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# Dual modification of TiO<sub>2</sub> nanorods for selective Photoelectrochemical Detection of Organic Compounds

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Keywords: Photoelectrochemical analysis; Surface Plasmon Resonance; Titanium Dioxide;

**Highlights:**

1. Hydrogenation of TiO<sub>2</sub> nanorod electrode enhances photoelectrochemical oxidation of organic compounds.
2. Au-nanoparticle modification of TiO<sub>2</sub> nanorod electrode enables photoelectrochemical oxidation of organic compound under visible light due to the localized surface plasmonic resonance (LSPR) effect.
3. Selective detection of organic compounds at the Au@H-TiO<sub>2</sub> photoelectrode is achieved by varying wavelength of the light irradiation.

**ABSTRACT.**

Selective detection of organic compounds in water body is both desirable and challenging for photoelectrocatalytic (PEC) sensors. In this work, tunable oxidation capability is designed and achieved by modifying titanium dioxide nanorod arrays (TiO<sub>2</sub>) photoelectrodes with nano-sized plasmonic gold (Au) particle deposition and subsequent hydrogenation treatment (*i.e.* Au@H-TiO<sub>2</sub>). The effective incorporation of Au nanoparticles onto the TiO<sub>2</sub> nanorods induces a plasmonic effect and extends light absorption from ultraviolet (UV) to the visible light range while the hydrogenation process dramatically improves PEC oxidation activity. Under visible light, the Au@H-TiO<sub>2</sub> electrode exhibits selective detection capability to labile organic compounds. This excellent selectivity is demonstrated by a wide linear relationship between photocurrent and the concentration of different types of sugars, including glucose, fructose, sucrose and lactose in the presence of various concentrations of the aromatic compound potassium hydrogen phthalate (KHP). Furthermore, the modified electrode can also indiscriminately detect all kinds of organic compounds in a rapid manner under UV irradiation due to the strong oxidation capability. Such a unique feature of the tunable oxidation capability bestows the Au@H-TiO<sub>2</sub> photoelectrodes a new generation of the PEC sensors for selective and collective degradation of organic compounds.

## Introduction

The photoelectrocatalysis (PEC) sensor can in-situ monitor the overall amount of organic compounds in water body as well as speciation of organic pollutants in a simple, accurate and low cost way [1, 2]. The PEC sensors are developed by using high performance TiO<sub>2</sub> photoelectrodes to collectively oxidate the organic compounds at under UV light [3]. To date, the selective oxidization of organic compounds is another important but challenging feature of photocatalytic (PC) and of PEC processes in advanced applications, including selective synthesis of desired organic compounds, selective removal of toxic pollutants and selective detection of expected organic compounds among mixtures [4-6]. The application of selective PC and PEC oxidation process would bestow selective detection capability for PEC sensors.

In recent studies of photocatalytic materials, it is well-established that nano-sized metals (such as Au, Pt, Ag, and Pd) can enable PC and PEC reactions under visible light due to surface plasmonic resonance (SPR) induced electron excitation [7-10]. The SPR hot electrons from the nano-sized noble metal can be rapidly injected into the TiO<sub>2</sub>, leading to enhanced oxidation efficiency [11, 12]. This facilitates the use of nano-sized metal modified TiO<sub>2</sub> photocatalysts for water splitting under visible and solar irradiation [13, 14]. It has also been recently reported that plasmonic catalysts play an important role in driving degradation of some labile organic compounds [15, 16]. Based on these findings, the oxidation power of organic compounds is logically tunable by the selection of UV light or visible light for the PC or PEC reactions. Theoretically, the combined use of different light spectra will enable the detection of different organic compounds in a mixed solution without a separation process such as high performance liquid chromatography (HPLC) [17].

Existing nano-sized Au modified TiO<sub>2</sub> photoelectrodes provide very limited PC and PEC efficiency for practical applications due to low energy conversion efficiency [18-21]. Low conversion efficiency is a common barrier in practical applications of PEC sensors of organic compounds, especially in situations where response time is critical. Hydrogenation processes are a potential solution as the hydrogenation of TiO<sub>2</sub> could produce oxygen vacancies and Ti<sup>3+</sup>. These in turn could significantly improve electrical conductivity and cause red-shift of light absorption resulting in better PEC performance [22-24]. Hydrogenated TiO<sub>2</sub> has a higher sensitivity and wider linear range for the determination of collective organic compounds due to its decreased intrinsic electrochemical resistance in the UV region[25].

In this work, we fabricate a composite photoanode by combining TiO<sub>2</sub> nanorod arrays with plasmonic Au nanoparticles (*i.e.* Au@TiO<sub>2</sub> photoanode) to achieve selective detection of organic compounds under visible light. The electrode is subjected to a hydrogenation treatment that could enhance electronic conductivity, accelerate transport of photoelectrons from the Au nanoparticles to the external circuit *via* TiO<sub>2</sub>, and ultimately boost PEC efficiency. The boosted hydrogenated Au@TiO<sub>2</sub> photoanode (*i.e.* Au@H-TiO<sub>2</sub> photoanode) is expected to be able to oxidize and sense glucose in the presence of potassium hydrogen phthalate (KHP). KHP is used to determine whether the Au@H-TiO<sub>2</sub> photoanode can selectively detect sugars in the presence of aromatic compounds without the use of separation processes. The selectivity of the photoanode can be tuned by varying the wavelength of the light irradiation. Under visible light irradiation, sugars can be detected while the aromatic compounds KHP remain intact. Under UV illumination, the photoanode can indiscriminately detect the overall amount of organic compounds. To the best of our knowledge, this is the first report of a PEC sensor based on the SPR effect and hydrogenation for selective

detection of specific organic compounds and collective determination of overall organic compounds.

## Experimental Section

TiO<sub>2</sub> nanorod array electrodes were grown on a fluorine-doped tin oxide (FTO) glass substrate using a hydrothermal method [26]. Briefly, 30 ml of hydrochloric acid (37 wt%) and deionized water (1:1 v/v) were mixed in a 100 ml Teflon-lined stainless steel autoclave. While vigorously stirring the HCl solution, 0.36 mL of titanium butoxide was added to the autoclave and a transparent solution was obtained after 0.5 h. The FTO substrate was then immersed in the mixture solution and placed at an angle against the Teflon-liner wall with the conducting side facing down. The TiO<sub>2</sub> nanorods grew on the FTO after a hydrothermal process at 170 °C for 6 h. The FTO substrate was taken out rinsed with deionized water and air dried. Finally, the sample was annealed in air at 500 °C for 3 h to increase the crystallinity of TiO<sub>2</sub> nanowires and improve the mechanical strength of the TiO<sub>2</sub> grown on the substrate.

Au nanoparticles were deposited on the TiO<sub>2</sub> nanorod array using a solution thermal reduction method. The TiO<sub>2</sub> nanorod array grown on the FTO substrate was immersed in 0.03M pH 7 HAuCl<sub>4</sub> solutions for 2 h. The TiO<sub>2</sub> array was taken out and washed by deionized water, air dried and annealed for 2 h at 300 °C. The as-grown TiO<sub>2</sub> nanorod arrays electrode and the Au nanoparticles modified TiO<sub>2</sub> nanorod arrays electrode are herein referred to as TiO<sub>2</sub> and Au@TiO<sub>2</sub>, respectively.

Hydrogenation treatment of the  $\text{TiO}_2$  and  $\text{Au@TiO}_2$  electrodes was carried out in a 30 bar hydrogen atmosphere in a steel reactor at 300 °C for 30 min. The hydrogenated  $\text{TiO}_2$  and  $\text{Au@TiO}_2$  electrodes are herein referred to as H- $\text{TiO}_2$  and Au@H- $\text{TiO}_2$ , respectively.

## **Characterization**



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12 April. 2017

*Prof. Yasuhiro Shimizu*  
*Editor, Sensors & Actuators: B. Chemical*

**RE: Manuscript ID: SNB-D-17-01147**

Dear Prof. Shimizu,

Enclosed please find the revised article.

**Title:** *Dual modification of TiO<sub>2</sub> nanorods for selective Photoelectrochemical Detection of Organic Compounds*

**Authors:** *Yazhou Wang, Meng Zu, Sheng Li, Teera Butburee, Lianzhou Wang, Feng Peng and Shanqing Zhang\**

Thanks for the reviewers' and editors' valuable comments on our work. Taking all the comments and suggestions into our consideration, we have addressed all the concerns of the reviewers and highlighted the changes in red in the manuscript. We strongly believe all comments have been appropriately addressed. We believe the quality of the revised manuscript has been improved substantially and hope it can soon be published in *Sensors & Actuators: B. Chemical*.

Referee: 1

*This manuscript by Wang et al. reported the application of Au nanoparticle decorated H-TiO<sub>2</sub> nanorods modified electrode with tunable oxidation ability for selective photoelectrochemical detection of sugars. The authors have clearly demonstrated that by controlling the wavelength of the light, Au@H-TiO<sub>2</sub> could effectively and selectively oxidize different types of sugars in the presence of aromatic compounds. Therefore, I would like to recommend its publication after considering the following points:*

1. *In Scheme 1, particular band position of H-TiO<sub>2</sub> and the oxidation potential of glucose should be provided for clarity. The mid-gap energy levels of Au@H-TiO<sub>2</sub> should also be marked to show that the photoexcited holes can't drive water oxidation.*

**REPLY:** We thank the reviewer for the positive comments. The scheme image and caption has been revised for clarity as suggested and mark in red on page 19 as shown in below.



Structural analyses of the TiO<sub>2</sub> and Au@TiO<sub>2</sub> electrodes were performed using (i) high-resolution X-ray diffractometer (XRD) with Cu-K $\alpha$  radiations (wavelength, 1.5406 Å) on a Bruker D8 System, (ii) scanning electron microscope (SEM) on JEOL JSM-7001F, and (iii) transmission electron microscopy (TEM) using a FEI Tecnai F30 TEM (operating at 300 kV). The UV–Vis diffusion reflectance (UV–Vis) spectra were recorded by a UV–Vis spectrometer (U3010, Hitachi) with an integrating sphere accessory.

### **PEC measurement**

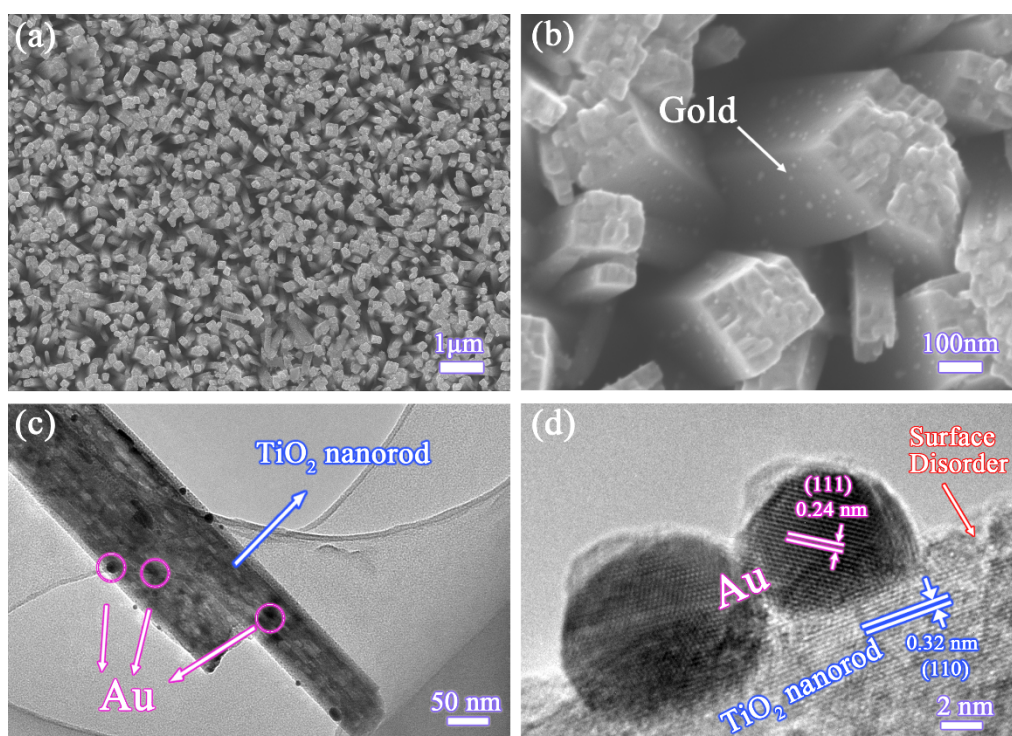
PEC experiments were carried out in a three-electrode PEC cell including an Ag/AgCl reference electrode and a platinum mesh auxiliary electrode. The working photoelectrodes were mounted in a special holder with an area of 0.78 cm<sup>2</sup> for visible and UV light illumination. A 0.1 M NaNO<sub>3</sub> solution was used as the supporting electrolyte solution. A potentiostat (voltammograph, CV-27, BAS) was used to conduct linear sweep voltammetry (LSV) and amperometric measurements. The light source was a 150 W xenon lamp system (HFC-150, TrustTech). A UV band-pass filter (UG 5, Schott) was used to remove the visible and infrared light while a UV light cut off filter ( $\lambda > 420$  nm, 500mW cm<sup>-2</sup>) was used to block the light in the UV region.

## **Results and discussion**

### **Characterization of photoelectrodes**

The TiO<sub>2</sub> nanorod arrays were firstly grown on a fluorine-doped tin oxide (FTO) glass substrate by a hydrothermal process followed by the deposition of Au nanoparticles, resulting in the Au@TiO<sub>2</sub> photoanode. Subsequent hydrogenation treatment leads to the Au@H-TiO<sub>2</sub> photoanode. The SEM micrographs of the Au@TiO<sub>2</sub> electrodes illustrate the uniform deposition of Au nanoparticles on the as-prepared TiO<sub>2</sub> nanorod arrays (see Figure S1, Supplementary Material) by the deposition–precipitation method. There is no significant morphological change between the

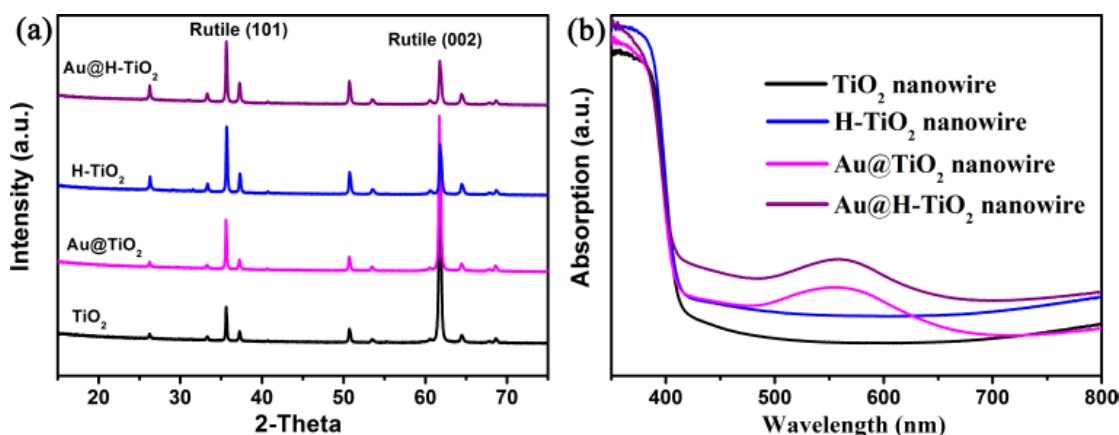
Au@TiO<sub>2</sub> and the Au@H-TiO<sub>2</sub> electrodes (see Figure 1 and S1), suggesting that the Au@TiO<sub>2</sub> sample is physically stable during the hydrogenation process. The TEM image in Figure 1c indicates that the Au nanoparticles deposited on the TiO<sub>2</sub> nanorod have a typical size of 5-10 nm, which is confirmed by energy-dispersive X-ray spectroscopy (see Figure S2 Supplementary Material). This also coincides with the observation of the HRTEM image in Figure 1d where two Au spherical nanoparticles have a diameter of 7-8 nm. Two distinct lattice fringes, the interface between the TiO<sub>2</sub> nanorod and Au nanoparticle regions can be assigned to Au (pink) and rutile TiO<sub>2</sub> (blue). Furthermore, dislocation of TiO<sub>2</sub> lattices could be observed in the area indicated by the red arrow where the thickness is ca. 1.5 nm. This surface lattice disorder which can be attributed to the hydrogenation treatment could yield mid-gap electronic levels that are responsible for the absorption of broader light wavelengths [27].



**Figure 1.** (a) Low and (b) high magnification SEM images of the Au@H-TiO<sub>2</sub> electrode, (c)

Low and (b) high magnification HRTEM images of the Au@H-TiO<sub>2</sub> electrode.

The surface disorder is also reflected in the significant decrease in the XRD (002) peak after the hydrogen treatment (Figure 2a). This can indicate the increase of oxygen vacancy density in the TiO<sub>2</sub> structure which induces improvement in the electric conductivity due to the increase in donor density. The dominant peak (002) diffraction at 63.2° and the peak (101) at 36.5° (JCPDS No. 88-1175) suggest that the crystalline phase of the H-TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes remain mainly rutile. No other change in the XRD spectra implies that the FTO substrate is not affected by the hydrogenation process.



**Figure 2.** (a) XRD patterns of the TiO<sub>2</sub>, H-TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes and (b) UV-Vis spectra of the TiO<sub>2</sub>, H-TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes.

The nano-sized Au deposition and hydrogenation treatment allow visible light absorption by the PEC electrode through the introduction of the SPR effect and mid-gap electric state. The UV-Vis diffuse absorbance spectra of H-TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> are used to study the optical properties of the PEC electrodes and contrast with the as-prepared TiO<sub>2</sub> electrode (Figure 2b). While the TiO<sub>2</sub> electrode strongly absorbs light only in the UV region due to the large band gap (3.0 eV for rutile), the Au@TiO<sub>2</sub> electrode shows another absorption band centered at 560 nm that can be attributed to the typical SPR effect of Au nanoparticles. Moreover, noticeable enhancement of UV and visible light absorption can be observed in H-TiO<sub>2</sub> and Au@H-TiO<sub>2</sub>. This result

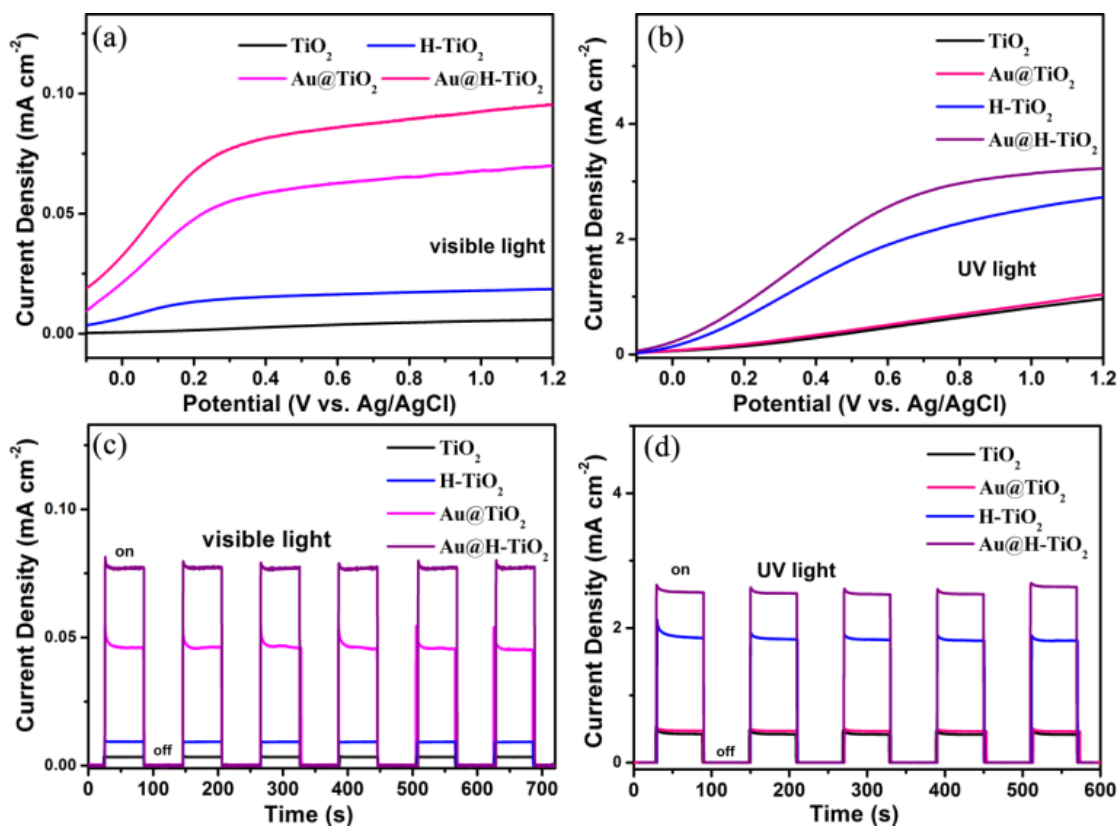
confirms that the hydrogenation of TiO<sub>2</sub> could induce mid-gap energy levels to absorb visible light [28]. Overall, the significant absorption enhancement of the Au@H-TiO<sub>2</sub> electrode in both UV and visible light regions is beneficial to PEC performance.

### PEC sensor

The capability of the PEC electrodes to photodegrade organic compounds was assessed in 0.1 M NaNO<sub>3</sub> solution as shown in Figure 3. The PEC profiles of different photoelectrodes (Figure 3a, c) were obtained under visible light using a band pass filter ( $\lambda > 420$  nm). Because the photocurrents can be considered as the PEC reaction rate of the PEC oxidation reaction, the photocurrents of the TiO<sub>2</sub>, H-TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes can be used to evaluate their PEC oxidation activity. A set of linear sweep voltammetry (LSV) curves are recorded in the potential range between -0.1 V and 1.2 V versus Ag/AgCl in Figure 3a. Upon illumination by visible light, the photocurrents increase linearly with increasing applied potential in the photoelectrodes. The H-TiO<sub>2</sub> electrode produces a slightly enhanced photocurrent under the same visible irradiation compared with TiO<sub>2</sub> electrode. This is in line with the working principle of hydrogenation, *i.e.* the creation of mid-gap energy levels facilitates the absorption of visible light. The PEC performance of the Au@TiO<sub>2</sub> electrode in the visible region is remarkably better than the TiO<sub>2</sub> and H-TiO<sub>2</sub> electrodes due to the SPR effect. As expected, the Au@H-TiO<sub>2</sub> electrode has the highest photocurrent compared with the other electrodes, which could be attributed to the synergy of the hydrogenation treatment and the SPR effect of the Au nanoparticles.

Although the added energy levels (resulting from hydrogen treatment) of the Au@H-TiO<sub>2</sub> electrode could contribute to the visible light PEC performance, most photoexcited holes located at mid-gap energy levels do not have sufficient activation energy to drive the water oxidation. Therefore, the significant enhancement of photocurrents using the Au@H-TiO<sub>2</sub> electrode is very likely due to the efficient separation of photoexcited electron-hole pairs (resulting from SPR effect

of Au nanoparticles), which is attributed to the improved electrical conductivity of hydrogenated TiO<sub>2</sub>. This coincides with observations of the transient photocurrent measurements in Figure 3c, where a constant potential of 0.6 V is applied because the electrochemical currents of both electrodes are stable when the potential above 0.6 V in LSV. The pristine TiO<sub>2</sub> electrode generates a small photocurrent (2.5  $\mu\text{A cm}^{-2}$ ), while a dramatically larger photocurrent (77.8  $\mu\text{A cm}^{-2}$ ) is observed for the Au@H-TiO<sub>2</sub> electrode (vs. 0.6 V Ag/AgCl).



**Figure 3.** The LSV of the TiO<sub>2</sub>, H-TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes under (a) visible light and (b) UV light at a scanning rate of 10 mV s<sup>-1</sup>. Photocurrent profiles at 0.6 V in the dark and under (c) visible light and (d) UV light.

The LSV and transient photocurrent measurements under UV light are also performed in 0.1 M NaNO<sub>3</sub> solution and are shown in Figure 3b and d. The photocurrents of the hydrogenated samples (Au@H-TiO<sub>2</sub> and the H-TiO<sub>2</sub>) are much higher than the non-hydrogenated electrodes respectively

under UV light (Figure 3b and d), which is due to the hydrogenation-enhanced conductivity. The highest photocurrent ( $2.5 \text{ mA cm}^{-2}$  vs.  $0.6 \text{ V Ag/AgCl}$ ) of the Au@H-TiO<sub>2</sub> electrode than the H-TiO<sub>2</sub> resulted from *Schottky* barriers between TiO<sub>2</sub> and Au that facilitate the separation of photoelectron and hole, rather than the SPR effect as it is not active under UV light [29].

To confirm the mechanism of photocurrent enhancement by hydrogenation and to quantitatively quantify the photoelectron transfer performance of the photoelectrodes, the PEC reaction resistance is measured by a series of LSVs of the Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes under visible light illumination at different light intensities (see Figure S3). Compared to typical Ohmic resistance, the PEC reaction resistance ( $R_0$ ) is an intrinsic property of the electrode during the PEC reaction. The  $R_0$  can be obtained by the calculation using the photocurrent curves of Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes under visible light illumination with different light intensity according to the Equation S1 (see supporting information). The calculated  $R_0$  values for the Au@TiO<sub>2</sub> and Au@H-TiO<sub>2</sub> electrodes are 152.4 and 28.5  $\Omega$ , respectively. The significant decreased resistance of the Au@H-TiO<sub>2</sub> electrode is due to the oxygen vacancies from the hydrogenation treatment. The lower PEC resistance could be beneficial to electron transport and the separation of photoelectron-hole pairs. Under visible light the SPR photo-excited electrons from the Au particles at the Au@H-TiO<sub>2</sub> electrode can swiftly transfer to the counter electrode through H-TiO<sub>2</sub> leading to higher photocurrent compared with Au@TiO<sub>2</sub> [30]. This suggests that the enhancement of Au@H-TiO<sub>2</sub> electrodes is mainly due to the boosted conductivity of hydrogenated TiO<sub>2</sub> resulting from oxygen vacancy. Good electronic conductivity can improve the efficiency of electron transfer and reduce the recombination of electron-hole pairs to enhance the PEC degradation performance.

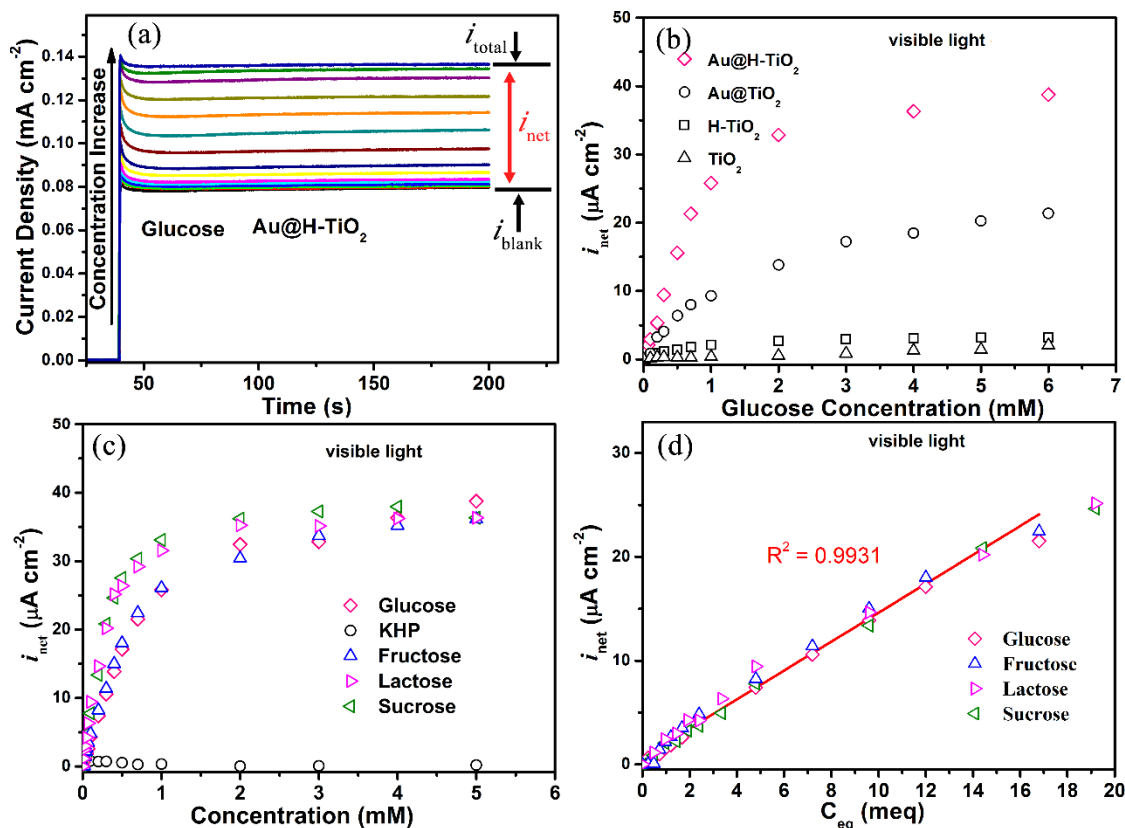
### **Feasibility of PEC sensor application**

The photodegrading organic compound performance of Au@H-TiO<sub>2</sub> is firstly characterized in 0.1 M NaNO<sub>3</sub> solution under a constant applied potential of +0.60 V and visible irradiation. As seen in Figure 4a, under the visible light, there is a stable background current ( $i_{\text{blank}}$ ) resulting from water oxidation at the surface of the electrode. Different photocurrents ( $i_{\text{total}}$ ) can be detected for glucose with diverse concentrations, and a net steady-state current ( $i_{\text{net}}$ ) can be obtained by subtracting  $i_{\text{blank}}$  from  $i_{\text{total}}$ .

$$i_{\text{net}} = i_{\text{total}} - i_{\text{blank}} \quad (1)$$

Because  $i_{\text{net}}$  represents the oxidation rate of the corresponding organic compounds using the different electrodes, it can be used to characterize the contribution of the SPR effect and hydrogenation treatment to PEC oxidation of a certain organic compounds as shown in Figure 4b. With the increase of glucose concentration, the  $i_{\text{net}}$  at TiO<sub>2</sub> and H-TiO<sub>2</sub> electrodes remain zero, which is attributed to the inability of TiO<sub>2</sub> and H-TiO<sub>2</sub> to PEC oxidize glucose under the visible light. In contrast, with the introduction of the plasmonic effect, the linearly increased  $i_{\text{net}}$  at the Au@TiO<sub>2</sub> electrode illustrates that the labile organic compounds, e.g. glucose, can be PEC oxidized by hot-hole at the plasmonic Au nanoparticles. Hydrogenation treatment further improves PEC performance, evidenced by the fact that the Au@H-TiO<sub>2</sub> electrode not only has the perfect linear relationship between  $i_{\text{net}}$  and glucose concentration but also presents the highest sensitivity towards all sugars (see Figure 4b and c). The calibration curves of  $i_{\text{net}}$  values versus the concentration of different types of sugars for Au@H-TiO<sub>2</sub> are plotted in Figure 4c. The Au@H-TiO<sub>2</sub> electrode presents an excellent linear calibration line from 0 to 1.0 mM due to the limiting step of mass transport of organic compounds. When the concentration of glucose, fructose, lactose and sucrose increase over 1.0 mM, the Au@H-TiO<sub>2</sub> electrode reaches its oxidation capacity and the photocurrents become steady. This result suggests excellent PEC performance of the Au@H-

TiO<sub>2</sub> electrode in photodegrading labile organic compounds under visible irradiation. Under visible illumination, however, the Au@H-TiO<sub>2</sub> electrode is non-photoactive to the varying concentration of KHP because KHP is chemically stable [31]. This represents a high selectivity feature of Au@H-TiO<sub>2</sub>, which can be used as PEC sensor to selectively detect labile organic compounds.



**Figure 4.** The PEC degradation of organic compounds under visible light: (a) Typical photocurrent profiles of the Au@H-TiO<sub>2</sub> electrode in various concentrations of glucose, (b) the plot of  $i_{net}$  against different concentrations of glucose for Au@H-TiO<sub>2</sub>, Au@TiO<sub>2</sub>, H-TiO<sub>2</sub> and TiO<sub>2</sub> electrodes under visible light, (c) the plot of  $i_{net}$  against different concentrations of glucose, fructose, lactose, sucrose and KHP for the Au@H-TiO<sub>2</sub> electrode, and (d) relationship between  $i_{net}$  and equivalent concentration ( $C_{eq}$ ) of glucose, fructose, lactose, sucrose and KHP, where  $C_{eq}$  (meq) =  $nC_M$  (mM) in 0.1 M NaNO<sub>3</sub> solution.



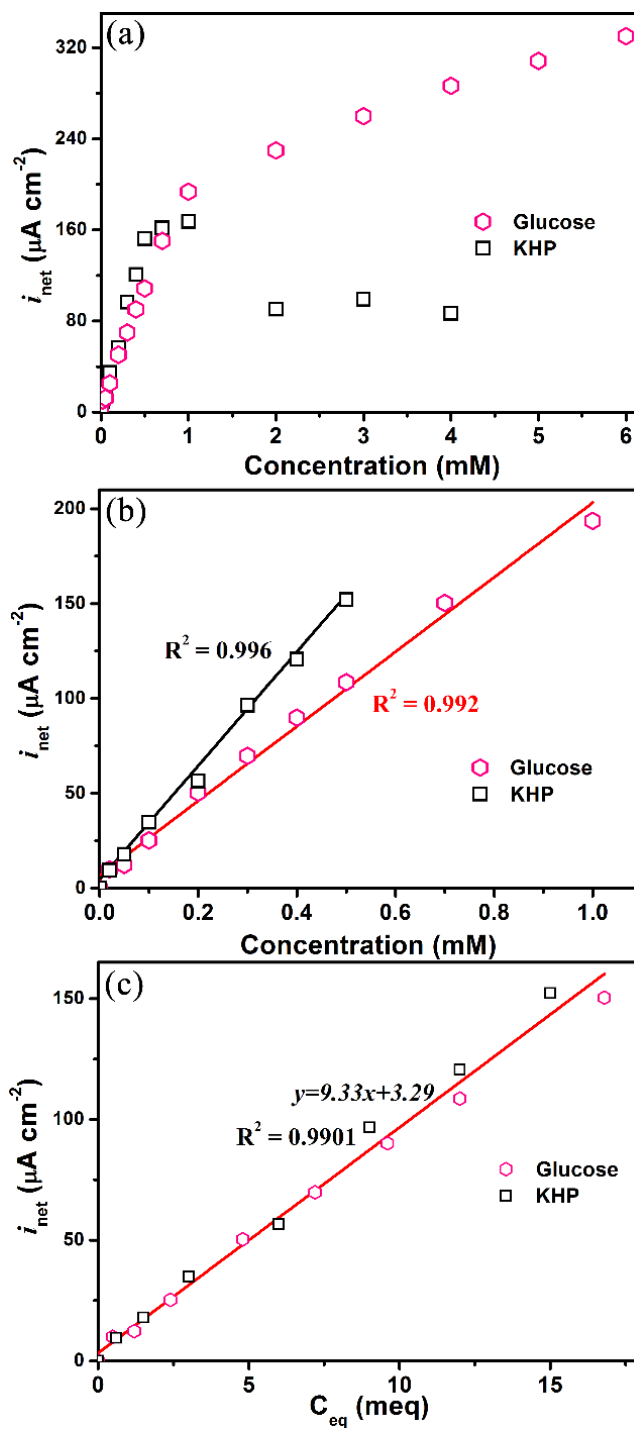
Additionally, the Au@H-TiO<sub>2</sub> electrode shows a higher sensitivity to lactose and sucrose than to glucose and fructose when the  $i_{\text{net}}$  values are plotted against the concentrations of different types of sugars (Figure 4c). This is due to the larger oxidation number of lactose (48 e) and sucrose (48 e) than fructose (24 e) and glucose (24 e). To calibrate the  $i_{\text{net}}$  curves, molar equivalent concentrations ( $C_{\text{eq}}$ , with a unit of meq) can be calculated by molar concentration ( $C_M$ ) with its corresponding oxidation number  $n$ .

$$C_{\text{eq}} = nC_M \quad (2)$$

Subsequently, the  $i_{\text{net}}$  value from Figure 4c were normalized and plotted against  $C_{\text{eq}}$  (Figure 4d). As expected, the linear fit of the data (in 0–20 meq) resulted in a  $R^2$  value of 0.9931. This excellent linear relationship suggests that the Au@H-TiO<sub>2</sub> photoanode is able to selectively oxidize different types of sugars to the same extent. This process is equivalent to “wet burning” the organic compounds at the photoanode surface.

In our tuneable PEC detection system, the number of types of detectable organic compounds can be increased by non-selective photodegradation under UV irradiation instead of visible light. Calibration curves of  $i_{\text{net}}$  values of UV PEC measurements versus the concentration of glucose or KHP for Au@H-TiO<sub>2</sub> electrodes are plotted in Figure 5. The  $i_{\text{net}}$  values increase with the increase in glucose and KHP concentration (Figure 5a), suggesting that either glucose or KHP can be degraded at the Au@H-TiO<sub>2</sub> electrode under UV illumination. An almost linear relationship between the  $i_{\text{net}}$  values of the Au@H-TiO<sub>2</sub> electrode and concentration can be clearly observed from 0 to 1.0 mM for both glucose and KHP (Figure 5b). Different from the glucose oxidation, KHP is a much more persistent organic compound than glucose. Therefore, the high concentration KHP lead to the oversupply of KHP to the TiO<sub>2</sub> surface. Due to the strong adsorption capability of KHP, the excessive KHP will be adsorbed onto the TiO<sub>2</sub> surface, leading to a typical poisoning

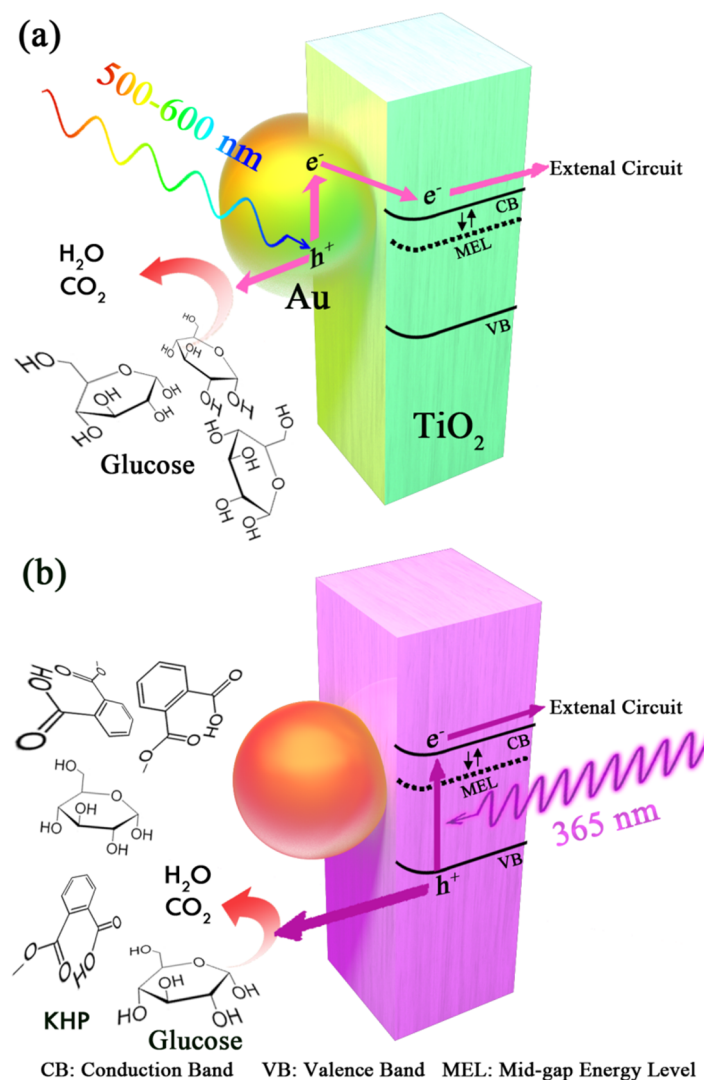
or inhibition effect to the electrode.[31] As a result, photocurrents decrease with the increased KHP concentrations in Fig. 5a. Due to the larger oxidation number of KHP (30 e) compared to glucose (24 e), the Au@H-TiO<sub>2</sub> electrode shows a higher sensitivity to KHP than to glucose. After conversion into TiO<sub>2</sub> photoanode is able to indiscriminately oxidize both types of organic compounds to water and CO<sub>2</sub> under UV illumination (Figure 5c). The linear relationship is of primary importance to analytical chemistry because it enables the Au@H-TiO<sub>2</sub> electrode to detect not only an individual organic compound but also aggregative parameters of organic compounds (*e.g.* COD in wastewater) with UV illumination. This characteristic allows the Au@H-TiO<sub>2</sub> to work as a universal sensor for organic compounds under UV irradiation and provides high selectivity for organic compounds detection, such as different kinds of sugars, under visible light. This tuneable feature could enable the Au@H-TiO<sub>2</sub> electrode to distinguish a specific organic compound from among several different organic compounds.



**Figure 5.** (a) Plots of  $i_{\text{net}}$  against different concentrations of glucose and KHP for Au@H-TiO<sub>2</sub> under UV light, (b) relationship between  $i_{\text{net}}$  and molar concentration  $C_M$ , (c) relationship between  $i_{\text{net}}$  and equivalent concentration  $C_{\text{eq}}$ , where  $C_{\text{eq}}$  (meq) =  $nC_M$  (mM) in 0.1 M NaNO<sub>3</sub> solution.

### **Application of PEC sensor in mixture solution**

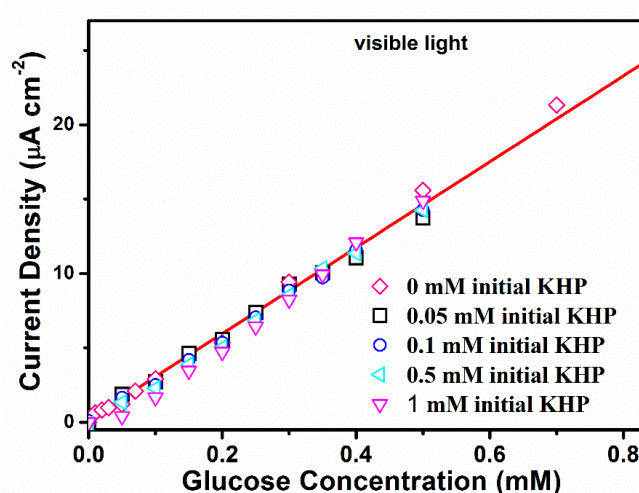
From the PEC performance under visible and UV illumination, the Au@H-TiO<sub>2</sub> can deliver light-directed selective and collective degradation of organic compounds as illustrated in Scheme 1. This selective degradation feature can be tuned by the selection of the irradiation wavelength. On one hand, with illumination by UV light, the Au@H-TiO<sub>2</sub> electrode can non-discriminately oxidize organic compounds, imparting the electrode as a universal sensor. On the other hand, the Au@H-TiO<sub>2</sub> photoelectrode is able to oxidize labile organic compounds in the presence of KHP due to insufficient oxidation ability caused by the LSPR effect. This property can be utilized to detect glucose in the presence of aromatic compounds without the need for separation processes. It is well established that the hydrogenation process could generate mid-gap energy levels (an example is shown in Scheme 1) [23]. Such mid-gap energy levels facilitate the absorption of longer wavelength of light. However, if the energy gap of the absorbed light is lower than water oxidation potential (1.23 eV, vs. NHE), the oxidation of water will not occur.



“**Scheme 1.** Tunable oxidation capability of the Au@H-TiO<sub>2</sub> photoelectrode: selective oxidation of labile organic compounds (a) under visible light and collective oxidation of various organic compounds (b) under UV light illumination (365 nm). The black dash lines between the upper conduction band (CB) and lower valence band (VB) represent a possible mid-gap energy level (MEL) due to the oxygen vacancy that generated by the hydrogenation process.”

To confirm the validity of detecting sugars in a mixed solution, the Au@H-TiO<sub>2</sub> electrode is applied in a glucose sensor with different initial concentrations of KHP under visible light. The calibration curves of  $i_{\text{net}}$  values versus the concentration of glucose in the presence of different

concentrations of KHP are plotted in Figure 6. In the absence of KHP, the obvious linear relationship of the  $i_{\text{net}}$  values of the Au@H-TiO<sub>2</sub> electrode can be clearly observed with the increased concentration of glucose. To assess the selective PEC detection of the Au@H-TiO<sub>2</sub> electrode, KHP of different concentrations is added as the initial electrolyte solution. The nearly perfect linear relationship between the  $i_{\text{net}}$  values of the Au@H-TiO<sub>2</sub> electrode with KHP concentrations from 0.05 mM to 1 mM is clearly observed. The negligible changes in  $i_{\text{net}}$  values in Figure 6 illustrate that the presence of KHP does not affect the detection of glucose. The Au@H-TiO<sub>2</sub> electrode can be an excellent sensor to sensitively and selectively detect glucose in KHP solutions.



**Figure 6.** Relationship between  $i_{\text{net}}$  and glucose concentration in the presence of different concentrations of KHP at the Au@H-TiO<sub>2</sub> electrode under visible light.

## Conclusions

TiO<sub>2</sub> nanorod arrays were synthesized and modified by plasmonic Au nanoparticles and hydrogenation treatments to enable the utilization of visible light for photoelectrocatalysis and enhance the electronic conductivity, respectively. The resultant Au@H-TiO<sub>2</sub> electrode could achieve selective PEC oxidation of sugars under visible light and collective PEC degradation of

various types of organic compounds under UV illumination. In this work, the Au@H-TiO<sub>2</sub> electrode has been developed as a versatile PEC sensor: it is capable of sensitively detecting sugars in the presence of aromatic compounds such as KHP under visible light without the need for solution separation, and determining collective organic compounds under UV illumination. This unique tunable detection capability of the Au@H-TiO<sub>2</sub> electrode will facilitate its use in new generation PEC sensors for organic compounds.

**Supporting Information.** The calculation of PEC reaction resistance, SEM images of TiO<sub>2</sub>, H-TiO<sub>2</sub> and Au@TiO<sub>2</sub> electrodes and EDS of Au@H-TiO<sub>2</sub> electrode are supported in supporting information.

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## REFERENCES

- [1] S. Zhang, D. Jiang, H. Zhao, Development of Chemical Oxygen Demand On-Line Monitoring System Based on a Photoelectrochemical Degradation Principle, *Environ Sci Technol*, 40(2006) 2363-8.
- [2] S. Zhang, L. Li, H. Zhao, A Portable Photoelectrochemical Probe for Rapid Determination of Chemical Oxygen Demand in Wastewaters, *Environ Sci Technol*, 43(2009) 7810-5.
- [3] L. Wang, T. Sasaki, Titanium Oxide Nanosheets: Graphene Analogues with Versatile Functionalities, *Chem Rev*, 114(2014) 9455-86.
- [4] S. Sarina, H. Zhu, Z. Zheng, S. Bottle, J. Chang, X. Ke, et al., Driving selective aerobic oxidation of alkyl aromatics by sunlight on alcohol grafted metal hydroxides, *Chemical Science*, 3(2012) 2138-46.
- [5] M.A. Lazar, W.A. Daoud, Achieving selectivity in TiO<sub>2</sub>-based photocatalysis, *RSC Adv*, 3(2013) 4130-40.
- [6] Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Dai, M.-H. Whangbo, Facile in situ synthesis of visible-light plasmonic photocatalysts M@TiO<sub>2</sub> (M = Au, Pt, Ag) and evaluation of their photocatalytic oxidation of benzene to phenol, *J Mater Chem*, 21(2011) 9079-87.
- [7] Y. Tian, T. Tatsuma, Mechanisms and Applications of Plasmon-Induced Charge Separation at TiO<sub>2</sub> Films Loaded with Gold Nanoparticles, *J Am Chem Soc*, 127(2005) 7632-7.
- [8] S. Pradhan, D. Ghosh, S. Chen, Janus Nanostructures Based on Au-TiO<sub>2</sub> Heterodimers and Their Photocatalytic Activity in the Oxidation of Methanol, *ACS Appl Mater Interfaces*, 1(2009) 2060-5.
- [9] L. Liu, T.D. Dao, R. Kodiyath, Q. Kang, H. Abe, T. Nagao, et al., Plasmonic Janus-Composite Photocatalyst Comprising Au and C-TiO<sub>2</sub> for Enhanced Aerobic Oxidation over a Broad Visible-Light Range, *Adv Funct Mater*, 24(2014) 7754-62.
- [10] T. Jiang, C. Jia, L. Zhang, S. He, Y. Sang, H. Li, et al., Gold and gold-palladium alloy nanoparticles on heterostructured TiO<sub>2</sub> nanobelts as plasmonic photocatalysts for benzyl alcohol oxidation, *Nanoscale*, 7(2015) 209-17.
- [11] S.T. Kochuveedu, Y.H. Jang, D.H. Kim, A study on the mechanism for the interaction of light with noble metal-metal oxide semiconductor nanostructures for various photophysical applications, *Chem Soc Rev*, 42(2013) 8467-93.
- [12] A. Furube, L. Du, K. Hara, R. Katoh, M. Tachiya, Ultrafast Plasmon-Induced Electron Transfer from Gold Nanodots into TiO<sub>2</sub> Nanoparticles, *J Am Chem Soc*, 129(2007) 14852-3.
- [13] M.A. Lazar, S. Varghese, S.S. Nair, Photocatalytic water treatment by titanium dioxide: recent updates, *Catalysts*, 2(2012) 572-601.
- [14] M. Zhang, C. Chen, W. Ma, J. Zhao, Visible-Light-Induced Aerobic Oxidation of Alcohols in a Coupled Photocatalytic System of Dye-Sensitized TiO<sub>2</sub> and TEMPO, *Angew Chem*, 120(2008) 9876-9.
- [15] S.-i. Naya, A. Inoue, H. Tada, Self-Assembled Heterosupramolecular Visible Light Photocatalyst Consisting of Gold Nanoparticle-Loaded Titanium(IV) Dioxide and Surfactant, *J Am Chem Soc*, 132(2010) 6292-3.
- [16] X. Lang, X. Chen, J. Zhao, Heterogeneous visible light photocatalysis for selective organic transformations, *Chem Soc Rev*, 43(2014) 473-86.
- [17] L. Li, S. Zhang, H. Zhao, A low cost universal photoelectrochemical detector for organic compounds based on photoelectrocatalytic oxidation at a nanostructured TiO<sub>2</sub> photoanode, *J Electroanal Chem*, 656(2011) 211-7.



- [18] W.-W. Zhao, C.-Y. Tian, J.-J. Xu, H.-Y. Chen, The coupling of localized surface plasmon resonance-based photoelectrochemistry and nanoparticle size effect: towards novel plasmonic photoelectrochemical biosensing, *Chem Commun*, 48(2012) 895-7.
- [19] J. Fang, S.-W. Cao, Z. Wang, M.M. Shahjamali, S.C.J. Loo, J. Barber, et al., Mesoporous plasmonic Au–TiO<sub>2</sub> nanocomposites for efficient visible-light-driven photocatalytic water reduction, *Int J Hydrogen Energ*, 37(2012) 17853-61.
- [20] T.C. Damato, C.C.S. de Oliveira, R.A. Ando, P.H.C. Camargo, A Facile Approach to TiO<sub>2</sub> Colloidal Spheres Decorated with Au Nanoparticles Displaying Well-Defined Sizes and Uniform Dispersion, *Langmuir*, 29(2013) 1642-9.
- [21] X. Zhang, Y. Liu, S.-T. Lee, S. Yang, Z. Kang, Coupling surface plasmon resonance of gold nanoparticles with slow-photon-effect of TiO<sub>2</sub> photonic crystals for synergistically enhanced photoelectrochemical water splitting, *Energ Environ Sci*, 7(2014) 1409-19.
- [22] T. Xia, X. Chen, Revealing the structural properties of hydrogenated black TiO<sub>2</sub> nanocrystals, *J Mater Chem A*, 1(2013) 2983-9.
- [23] X. Chen, L. Liu, P.Y. Yu, S.S. Mao, Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals, *Science*, 331(2011) 746-50.
- [24] R.B. Aggio, K. Ruggiero, S.G. Villas-Boas, Pathway Activity Profiling (PAPi): from the metabolite profile to the metabolic pathway activity, *Bioinformatics*, 26(2010) 2969-76.
- [25] S. Li, J. Qiu, M. Ling, F. Peng, B. Wood, S. Zhang, Photoelectrochemical Characterization of Hydrogenated TiO<sub>2</sub> Nanotubes as Photoanodes for Sensing Applications, *ACS Appl Mater Interfaces*, 5(2013) 11129-35.
- [26] B. Liu, E.S. Aydil, Growth of Oriented Single-Crystalline Rutile TiO<sub>2</sub> Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells, *J Am Chem Soc*, 131(2009) 3985-90.
- [27] J. Qiu, S. Li, E. Gray, H. Liu, Q.-F. Gu, C. Sun, et al., Hydrogenation Synthesis of Blue TiO<sub>2</sub> for High-Performance Lithium-Ion Batteries, *J Phys Chem C*, 118(2014) 8824-30.
- [28] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R.C. Fitzmorris, et al., Hydrogen-treated TiO<sub>2</sub> nanowire arrays for photoelectrochemical water splitting, *Nano Lett*, 11(2011) 3026-33.
- [29] Z. Zhang, J.T. Yates, Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces, *Chem Rev*, 112(2012) 5520-51.
- [30] C. Gomes Silva, R. Juárez, T. Marino, R. Molinari, H. García, Influence of Excitation Wavelength (UV or Visible Light) on the Photocatalytic Activity of Titania Containing Gold Nanoparticles for the Generation of Hydrogen or Oxygen from Water, *J Am Chem Soc*, 133(2010) 595-602.
- [31] Y. Han, S. Zhang, H. Zhao, W. Wen, H. Zhang, H. Wang, et al., Photoelectrochemical Characterization of a Robust TiO<sub>2</sub>/BDD Heterojunction Electrode for Sensing Application in Aqueous Solutions, *Langmuir*, 26(2009) 6033-40.

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