59. Xu X, Zhang B, Cui J, Xiong D, Shen Y, Chen W, Sun L, Cheng Y, Wang M. Efficient p-type dye-sensitized solar cells based on disulfide/thiolate electrolytes. *Nanoscale*, 2013, 5(17): 7963–7969
 60. Kojima A, Teshima K, Shirai Y, Miyasaka T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 2009, 131(17): 6050–6051
 61. Hsu H, Ji L, Du M, Zhao J, Yu E, Bard A. Optimization of PbI₂/MAPbI₃ perovskite composites by scanning electrochemical microscopy. *Journal of Physical Chemistry C*, 2016, 120(35): 19890–19895
 62. Alemu G, Li J, Cui J, Xu X, Zhang B, Cao K, Shen Y, Cheng Y, Wang M. Investigation on regeneration kinetics at perovskite/oxide interface with scanning electrochemical microscopy. *Journal of Materials Chemistry A, Materials for Energy and Sustainability*, 2015, 3(17): 9216–9222
 63. Jang J, Lee J, Ye H, Fan F, Bard A. Rapid screening of effective dopants for Fe₂O₃ photocatalysts with scanning electrochemical microscopy and investigation of their photoelectrochemical properties. *Journal of Physical Chemistry C*, 2009, 113(16): 6719–6724
 64. Currao A. Photoelectrochemical water splitting. *Chimia*, 2007, 61 (12): 815–819
 65. Acar C, Dincer I, Zamfirescu C. A review on selected heterogeneous photocatalysts for hydrogen production. *International Journal of Energy Research*, 2014, 38(15): 1903–1920
 66. Acar C, Dincer I. A review and evaluation of photoelectrode coating materials and methods for photoelectrochemical hydrogen production. *International Journal of Hydrogen Energy*, 2016, 41(19): 7950–7959
 67. Shi Q, Murcia-López S, Tang P, Flox C, Morante J, Bian Z, Wang H, Andreu T. Role of tungsten doping on the surface states in BiVO₄ photoanodes for water oxidation: tuning the electron trapping process. *ACS Catalysis*, 2018, 8(4): 3331–3342
 68. Yang Y, Niu S, Han D, Liu T, Wang G, Li Y. Progress in developing metal oxide nanomaterials for photoelectrochemical water splitting. *Advanced Energy Materials*, 2017, 7(19): 1700555
 69. Zhang X, Zhang B, Zuo Z, Wang M, Shen Y. N/Si co-doped oriented single crystalline rutile TiO₂ nanorods for photoelectrochemical water splitting. *Journal of Materials Chemistry A, Materials for Energy and Sustainability*, 2015, 3(18): 10020–10025
 70. Zhang X, Yang H, Zhang B, Shen Y, Wang M. BiOI-TiO₂ nanocomposites for photoelectrochemical water splitting. *Advanced Materials Interfaces*, 2016, 3(1): 1500273
 71. Harrison S, Hayne M. Photoelectrolysis using type-II semiconductor heterojunctions. *Scientific Reports*, 2017, 7(1): 11638
 72. Wang H, Zhang L, Chen Z, Hu J, Li S, Wang Z, Liu J, Wang X. Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. *Chemical Society Reviews*, 2014, 43(15): 5234–5244
 73. Yang J, Wang D, Han H, Li C. Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Accounts of Chemical Research*, 2013, 46(8): 1900–1909
 74. Zhang X, Zhang B, Liu S, Kang H, Kong W, Zhang S, Shen Y, Yang B. RGO modified Ni doped FeOOH for enhanced electrochemical and photoelectrochemical water oxidation. *Applied Surface Science*, 2018, 436: 974–980
 75. Zhang X, Zhang B, Luo Y, Lv X, Shen Y. Phosphate modified N/Si co-doped rutile TiO₂ nanorods for photoelectrochemical water oxidation. *Applied Surface Science*, 2017, 391: 288–294
 76. Zhang X, Zhang B, Huang D, Yuan H, Wang M, Shen Y. TiO₂ nanotubes modified with electrochemically reduced graphene oxide for photoelectrochemical water splitting. *Carbon*, 2014, 80: 591–598
 77. Shi W, Zhang X, Brillet J, Huang D, Li M, Wang M, Shen Y. Significant enhancement of the photoelectrochemical activity of WO₃ nanoflakes by carbon quantum dots decoration. *Carbon*, 2016, 105: 387–393
 78. Shi W, Zhang X, Li S, Zhang B, Wang M, Shen Y. Carbon coated

- Cu₂O nanowires for photoelectrochemical water splitting with enhanced activity. *Applied Surface Science*, 2015, 358: 404–411
79. Zhang X, Zhang B, Cao K, Brillet J, Chen J, Wang M, Shen Y. A perovskite solar cell-TiO₂@BiVO₄ photoelectrochemical system for direct solar water splitting. *Journal of Materials Chemistry A, Materials for Energy and Sustainability*, 2015, 3(43): 21630–21636
 80. Chen Y S, Manser J S, Kamat P V. All solution-processed lead halide perovskite-BiVO₄ tandem assembly for photolytic solar fuels production. *Journal of the American Chemical Society*, 2015, 137(2): 974–981
 81. Brillet J, Yum J, Cornuz M, Hisatomi T, Solarska R, Augustynski J, Grätzel M, Sivula K. Highly efficient water splitting by a dual-absorber tandem cell. *Nature Photonics*, 2012, 6(12): 824–828
 82. Park H, Kweon K, Ye H, Paek E, Hwang G, Bard A. Factors in the metal doping of BiVO₄ for improved photoelectrocatalytic activity as studied by scanning electrochemical microscopy and first-principles density-functional calculation. *Journal of Physical Chemistry C*, 2011, 115(36): 17870–17879
 83. Leonard K, Nam K, Lee H, Kang S, Park H, Bard A. ZnWO₄/WO₃ composite for improving photoelectrochemical water oxidation. *Journal of Physical Chemistry C*, 2013, 117(31): 15901–15910
 84. Ye H, Park H, Bard A. Screening of electrocatalysts for photoelectrochemical water oxidation on W-doped BiVO₄ photocatalysts by scanning electrochemical microscopy. *Journal of Physical Chemistry C*, 2011, 115(25): 12464–12470
 85. Ye H, Lee J, Jang J, Bard A. Rapid screening of BiVO₄-based photocatalysts by scanning electrochemical microscopy (SECM) and studies of their photoelectrochemical properties. *Journal of Physical Chemistry C*, 2010, 114(31): 13322–13328
 86. Lu X, Hu Y, He H. Electron transfer kinetics at interfaces using secm (scanning electrochemical microscopy). In: Sur U K, ed. *Recent Trend in Electrochemical Science and Technology*. Rijeka: In Tech, 2012, 127–156
 87. Ahn H S, Bard A J. Surface interrogation scanning electrochemical microscopy of Ni_{1-x}Fe_xOOH (0 < x < 0.27) oxygen evolving catalyst: kinetics of the “fast” iron sites. *Journal of the American Chemical Society*, 2016, 138(1): 313–318
 88. Zhang B, Zhang X, Xiao X, Shen Y. Photoelectrochemical water splitting system—a study of interfacial charge transfer with scanning electrochemical microscopy. *ACS Applied Materials & Interfaces*, 2016, 8(3): 1606–1614
 89. Rastgar S, Wittstock G. Characterization of photoactivity of nanostructured BiVO₄ at polarized liquid-liquid interfaces by scanning electrochemical microscopy. *Journal of Physical Chemistry C*, 2017, 121(46): 25941–25948
 90. Ahn H S, Bard A J. Surface interrogation of CoP₁ water oxidation catalyst by scanning electrochemical microscopy. *Journal of the American Chemical Society*, 2015, 137(2): 612–615
 91. Zigah D, Rodríguez-López J, Bard A J. Quantification of photoelectrogenerated hydroxyl radical on TiO₂ by surface interrogation scanning electrochemical microscopy. *Physical Chemistry Chemical Physics*, 2012, 14(37): 12764–12772
 92. Park H, Leonard K, Bard A. Surface interrogation scanning electrochemical microscopy (SI-SECM) of photoelectrochemistry at a W/Mo-BiVO₄ semiconductor electrode: quantification of hydroxyl radicals during water oxidation. *Journal of Physical Chemistry C*, 2013, 117(23): 12093–12102
 93. Cho S, Park H, Lee H, Nam K, Bard A. Metal doping of BiVO₄ by composite electrodeposition with improved photoelectrochemical water oxidation. *Journal of Physical Chemistry C*, 2013, 117(44): 23048–23056
 94. Krumov M R, Simpson B H, Counihan M J, Rodríguez-López J. *In situ* quantification of surface intermediates and correlation to discharge products on hematite photoanodes using a combined scanning electrochemical microscopy approach. *Analytical Chemistry*, 2018, 90(5): 3050–3057
 95. Kim J Y, Ahn H S, Bard A J. Surface interrogation scanning electrochemical microscopy for a photoelectrochemical reaction: water oxidation on a hematite surface. *Analytical Chemistry*, 2018, 90(5): 3045–3049



Xiaofan Zhang received her Ph.D. degree in Photoelectric Information Engineering from Huazhong University of Science and Technology in 2015. She joined Henan Provincial Key Laboratory of Nanocomposite and Applications and Institute of Nanostructured Functional Materials at Huanghe Science and Technology College in 2015. Now she is a lecturer, working in School of Environment and Civil Engineering of Dongguan University of Technology from 2018. Her research interests are related to energy conversion, and focus on solar water splitting, dynamics investigation of photoelectrochemical interfacial reaction and electrocatalysis.



Man Liu received her M.Sc degree from the College of Chemistry and Molecular Engineering at Zhengzhou University in 2013. Currently, she works on Henan Provincial Key Laboratory of Nano-composite and Applications of Huanghe Science and Technology College. Her research interests mainly focus on analysis of materials by means of NMR spectrometer, mass spectrograph, X-ray diffraction (XRD), scanning electron microscopy(SEM), transmission electron microscopy (TEM).



Weiqian Kong obtained her M.Sc degree from Institute of Functional Nano & Soft Materials (FUNSOM) in Soochow University in 2015. Then she works as a teaching assistant until now in Henan Provincial Key Laboratory of Nanocomposite and Applications, Institute of Nanostructured Functional Materials of Huanghe Science and Technology College. Her research interests focus on carbon nanomaterials and their applications in detection and catalysis, photoelectrochemical water splitting, energy and environmental applications.



Hongbo Fan received his B.Sc. degree from Henan Normal University in 1983, his M.Sc. and Ph.D. degrees from Huazhong University of Science and Technology in 1996 and 2003, respectively. He worked as a postdoctoral research fellow at South China University of Technology from 2003 to 2005. Prof. Fan joined Dongguan University of Technology in 2005. Currently,

he is the dean of School of Environment and Civil Engineering and the director of Dongguan Clean Production Technology Center. His research interests are related to energy storage materials, intelligence materials, as well as energy efficiency and environmental protection, and so on.