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Probing polarization modes of Ag nanowires with hot electron detection on Au/TiO_2 nanodiodes

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We report the effect of surface plasmons of silver nanowires (AgNWs) on the generation of hot electrons. The AgNWs were deposited on ultra-thin Au/TiO_2 Schottky nanodiodes using a spraying method. As surface coverage of the AgNWs on the thin gold film increased, the short-circuit current under illumination increased, showing the effect of the AgNWs on the energy conversion efficiency. Detection of the hot electron flow enhanced by the AgNWs on the Au/TiO_2 nanodiodes provides evidence of transverse (3.28 eV) and bulk silver (3.52 eV) plasmon modes that were confirmed by the measurement of the absorbance spectra of the AgNWs. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799156]

Nanostructured noble metals have been attractive for their unusual optical properties and widely utilized for effective light capture and solar energy conversion. Energy conversion in an ultrathin metal film on oxides, based on the excitation of charged carriers at the ultrathin metal surface during exothermic reactions or under illumination, has been studied for several decades.[1–5] The energy conversion phenomena associated with fast electrons have been demonstrated in catalytic reactions and photon absorption on metal films.[6–12] Nienhaus *et al.* directly detected charged carriers excited at the surface with a Schottky diode consisting of an ultrathin metal film and silicon, where the metal surface was exposed to hydrogen and deuterium atoms.[6] Gadzuk *et al.* suggested a theoretical model for the electronic nonadiabatic effects to account for the generation of energetic charged carriers during exothermic reactions.[13] The energetic charged carriers can be generated by absorption of photons and can be detected at the thin metal surface on oxide layers.[2,9,10] These energetic charged carriers are often called hot electrons.[1,4,8,13–16] Pump-probe experiments at femtosecond time scales reveal the presence of hot electrons with a kinetic energy of 1–3 eV that have elastic mean free paths in metals in the range of approximately 10 nm.

The generation of hot electrons by photon absorption on nanostructured noble metals can be a remarkable candidate for energy conversion because of the enhancement of photon absorption by collective charge oscillations, i.e., localized surface plasmons (LSPs) confined to the surface of nanostructured noble metals.[11] The properties of LSPs depend on the size, shape, and dielectric materials surrounding the metals.[17–20] Recently, nanostructured noble metals have gained significance for photovoltaic systems because of facile tunability of the optical cross section of the nanostructured noble metals. Absorption and scattering cross sections have been reported as a function of incident photon energy on nanodisks made of Ag, Au, Pt, and Pd with various diameters; the optical properties of the nanodisks can be tuned by the diameter of the nanodisks because of the branching ratio of the radiative to nonradiative LSPs decay channels.[21] Recently, it was also shown, both experimentally and theoretically, that LSPs on metal nanostructures enhance the hot electron flows across the Schottky barrier via internal photoemission.[11,22–25] Our previous work showed that the enhanced hot electron flows were directly observed on metal/semiconductor nanodiodes after modification of the thin film metal surface, such as continuous nano-sized islands and adsorption of dye molecules on the surface.[11,23] Knight *et al.* utilized hot electron-hole pairs generated from the decay of LSPs for photon detection using plasmonic antennas.[22] Thomas *et al.* reported the theoretical efficiency limit of plasmon-enhanced internal photoemission based on fundamental electronic properties of metallic absorbers and suggested a strategy to overcome the theoretical limit by modifying the electron density of states of the absorber via employment of alloys and quantum confinement effects.[24–26]

In our approach, we investigated the direct relationship between LSPs of nanowire-shaped noble metals and the generation of hot electrons to understand the energy conversion of nanostructured noble metals on an ultra-thin metal surface. The silver nanowires (AgNWs) were synthesized using the polyol process[27] and deposited on metal/semiconductor Schottky diodes as an absorbing layer for high photon energy. The photocurrent was detected on the AgNWs on metal/semiconductor Schottky diodes and the incident photon-to-electron conversion efficiency (IPCE) exhibited polarization modes of the AgNWs. The results show the effect of the AgNW's surface plasmons on the hot electron flows generated by photon absorption.

The metal/semiconductor Schottky diode of Au/TiO_2 has been fabricated to detect hot electron flow. Details of the device fabrication are described elsewhere.[8,28,29] First, an insulating p-type (100) silicon wafer covered by 500 nm SiO_2 is prepared for the vertically oriented Au/TiO_2 Schottky diodes. The role of the 500 nm SiO_2 layer is to electrically insulate the silicon wafer and titanium oxide layer. A

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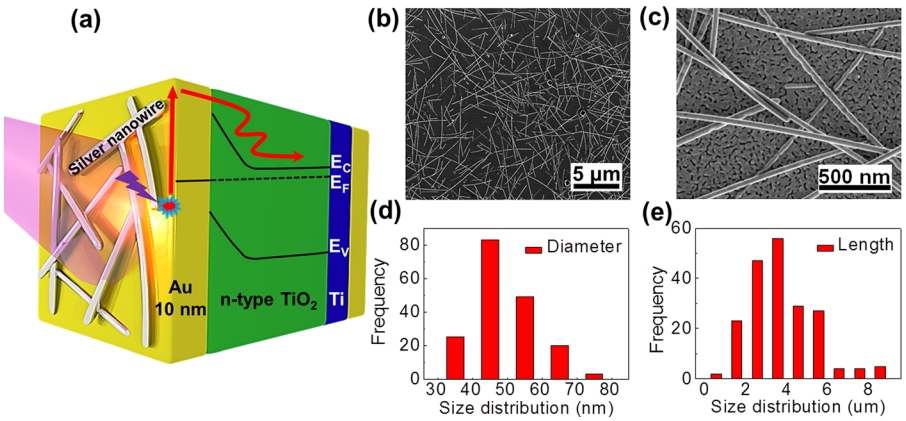

FIG. 1. (a) Scheme for hot electron flow generated by surface plasmons on AgNWs from photon absorption on the AgNWs deposited on the Au/TiO_2 diode and the energy band diagram for Schottky diode-based hot electron detection. (b), (c) Scanning electron microscopy images of the AgNW-deposited thin gold film (10 nm thickness) on the Au/TiO_2 diode. (d) Plot of the size distribution of the diameter of the AgNWs. (e) Plot of the size distribution of the length of the AgNWs.

4×6 mm, 200 nm-thick film of titanium oxide is then deposited onto the silicon oxide through an aluminum shadow mask using a multi-target sputtering system. To control the sheet resistance of the titanium oxide film, the wafer is then annealed in air at 450 °C for 3 h; this annealing changes the concentration of the oxygen vacancies as a dopant in the TiO_2 film for n-type TiO_2. The next step is deposition of a 50 nm-thick film of titanium and then a 150 nm film of gold, which constitute the nanodiode's two ohmic electrodes, through a second mask using electron beam evaporation. Finally, a thin gold film (10 ± 2 nm thick) is deposited through a third mask for formation of the Schottky contact.

The AgNWs were synthesized using the polyol process.[27] 5.86 g of poly(vinyl pyrrolidone) (PVP) (Mw 55 000) was added to 190 ml glycerol and the mixture was heated in a clean beaker at 150 °C for 2 h to remove any moisture remaining in the PVP. The solution was then moved to a clean two-neck flask and cooled down to 55 °C. Next, 0.059 g of sodium chloride, 0.5 ml of deionized water, and 10 ml of glycerol were added to the prepared PVP and glycerol solution, along with 1.58 g of silver nitrate. The suspension was rapidly heated to 155 °C (within 10 min) and kept there for 20 min for further reaction. During the whole process, a magnetic bar was used to gently stir the solution. The final product was centrifuged for 30 min at 6000 rpm and then redispersed in methanol. We repeated the centrifugation and redispersion steps twice more. Finally, the washed AgNWs were stored in methanol. We kept the suspension on a shaker to prevent aggregation. The AgNWs were deposited on the Au/TiO_2 surface using a spraying method. The surface coverage of the AgNWs was precisely controlled by changing the number of paths the spray nozzle moved forward and backward. The photocurrent was measured with a source-meter (Keithley Instrumentation, 2400) under illumination from a tungsten-halogen lamp with a normal incidence angle. The lamp power was 9 mW/cm^2 and the distance from the lamp to the diode was 10 cm. In order to measure the IPCE of the diodes, the short circuit current was measured as a function of incident photon energy. The optical properties of the AgNWs were characterized using a UV-VIS spectrophotometer (UV-3600, Shimadzu); the AgNWs were deposited on a (1/16 in. thick) quartz substrate and the instrument was used in standard setup mode. A clean quartz substrate was used as a reference to remove the absorption and reflection of the quartz substrate.

The nanostructure of the AgNWs was employed to demonstrate the effect of the AgNWs on hot electron flow. Since the high aspect ratio of the AgNWs gives rise to a clear signature of polarization modes, the measurement of photocurrent on AgNWs on metal/semiconductor nanodiodes can reveal the evidence of hot electron flow and, at the same time, polarization modes generated by the AgNWs.[30–33] The energy band diagram of the AgNW-deposited diode is described in Fig. 1(a). To generate and detect hot electrons, the energetic charge carriers need enough energy to pass through the 10 nm-thick gold film and travel over the Schottky barrier and into the TiO_2 conduction band. We describe a scheme for light absorption of ultra-violet wavelength via LSPs on the AgNWs. Figures 1(b) and 1(c) are scanning electron microscopy (SEM) images of AgNWs on Au/TiO_2 at two different magnifications, showing the AgNWs with a surface coverage of 15.1%. The size distributions of the diameter and the length of the AgNWs are obtained based on the SEM images (Figs. 1(d) and 1(e),

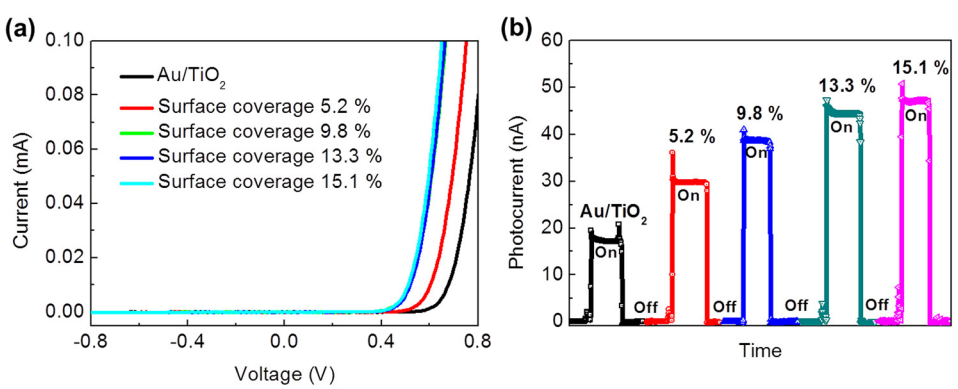

FIG. 2. (a) I-V curves of Au/TiO_2 diodes after deposition of the AgNWs showing that the rectifying behavior of the diode was well maintained. (b) Plot of the short-circuit photocurrent measured on the AgNWs deposited on the Au/TiO_2 diode under illumination from a tungsten-halogen lamp. The short-circuit currents increase with subsequent depositions of AgNWs on the diode.

respectively), where the average diameter and length of the AgNWs are approximately 44 nm and 3.2 μm, respectively, indicating that the aspect ratio of the AgNWs is roughly 73:1.

Figure 2(a) shows current-voltage (I-V) characteristic curves of Au/TiO_2 diodes measured after deposition of the AgNWs at several different concentrations. Surface coverage in Fig. 2(a) represents the fraction of the AgNWs covering the thin gold film. Because the Schottky barrier of Ag/TiO_2 (0.8 eV) is lower than Au/TiO_2 (1.1 eV),[34–37] the effective Schottky barrier decreases as the concentration of the AgNWs increases, due to the direct contact between the AgNWs and TiO_2. In the range of surface coverage from 9.8% to 15.1%, the shapes of the I-V curves remain almost consistent and the rectifying behavior of the diode was well preserved, as shown in Fig. 2(a). The photocurrent was measured after each AgNW deposition step under illumination with a tungsten-halogen lamp (9 mW/cm^2) at a normal incidence angle (Fig. 2(b)).

Deposition of the AgNWs on the thin gold film enhanced the photocurrent, but the photocurrent eventually became saturated because the thick AgNW film could block the incident light from propagating to the thin gold and TiO_2 films as absorbing layers. Figures 3(a) and 3(b) show SEM images of the AgNWs on the thin gold film. The amount of AgNWs was precisely adjusted by an automated spraying system. The frequency of the AgNWs in Fig. 3(a) is smaller than that of Fig. 3(b). The uniform deposition of the AgNWs on the surface is confirmed, as shown in Fig. 3. To confirm the optical properties of the AgNWs, the absorbance spectra of AgNWs deposited on quartz were measured (Fig. 3(c)). The absorbance spectrum of the surface coverage at 15.1% on quartz clearly shows a well-resolved maximum at 3.48 eV and a shoulder at approximately 3.30 eV, whereas the surface coverage at 5.2% does not show two well-defined peaks (Fig. 3(c)). As the deposited amount of AgNWs increases, the two growing peaks could be attributed to the polarization modes of the LSPs of the AgNWs.[38] To confirm the hot electron flow generated by the AgNWs, we measured IPCE as a function of incident photon energy on the AgNW-deposited Au/TiO_2 diodes with the thin gold film. Figure 4(a) compares the IPCE of the AgNW-deposited diode with that of the reference diode having no AgNWs. The plot comparing the IPCE shows increases at two points at around 3.52 eV and 3.28 eV. To magnify the increment of the IPCE plots, Fig. 4(b) is obtained by subtracting the IPCE of the reference diode from that of the diode with adsorbed AgNWs. Clear peaks are present at 3.52 eV and 3.28 eV, which positions are consistent with those in the absorbance spectra of the AgNWs (3.48 eV and 3.30 eV), as shown in Fig. 3(c). The two peaks observed in the IPCE and absorbance spectra are most likely associated with the bulk plasmon of the silver film and the transverse modes generated by the aspect ratio of the AgNWs, respectively. Sun *et al.* observed the plasmon resonances, according to the aspect ratio of the AgNWs, increased with the elongation of growth time.[38,39] As the aspect ratio increases from nanoparticles to nanowires, the longitudinal plasmon mode red-shifted significantly, as predicted by discrete dipole approximation (DDA) calculations and, finally, disappeared when the aspect ratio was greater than 5. However, the position of the transverse plasmon mode stayed relatively constant at 380 nm. At the same time, optical signatures similar to bulk silver appeared, as indicated by a shoulder around 350 nm, which could be attributed to the plasmon resonance of the bulk silver film. The polarization modes of the plasmon resonances of the extinction spectra were detected with a polarized UV-VIS spectrometer by Tao *et al.*[40] The close-packed AgNWs, approximately 50 nm in diameter and 2–3 μm in length, exhibited plasmon resonance modes at 350 nm (bulk

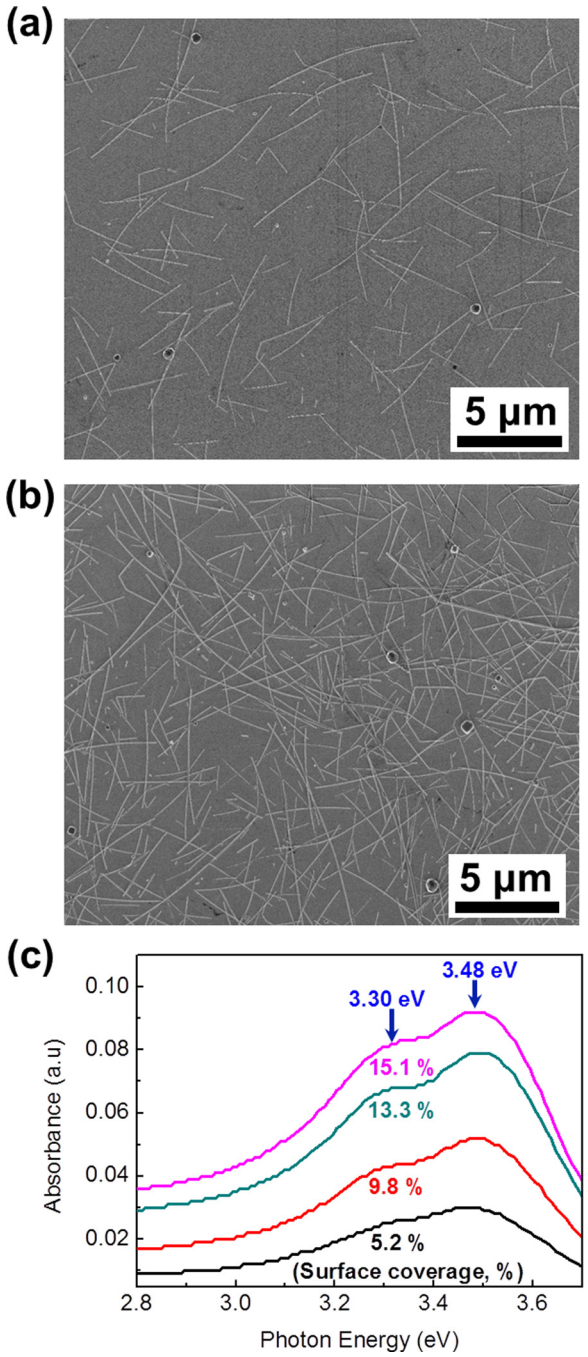

FIG. 3. Scanning electron microscopy images of the AgNW-deposited thin gold film (10 nm thickness) in the Au/TiO_2 diode. (a) 5.2% surface coverage, (b) 15.1% surface coverage. (c) UV-VIS spectra of the AgNWs deposited on quartz. Bare quartz was set up as a reference to subtract out the absorption of the quartz. The absorbance spectra exhibit two peaks at 3.3 eV and 3.48 eV. As the surface coverage of the AgNWs increases, the spectra signal is enhanced and the two peaks in the spectra become clearer.

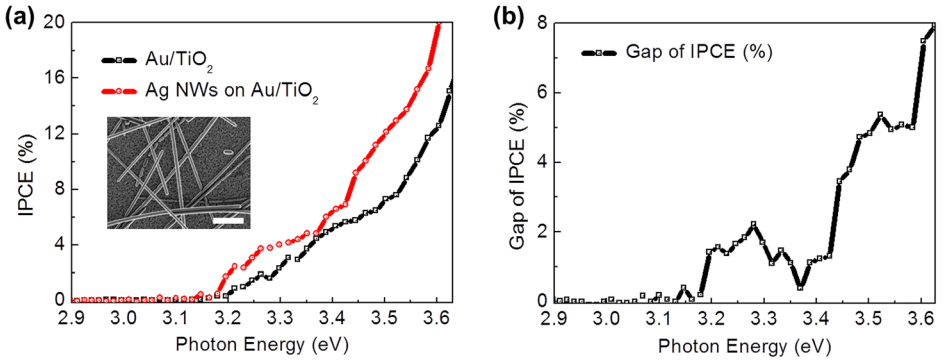

FIG. 4. (a) IPCE plots as a function of photon energy measured on the Au/TiO_2 diode with a 10 nm metal film showing the overall enhancement of the IPCE after deposition of the AgNWs. (Scale bar of inset is 500 nm.) (b) The difference (gap) between the IPCE plots of the AgNW-deposited diode and the reference diode without the AgNWs. This gap shows clear peaks at around 3.52 eV and 3.28 eV, which are in good agreement with the peak positions of the UV-VIS spectra of the AgNWs.

plasmon mode of silver) and 380 nm (transverse plasmon mode). We also note that the spatially non-local effect in the AgNWs has transverse surface plasmon modes that interact with the longitudinal bulk modes, modifying the surface plasmon dispersion relationship.[41,42] The effect becomes especially noticeable when the AgNWs get thinner. The effect of the spatially non-local effect in the AgNWs can be further studied by varying the diameter of the AgNWs.

The apparent peaks of the IPCE plot after deposition of the AgNWs suggest that hot electron detection can be utilized to reveal the polarization modes of surface plasmons. The presence of AgNWs has significance in the generation of hot electrons through direct energy conversion, which was enhanced by surface plasmon resonances on nanostructured noble metals, as illustrated in Fig. 2(b). In addition, using the polarization dependency based on the surface plasmon resonances is a promising way to investigate the direct energy conversion and to utilize the nanostructured noble metal as an energy harvesting material due to the easy tunability of the optical properties.

In conclusion, the hot electron flow generated by AgNWs was detected on the metal/semiconductor diode by measuring photocurrent as a function of the incident photon energy. The aspect ratio of the AgNWs produced the polarization modes of the surface plasmon resonances. The absorbance spectra of the AgNW film deposited on quartz substrates were measured using the UV-VIS spectrometer, revealing the plasmon modes of the bulk silver and the transverse by the LSPs of the AgNWs. The peaks originating from amplified hot electrons in the IPCE plot correspond with those of absorbance spectra, implying direct energy conversion from the bulk silver and the transverse plasmon modes to hot electrons. The strong correlation of the photocurrent and UV-VIS spectra shows the possibility for manipulating the energy conversion in a specific range of the photon energy.

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[1]G. A. Somorjai, K. M. Bratlie, M. O. Montano, and J. Y. Park, J. Phys. Chem. B **110**(40), 20014 (2006).
[2]A. Furube, L. Du, K. Hara, R. Katoh, and M. Tachiya, J. Am. Chem. Soc. **129**(48), 14852 (2007).
[3]J. R. Trail, M. C. Graham, D. M. Bird, M. Persson, and S. Holloway, Phys. Rev. Lett. **88**(16), 166802 (2002).
[4]Y. Huang, A. M. Wodtke, H. Hou, C. T. Rettner, and D. J. Auerbach, Phys. Rev. Lett. **84**(13), 2985 (2000).
[5]S. K. Dasari, M. A. Hashemian, J. Mohan, and E. G. Karpov, Chem. Phys. Lett. **553**, 47 (2012).
[6]H. Nienhaus, H. S. Bergh, B. Gergen, A. Majumdar, W. H. Weinberg, and E. W. McFarland, Phys. Rev. Lett. **82**(2), 446 (1999).
[7]L. Hellberg, J. Stromquist, B. Kasemo, and B. I. Lundqvist, Phys. Rev. Lett. **74**(23), 4742 (1995).
[8]J. Y. Park and G. A. Somorjai, J. Vac. Sci. Technol. B **24**(4), 1967 (2006).
[9]Y. Tian and T. Tatsuma, J. Am. Chem. Soc. **127**(20), 7632 (2005).
[10]Y. Tian, H. Notsu, and T. Tatsuma, Photochem. Photobiol. Sci. **4**(8), 598 (2005).
[11]Y. K. Lee, C. H. Jung, J. Park, H. Seo, G. A. Somorjai, and J. Y. Park, Nano Lett. **11**(10), 4251 (2011).
[12]G. A. Somorjai, H. Frei, and J. Y. Park, J. Am. Chem. Soc. **131**(46), 16589 (2009).
[13]J. W. Gadzuk, J. Phys. Chem. B **106**(33), 8265 (2002).
[14]B. Kasemo, E. Tornqvist, J. K. Norskov, and B. I. Lundqvist, Surf. Sci. **89**(1–3), 554 (1979).
[15]H. Nienhaus, Surf. Sci. Rep. **45**(1–2), 3 (2002).
[16]J. Y. Park, J. R. Renzas, A. M. Contreras, and G. A. Somorjai, Top. Catal. **46**(1–2), 217 (2007).
[17]K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. B **107**, 668 (2003).
[18]S. Eustis and M. A. El-Sayed, Chem. Soc. Rev. **35**(3), 209 (2006).
[19]I. O. Sosa, C. Noguez, and R. G. Barrera, J. Phys. Chem. B **107**(26), 6269 (2003).
[20]C. J. Murphy, T. K. San, A. M. Gole, C. J. Orendorff, J. X. Gao, L. Gou, S. E. Hunyadi, and T. Li, J. Phys. Chem. B **109**(29), 13857 (2005).
[21]C. Langhammer, B. Kasemo, and I. Zoric, J. Chem. Phys. **126**(19), 194702 (2007).
[22]M. W. Knight, H. Sobhani, P. Nordlander, and N. J. Halas, Science **332**(6030), 702 (2011).
[23]Y. K. Lee, J. Park, and J. Y. Park, J. Phys. Chem. C **116**(35), 18591 (2012).
[24]T. P. White and K. R. Catchpole, Appl. Phys. Lett. **101**, 073905 (2012).
[25]M. Shanthil, R. Thomas, R. S. Swathi, and K. G. Thomas, J. Phys. Chem. Lett. **3**(11), 1459 (2012).
[26]P. V. Kamat, J. Phys. Chem. C **112**(48), 18737 (2008).
[27]C. Yang, H. W. Gu, W. Lin, M. M. Yuen, C. P. Wong, M. Y. Xiong, and B. Gao, Adv. Mater. **23**(27), 3052 (2011).
[28]J. Y. Park, H. Lee, J. R. Renzas, Y. W. Zhang, and G. A. Somorjai, Nano Lett. **8**(8), 2388 (2008).
[29]J. Y. Park and G. A. Somorjai, ChemPhysChem **7**(7), 1409 (2006).
[30]L. J. E. Anderson, C. M. Payne, Y. R. Zhen, P. Nordlander, and J. H. Hafner, Nano Lett. **11**(11), 5034 (2011).
[31]Z. P. Li, K. Bao, Y. R. Fang, Y. Z. Huang, P. Nordlander, and H. X. Xu, Nano Lett. **10**(5), 1831 (2010).
[32]H. Wei, F. Hao, Y. Z. Huang, W. Z. Wang, P. Nordlander, and H. X. Xu, Nano Lett. **8**(8), 2497 (2008).
[33]G. Schider, J. R. Krenn, W. Gotschy, B. Lamprecht, H. Ditlbacher, A. Leitner, and F. R. Aussenegg, J. Appl. Phys. **90**(8), 3825 (2001).
[34]X. Wu and E. S. Yang, IEEE Electron Device Lett. **11**(7), 315 (1990).

[35]X. Wu, M. T. Schmidt, and E. S. Yang, Appl. Phys. Lett. **54**(3), 268 (1989).
[36]T. Q. Tuy and I. Mojzes, Appl. Phys. Lett. **56**(17), 1652 (1990).
[37]D. Spaltmann, J. Geurts, N. Esser, D. R. T. Zahn, W. Richter, and R. H. Williams, Semicond. Sci. Technol. **7**(3), 344 (1992).
[38]Y. Sun, Y. Yin, B. T. Mayers, T. Herricks, and Y. Xia, Chem. Mater. **14**(11), 4736 (2002).
[39]Y. G. Sun, B. Gates, B. Mayers, and Y. N. Xia, Nano Lett. **2**(2), 165 (2002).
[40]A. Tao, F. Kim, C. Hess, J. Goldberger, R. R. He, Y. G. Sun, Y. N. Xia, and P. D. Yang, Nano Lett. **3**(9), 1229 (2003).
[41]X. Y. He, J. Opt. Soc. Am. B **26**(9), A23 (2009).
[42]X. Y. He, J. Opt. Soc. Am. B **27**(11), 2298 (2010).