

# Tunable Wavelength Enhanced Photoelectrochemical Cells from Surface Plasmon Resonance

Hao Yang,<sup>†</sup> Zi-Han Wang,<sup>†</sup> Yan-Yu Zheng,<sup>†</sup> Lan-Qi He,<sup>†</sup> Chao Zhan,<sup>‡</sup> Xihong Lu,<sup>†</sup> Zhong-Qun Tian,<sup>‡</sup> Ping-Ping Fang,<sup>\*,†</sup> and Yexiang Tong<sup>†</sup>

<sup>†</sup>KLGHFI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

<sup>‡</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

## S Supporting Information

**ABSTRACT:** Photocatalysis is a promising technology for renewable energy production. Many photocatalysis have realized the visible-light-driven catalytic activity. However, it is still difficult to achieve the enhanced photocatalytic activity with tunable wavelength. We have designed tunable wavelength enhanced photoelectrochemical cells by tuning the surface plasmon resonance (SPR) peaks, which can be controlled by the aspect ratios of the Au nanorods, for both the cathode with the hydrogen evolution reaction and the anode with the electrooxidation of methanol reaction. The optimal photocatalytic activity of the hydrogen evolution and electrooxidation of the methanol can be realized only when the illuminating wavelength matches with the SPR peaks, which is quite selective to the illuminating wavelength. The blue shift of the SPR peak increases the photoelectrocatalytic effect whereas the red shift enhances the photothermal effect. Such studies provide a useful way for improving the photocatalytic activity and the selectivity of the photocatalytic reactions by adjusting the illuminating wavelength.

Solar energy conversion is a promising way to provide a sustainable energy source to meet the steadily increasing energy demand. Photocatalysis could be used to exploit the free energy of the sun in the search for new sustainable energy sources, which has now become the most promising green technology.<sup>1,2</sup> Solar energy can be converted and stored in chemical fuels with a photoelectrochemical system through photocatalytic reactions such as splitting water or reducing CO<sub>2</sub>.<sup>3,4</sup> Photocatalysis can not only produce H<sub>2</sub> or reduce CO<sub>2</sub>,<sup>5,6</sup> but also enhance the catalytic activity of reactions such as electrooxidation of methanol,<sup>1</sup> Suzuki coupling reaction<sup>7</sup> and so on. Currently, most of the photocatalytic reactions are easily realized under ultraviolet (UV) light irradiation, but are difficult to utilize the visible wavelengths that comprise most of the solar energy reaching the Earth's surface. In this regard, numerous efforts have been made to boost the visible-light-driven activity of these photocatalytic reactions from UV light to visible light and great progresses have been achieved.

Among the photocatalytic systems developed, plasmonic photocatalysis are one of the most extensively investigated

photocatalytic systems owing to their high solar energy utilization efficiency and possess great potential applications.<sup>8–10</sup> Surface plasmon resonance (SPR) effects have been widely used to construct visible-light-driven photocatalysts.<sup>11–13</sup> Tunable SPR ranging from visible to near-infrared has been achieved by tuning the aspect ratios of gold nanorods (Au NRs), which provides the possibility to enhance chemical reactions on their surface under light of particular frequencies illumination.<sup>14,15</sup> Nevertheless, the enhanced photocatalytic activity with such tunable wavelength is still very challenging and has not yet been realized. To make full utilization of the SPR absorption peaks to improve the photocatalytic activity of the corresponding reactions is still a great challenge. To realize the tunable wavelength enhanced photoelectrochemical cells with both the anode and the cathode tunable by the illuminating wavelength is even more difficult.

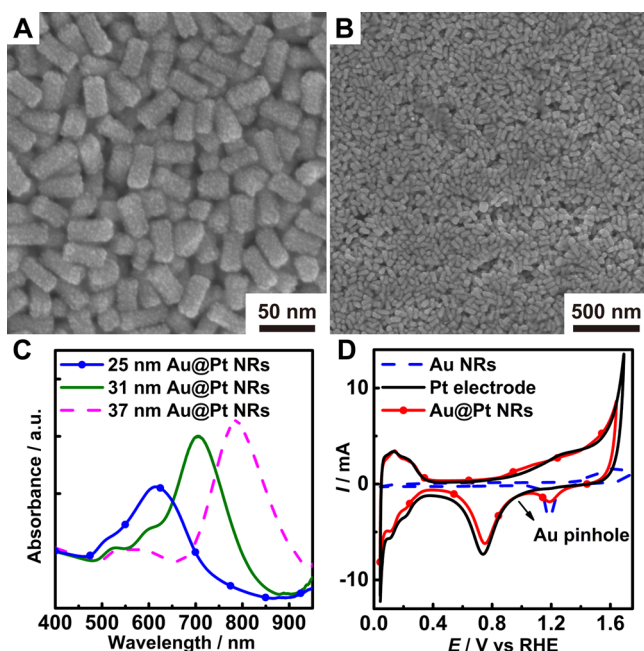
Herein, we realized the photoelectrochemical cells with tunable wavelength enhancement from Au nanorods coated by Pt clusters (denoted as Au@Pt NRs) with corresponding SPR peaks. The tunable wavelength enhanced photocatalytic activity for electroreduction of H<sub>2</sub>O to produce H<sub>2</sub>, and electrooxidation of methanol reactions could be readily realized by controlling the aspect ratios of the Au NRs with different SPR peaks. We systematically investigated the influence of the illuminating wavelength on the catalytic activity of the hydrogen evolution reaction and methanol electrooxidation reaction for Au@Pt NRs with different aspect ratios. Moreover, photoelectrochemical cells with the hydrogen evolution reaction as the cathode and methanol electrooxidation reaction as the anode were skillfully designed to investigate the tunable wavelength enhanced photocatalytic activity. The maximum photocatalytic activity enhancement was achieved by well matching the illumination wavelength with the SPR peaks of the Au@Pt NRs. Such photocatalytic activity was contributed by both the photoelectrocatalytic and the photothermal effects.

Au NRs with different plasmon resonance absorption peaks were first synthesized according to the literature,<sup>16</sup> and then coated with Pt clusters according to our previous work.<sup>17</sup> Detailed experiments are in S1 in the Supporting Information (SI). Scanning electron microscopy (SEM) and transmission

Received: September 29, 2016

Published: December 6, 2016

electron microscopy (TEM) images show that Pt clusters are successfully coated on the Au NRs, as shown in Figure 1A and



**Figure 1.** SEM images of 25 nm Au NRs on silicon (A) and on F-doped tin oxide coated glass (FTO) for electrochemical studies (B); (C) UV-vis absorption spectra of 25, 31 and 37 nm Au@Pt NRs on FTO; (D) CV curves of 31 nm Au NRs, 31 nm Au@Pt NRs and Pt electrode on FTO electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (pH = 0.76) with a scanning rate of 50 mV s<sup>-1</sup>.

S1 in the SI. The aspect ratios for these Au NRs are 2.5, 3.0 and 3.4, respectively. Figure 1B is the typical SEM images of the Au@Pt NRs on FTO, which are used as electrode for photocatalytic activity studies. As expected, we could tune the SPR peaks to be 613, 705 and 784 nm for 25, 31 and 37 nm Au@Pt NRs by adjusting the aspect ratios of the Au@Pt NRs (Figure 1C), respectively.

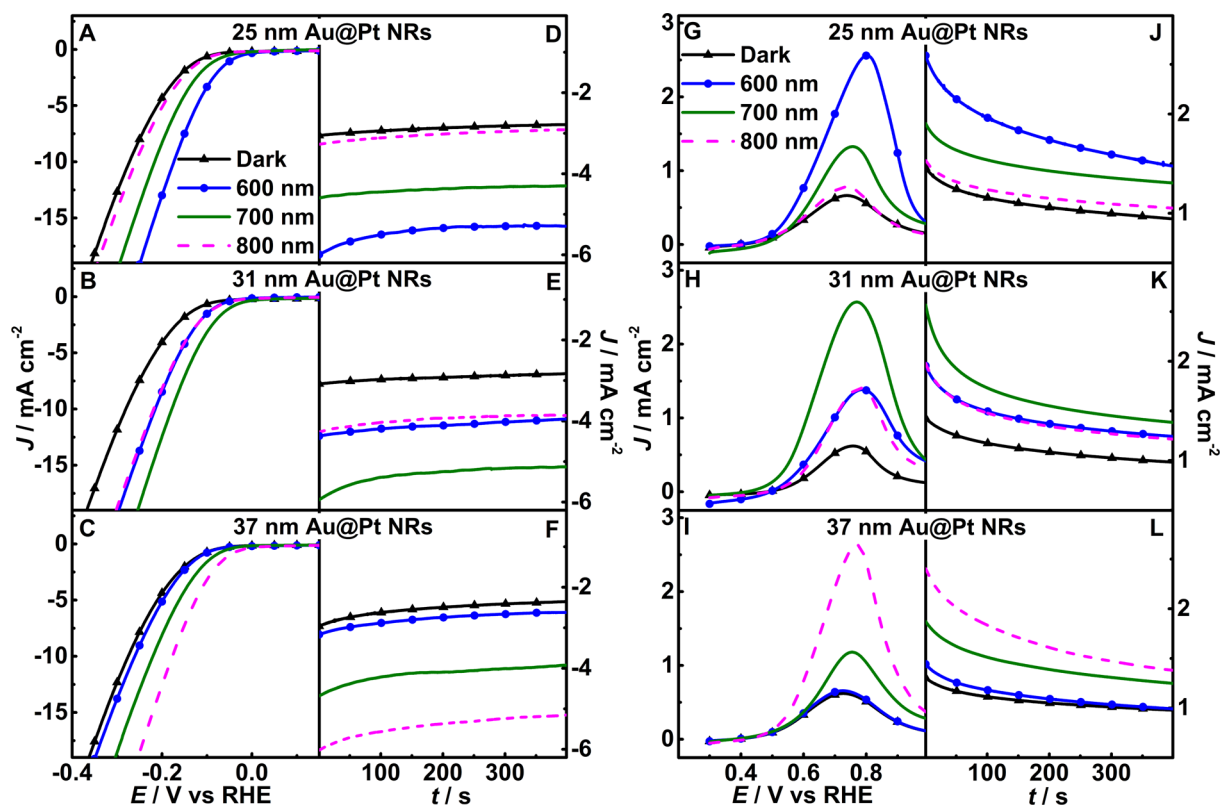
Electrochemical measurements were further used to identify the surface structure of the Au@Pt NRs. The reduction peak at about 1.2 V corresponds to the oxygen desorption on Au NRs whereas the peak at about 0.8 V compared to the reversible hydrogen electrode (RHE) corresponds to the oxygen desorption on Pt electrode in H<sub>2</sub>SO<sub>4</sub> solution according to the literature.<sup>18,19</sup> The cyclic voltammogram (CV) in Figure 1D shows the reduction peaks both at around 1.2 and 0.8 V for the Au@Pt NRs (Figure 1D), implicating that the Au sites were exposed on the surface,<sup>20</sup> instead of completely coated with Pt clusters.

The influences of the illuminating wavelength and SPR peak on the photocatalytic activity for the hydrogen evolution reaction by Au@Pt NRs with different aspect ratios were first investigated. Linear sweep voltammogram (LSV) curves of these Au@Pt NRs electrodes in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution under different illuminating wavelengths for each aspect ratio are shown in Figure 2A–C. The photocatalytic activity gradually increased with the illuminating time and then kept constant after about 30 min illumination (see S2 in the SI), and therefore we selected an illuminating time of 30 min for all the photocatalytic reactions. Interestingly, the catalytic activity enhancement is significantly dependent on the SPR peak and illuminating wavelength.

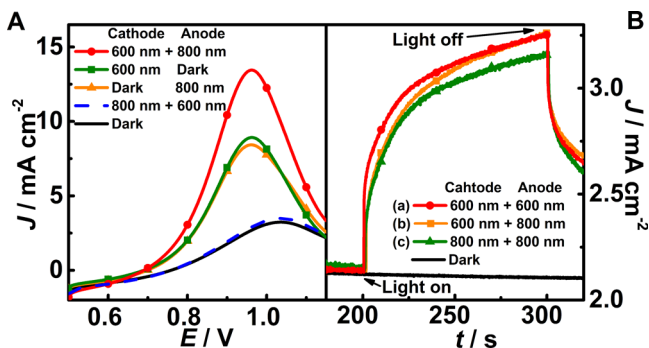
We analyzed the dependence of the photocatalytic activity on the SPR peak and illuminating wavelength in detail. LSV curves show that the 25 nm Au@Pt NRs with a SPR peak at about 613 nm exhibit the highest photocatalytic enhancement when the illuminating wavelength is at about 600 nm, whereas 700 and 800 nm wavelength illumination will make only weak catalytic activity enhancement (Figure 2A). This is due to the SPR absorption at 700 and 800 nm for the 25 nm Au@Pt NRs are weaker than at 600 nm (Figure 1C). Similarly, the 31 nm Au@Pt NRs with a SPR peak at about 708 nm exhibits the highest photocatalytic enhancement when the illuminating wavelength is at about 700 nm, and the 37 nm Au@Pt NRs with a SPR peak at about 784 nm exhibits the highest photocatalytic enhancement when the illuminating wavelength is at about 800 nm (Figure 2B,C). Additionally, the Pt clusters coated on nanoparticles without SPR exhibit weak photocatalytic activity (S3 in the SI), which indicates that the SPR from Au NRs is essential to enhance the photocatalytic activity. Therefore, the highest catalytic activity enhancement is achieved only when the illuminating wavelength matches with the SPR peak, which is further confirmed by the *I*–*t* curves collected at –0.10 V (Figure 2D–F). These results again demonstrate that the Au@Pt NRs yield the highest enhancement in photocatalytic activity when the illuminating wavelength matches well with their SPR peaks.

Next, we systematically investigated the influences of the illuminating wavelength and SPR peaks on the catalytic activity of the electrooxidation of methanol on the Au@Pt NRs. Similar as the hydrogen evolution reaction, the highest photocatalytic activity is achieved by illuminating the Au@Pt NRs with the corresponding SPR peak wavelength. Au@Pt NRs with a SPR peak at about 613, 705 and 784 nm exhibit the highest photocatalytic activity when the illuminating wavelength is 600, 700 and 800 nm, respectively (Figure 2G–I). *I*–*t* curves collected at 0.80 V also confirm that illuminating the Au@Pt NRs with a wavelength of the SPR peak gives the highest photocatalytic activity (Figure 2J–L). The photocatalytic activity will decrease when the illuminating wavelength is shifted away from the SPR peaks, which is similar to the photocatalytic activity of the hydrogen evolution reaction. Thus, the photocatalytic activity of the electrooxidation of methanol can be tuned by varying the illuminating wavelength taking advantage of the tunable SPR from Au@Pt NRs.

Lastly, a photoelectrochemical cell with the hydrogen evolution reaction as the cathode and electrooxidation of methanol reaction as the anode was designed to study the tunable wavelength enhanced photocatalytic activity. The 25 nm Au@Pt NRs with the absorption at about 613 nm were used as the cathode while the 37 nm Au@Pt NRs with the absorption at about 784 nm were used as the anode. The photocatalytic activity was enhanced by about 1 time when the cathode was illuminated with the 600 nm light or the anode was illuminated with the 800 nm light (Figure 3A), respectively. Most importantly, when the cathode was illuminated with the 600 nm light and the anode was illuminated with the 800 nm light at the same time, the photocatalytic activity was enhanced by almost 2 times (Figure 3A). However, if the cathode was illuminating with the 800 nm light and the anode was illuminating with the 600 nm light at the same time, a weak photocatalytic activity enhancement was gained (Figure 3A). *I*–*t* curves in S4 in the SI can further confirm these results. More group data of different anode and cathode illuminating with different wavelengths are listed in S5 in the SI. The maximum



**Figure 2.** (A–C) LSV curves of Au@Pt NRs with various absorption peaks in dark and illuminating with different wavelength for 30 min in a 0.5 M  $\text{H}_2\text{SO}_4$  solution (pH = 0.76) and (D–F) corresponding  $I-t$  curves at  $-0.10$  V for 400 s; (G–I) LSV curves of Au@Pt NRs with various absorption peaks in dark and illuminating with different wavelength for 30 min in a 1 M methanol + 0.5 M  $\text{H}_2\text{SO}_4$  solution (pH = 0.76) and (J–L) corresponding  $I-t$  curves at  $0.8$  V for 400 s.



**Figure 3.** (A) LSV curves of photoelectrochemical cells with 25 nm Au@Pt NRs as the cathode and the 37 nm Au@Pt NRs as the anode in a two-electrode configuration under different wavelength irradiation with a scanning rate of  $10 \text{ mV s}^{-1}$ . (B)  $I-t$  curves of the photoelectrochemical cells with different electrodes illuminating under the corresponding wavelength at  $0.90$  V for 400 s in a 1 M methanol + 0.5 M  $\text{H}_2\text{SO}_4$  solution (pH = 0.76) with light on 200 s.

photocatalytic activity enhancement is achieved only when the illuminating wavelengths match with the SPR peaks for all groups of anodes and cathodes, which is about 2 times higher than the photocatalytic activity without matching with the illuminating wavelength (Figure 3A). Therefore, the photocatalytic activity of the photoelectrochemical cells can be tuned by the illuminating wavelength, indicating its high selectivity to the illuminating wavelength.

We finally investigated the mechanism of the SPR enhanced catalytic activity for such photoelectrochemical cells. The

enhanced photocatalytic activity induced by SPR is caused by the photothermal and photoelectrocatalytic effects.<sup>1,21</sup> When the light was on, an immediate increase of the current was observed in the  $I-t$  curves (Figure 3B), which was contributed by the photoelectrocatalytic effect from the hot electrons.<sup>1</sup> Then the current began to increase as a result of the gradual increase of the temperature on the hot Au@Pt NRs surface due to the photothermal effect from the illumination (see S6 in the SI). Therefore, the photocatalytic activity of different Au@Pt NRs is contributed by both the photoelectrocatalytic and photothermal effects (Figure 3B).

$I-t$  curves with an immediate light on are used to calculate the quantitative contribution of the photoelectrocatalytic and photothermal effect according to our recent work (see S6 in the SI).<sup>1</sup> The current before switching on the light at 200 s was designed as  $i_0$  whereas the current after immediate illumination for 2 s was designed as  $i_1$ , and the contribution ratio for the photoelectrocatalytic effect would be  $(i_1 - i_0)/i_1$ . The 600 + 600 nm, 600 + 800 nm, 800 + 800 nm group exhibit a photoelectrocatalytic effect of about 19%, 14% and 11% (Figure 3B), respectively. The final temperature on the hot Au@Pt NRs surface after illuminating for 30 min is calculated from  $\nu_{\text{N}=\text{C}}$  of 4-methoxyphenyl isocyanide in surface enhanced Raman spectroscopy (see S6 in the SI). The hot spot temperature of different electrode, the quantitative contribution of the photoelectrocatalytic effect and the current density are summarized in Table 1. The final temperature for the 600 and 800 nm illuminating electrodes are 82 and 90 °C, but the final photocurrent density is 13.8 and 12.6  $\text{mA cm}^{-2}$ , indicating the short wavelength makes a higher photocatalytic activity

**Table 1. Photothermal Effect and Photoelectrocatalytic Effect for the Photoelectrochemical Cells with Various Au@Pt Electrodes**

illuminating wavelength		hot spot temperature (°C)		PEC effect <sup>a</sup> (%)	$J^b$ (mA cm <sup>-2</sup> )
cathode	anode	cathode	anode		
600 on 25 nm Au@Pt	600 on 25 nm Au@Pt	82	82	19	13.8
600 on 25 nm Au@Pt	800 on 37 nm Au@Pt	82	90	14	13.44
800 on 37 nm Au@Pt	800 on 37 nm Au@Pt	90	90	11	12.6

<sup>a</sup>Photoelectrocatalytic effect calculated by the  $I-t$  curves in Figure 3B and detail of the calculation can be seen in S6 in the SI. <sup>b</sup> $J$  is the peak current density of photoelectrochemical cells with various Au@Pt electrode in Figure S5 in the SI.

enhancement. Therefore, the blue shift of the SPR peak increases the photoelectrocatalytic effect whereas the red shift enhances the photothermal effect.

In conclusion, we have realized a tunable wavelength enhanced photoelectrochemical cell by tuning the SPR peaks of the Au@Pt NRs. The photocatalytic activity of the hydrogen evolution reaction and methanol electrooxidation reaction can be tuned by matching the SPR peaks with the illuminating wavelength. The highest photocatalytic activity enhancement is achieved when the illuminating wavelength is 600, 700 and 800 nm for the 25, 31 and 37 nm Au@Pt NRs, which matches with the SPR peaks of the Au@Pt NRs. The photocatalytic activity of the photoelectrochemical cells can be enhanced by 2-fold when the illuminating wavelength matches with the SPR peaks of the electrode. Both of photocatalytic activity of the cathode and the anode can be regulated by the matching of the illuminating wavelength with the SPR peaks. The photocatalytic activity is contributed by the photothermal and photoelectrocatalytic effects with a ratio of about 4 to 1. The shorter wavelength SPR peak can achieve higher photocatalytic activity. Such tunable wavelength enhanced catalytic activity provides a way to match the absorption of molecule, SPR peaks and illuminating wavelength to enhance both the photocatalytic activity and the selectivity, which would be very promising in the solar-energy harvesting and conversion reactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10205.

Experimental details; TEM images; electrochemical data of Au@Pt NRs under different illumination time; photoelectrochemical cell with different electrode; calculation of the temperature of the Au@Pt NRs surface (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*fangpp3@mail.sysu.edu.cn

### ORCID

Hao Yang: 0000-0002-9551-747X

Ping-Ping Fang: 0000-0001-9608-770X

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundations of China (Grant Nos. 21405182, 21476271, 21461162003 and 21403306), the National Basic Research Program of China (Grant Nos. 2015CB932300 and 2015CB932301) and the Natural Science Foundations of Guangdong Province (S2013030013474 and 2014KTSCX004).

## ■ REFERENCES

- (1) Yang, H.; He, L. Q.; Hu, Y. W.; Lu, X.; Li, G. R.; Liu, B.; Ren, B.; Tong, Y.; Fang, P. P. *Angew. Chem., Int. Ed.* **2015**, *54*, 11462.
- (2) Kale, M. J.; Avanesian, T.; Xin, H.; Yan, J.; Christopher, P. *Nano Lett.* **2014**, *14*, 5405.
- (3) Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. *J. Am. Chem. Soc.* **2016**, *138*, 4354.
- (4) Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.-T.; Zhong, J.; Kang, Z. *Science* **2015**, *347*, 970.
- (5) Liu, H.; Meng, X.; Dao, T. D.; Zhang, H.; Li, P.; Chang, K.; Wang, T.; Li, M.; Nagao, T.; Ye, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 11545.
- (6) Zheng, Z.; Tachikawa, T.; Majima, T. *J. Am. Chem. Soc.* **2015**, *137*, 948.
- (7) Wang, F.; Li, C.; Chen, H.; Jiang, R.; Sun, L.-D.; Li, Q.; Wang, J.; Yu, J. C.; Yan, C.-H. *J. Am. Chem. Soc.* **2013**, *135*, 5588.
- (8) Zheng, Z.; Tachikawa, T.; Majima, T. *J. Am. Chem. Soc.* **2014**, *136*, 6870.
- (9) Wu, B.; Liu, D.; Mubeen, S.; Chuong, T. T.; Moskovits, M.; Stucky, G. D. *J. Am. Chem. Soc.* **2016**, *138*, 1114.
- (10) Kale, M. J.; Christopher, P. *Science* **2015**, *349*, 587.
- (11) Zhang, J.; Jin, X.; Morales-Guzman, P. I.; Yu, X.; Liu, H.; Zhang, H.; Razzari, L.; Claverie, J. P. *ACS Nano* **2016**, *10*, 4496.
- (12) Brongersma, M. L.; Halas, N. J.; Nordlander, P. *Nat. Nanotechnol.* **2015**, *10*, 25.
- (13) Robotjazi, H.; Bahauddin, S. M.; Doiron, C.; Thomann, I. *Nano Lett.* **2015**, *15*, 6155.
- (14) Boerigter, C.; Campana, R.; Morabito, M.; Linic, S. *Nat. Commun.* **2016**, *7*, 10545.
- (15) Nishijima, Y.; Ueno, K.; Yokota, Y.; Murakoshi, K.; Misawa, H. *J. Phys. Chem. Lett.* **2010**, *1*, 2031.
- (16) Zhang, L.; Xia, K.; Lu, Z.; Li, G.; Chen, J.; Deng, Y.; Li, S.; Zhou, F.; He, N. *Chem. Mater.* **2014**, *26*, 1794.
- (17) Fang, P.-P.; Duan, S.; Lin, X.-D.; Anema, J. R.; Li, J.-F.; Buriez, O.; Ding, Y.; Fan, F.-R.; Wu, D.-Y.; Ren, B.; Wang, Z. L.; Amatore, C.; Tian, Z.-Q. *Chem. Sci.* **2011**, *2*, 531.
- (18) Zhang, J.; Huang, M.; Ma, H.; Tian, F.; Pan, W.; Chen, S. *Electrochem. Commun.* **2007**, *9*, 1298.
- (19) Marković, N. M.; Grgur, B. N.; Ross, P. N. *J. Phys. Chem. B* **1997**, *101*, 5405.
- (20) Tian, Z.-Q.; Ren, B.; Li, J.-F.; Yang, Z.-L. *Chem. Commun.* **2007**, 3514.
- (21) Sarina, S.; Zhu, H. Y.; Xiao, Q.; Jaatinen, E.; Jia, J.; Huang, Y.; Zheng, Z.; Wu, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 2935.