Photocatalysis

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Controlling the Selectivity of the Surface Plasmon Resonance Mediated Oxidation of *p*-Aminothiophenol on Au Nanoparticles by Charge Transfer from UV-excited TiO_2**

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Abstract: *Although catalytic processes mediated by surface plasmon resonance (SPR) excitation have emerged as a new frontier in catalysis, the selectivity of these processes remains poorly understood. Here, the selectivity of the SPR-mediated oxidation of p-aminothiophenol (PATP) employing Au NPs as catalysts was controlled by the choice of catalysts (Au or TiO_2-Au NPs) and by the modulation of the charge transfer from UV-excited TiO_2 to Au. When Au NPs were employed as catalyst, the SPR-mediated oxidation of PATP yielded p,p-dimercaptobenzene (DMAB). When TiO_2-Au NPs were employed as catalysts under both UV illumination and SPR excitation, p-nitrophenol (PNTP) was formed from PATP in a single step. Interestingly, PNTP molecules were further reduced to DMAB after the UV illumination was removed. Our data show that control over charge-transfer processes may play an important role to tune activity, product formation, and selectivity in SPR-mediated catalytic processes.*

Nanomaterials that display both high catalytic activities and selectivities are of great importance in the field of heterogeneous catalysis, as they make it possible to minimize the formation of side products and the need for several purification steps.[1,2] As an example, catalytic routes for the synthesis of aromatic azocompounds from the oxidation of anilines or the reduction of nitroaromatics under mild conditions offer high yields but selectivities remain challenging.[3,4] Nonetheless, this is of great importance as they represent high-value compounds that are widely employed in industry.[3–5]

Recently, catalytic processes mediated or enhanced by the surface plasmon resonance (SPR) excitation in plasmonic nanomaterials, such as gold (Au) and silver (Ag), have emerged as a new frontier in heterogeneous catalysis.[6–10] This approach allows for the use of light as the energy input to drive chemical transformations. The oxidation of *p*-aminothiophenol (PATP) to *p*,*p*-dimercaptoazobenzene (DMAB) has been widely used as a model reaction to probe SPR-mediated catalytic activities of Au and Ag NPs.[11–15] In this process, it has been shown that the transfer of hot electrons from the SPR-excited metal NPs to adsorbed O_2 molecules from air is responsible for O_2 activation, which generates $^3O_2$ species that subsequently drive the PATP oxidation.[11–16] Although several examples have been reported on the SPR-mediated or SPR-enhanced catalysis of Au and Ag NPs, studies on the selectivity of these processes remain scarce and challenging despite its great importance in catalysis. As the activation of molecular oxygen (O_2) represents a critical step in this and several other oxidation reactions, the control over the charge states in the metal may represent an effective approach to tune its activities and selectivities.[6,17–20] In order to control the charge states in a metal, however, it is necessary to introduce an additional electron source into the system. In this context, charge transfer from a semiconducting material, such as TiO_2, represents an intuitive strategy.[21,22]

Here, we show that the selectivity in SPR-mediated oxidation of PATP by Au NPs can be controlled by maneuvering its charge state via charge transfer from UV-excited TiO_2 to Au. More specifically, while the SPR-mediated oxidation of PATP in Au NPs led to the formation of DMAB, the use of TiO_2-Au NPs as catalysts under both UV and SPR excitation led to a one-step oxidation of PATP to *p*-nitrophenol (PNTP). Moreover, PNTP could be further reduced to DMAB on the TiO_2-Au NPs when the UV-excitation was turned off.

Figure 1 a and b shows SEM images for the Au NPs and TiO_2 colloidal spheres decorated with Au NPs (TiO_2-Au) that were employed as catalysts in the SPR-mediated oxidation of PATP. The TiO_2-Au colloidal spheres were obtained by a protocol recently developed in our group that consists of the use of TiO_2 colloidal spheres as physical templates for Au deposition.[23] Figure 1 a shows that the TiO_2-Au material displayed a spherical shape of relatively uniform size with a diameter of about 200 nm and comprised of 20 nm Au NPs at the surface. Moreover, the deposited Au NPs were uniformly distributed over the TiO_2 surface without significant aggregation. In order to compare the catalytic activity of the TiO_2-Au material with their Au NPs counterpart, Au NPs were synthetized under similar experimental conditions as described in Figure 1 a, but in the absence of TiO_2. Figure 1 b shows that the size of the Au NPs was similar to those described in in TiO_2-Au material (about 20 nm).

After the synthesis, the Au and TiO_2-Au materials were employed as catalysts towards the SPR-mediated oxidation of PATP as a model reaction. In this transformation, the transfer of electrons from Au to adsorbed O_2 molecules represents the crucial step for O_2 activation, which in turn contributes to the

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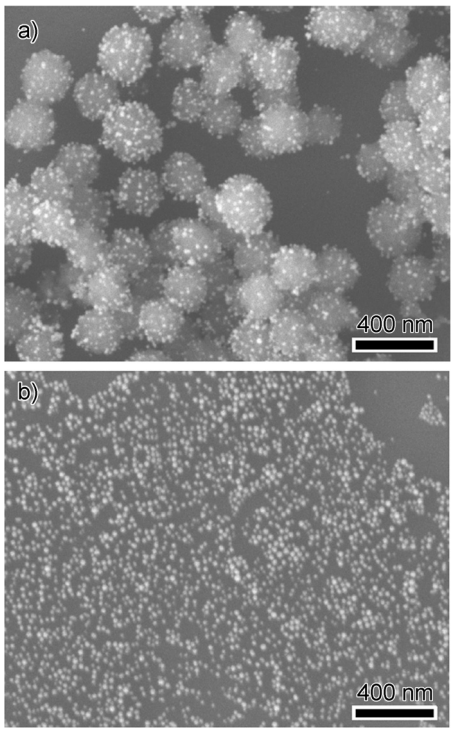

Figure 1. SEM images of a) TiO_2-Au and b) Au NPs employed as catalysts for the SPR-mediated oxidation of PATP.

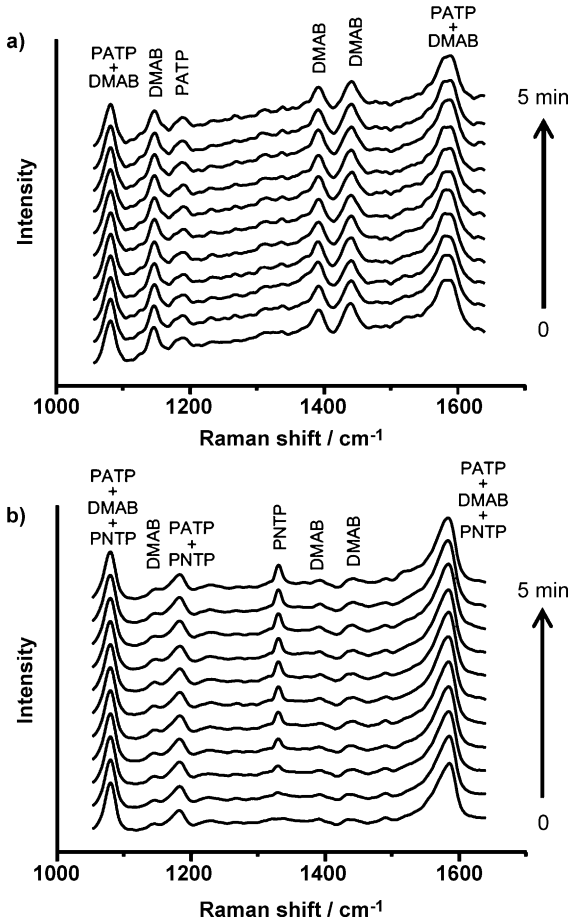

Figure 2. Time-dependent SERS spectra for a) Au and b) TiO_2-Au NPs that had been functionalized with PATP. The initial spectra (0 s) were recorded without UV illumination. After this initial spectrum was registered, the UV light was turned on and the subsequent SERS spectra recorded in 30 s intervals (bottom to top). All spectra were acquired at a 5 s irradiation time, 0.13 mW laser power, and at 632.8 nm excitation. All spectra were normalized employing the 1081 cm^{-1} signal as reference.

PATP oxidation.[12,15] Here, as a result of the SPR excitation on Au NPs, free electrons can transiently occupy the higher empty states above the Fermi level, the so-called hot electrons. If a nearby electron acceptor molecule, such as O_2 from air, with a suitable energy level is present, hot electrons can be transferred from the metal to the molecule to drive chemical transformations.[12,21] In addition to the SPR excitation, we were interested in investigating the effect of UV excitation in TiO_2-Au materials over the SPR-mediated performances. Would it be possible to employ charge-transfer processes between TiO_2 and Au NPs to control selectivity and product formation?

Figure 2a shows the SERS spectra for Au NPs that had been functionalized with PATP molecules as a function of time registered at 30 s intervals (from bottom to top). In this figure, after the initial spectra were recorded (0 s), the samples were exposed to UV illumination and the subsequent SERS spectra were recorded. The oxidation of PATP to DMAB by activated oxygen ($^3O_2$) can be clearly observed in the initial SERS spectra (at 0 s, without UV illumination). The bands which appeared at 1081, 1182, 1489, and 1593 cm^{-1} are assigned to A_1 modes of PATP, and those which appeared at 1081, 1142, 1390, 1433, and 1575 cm^{-1} are assigned to the A_g modes of DMAB.[16,24] In this case, the product conversion can be probed by monitoring the DMAB:PATP + DMAB 1433:1081 cm^{-1} intensity ratios.[11,12,17] It can be observed that no significant changes as a function of time were detected in the DMAB:PATP + DMAB intensity ratios after UV exposure, in agreement with the presence of only Au NPs in the substrate (see Figure S1a in the Supporting Information). This rules out the possibility that UV exposure may generate local heating or hot electrons at the metal surface that could contribute to PATP oxidation. Therefore, the UV illumination power employed in our measurements was small enough (about 1 $mW\,cm^{-2}$) so that no conversion was induced on individual Au NPs as catalysts.

The SERS spectra measured for TiO_2-Au NPs that had been functionalized with PATP are shown in Figure 2b, and displayed remarkably distinct spectral features relative to those described for Au NPs (Figure 2a). The initial spectra (0 s, no UV exposure) displayed only the characteristic peaks assigned to PATP (the intensity of the bands assigned to DMAB were very low). This is in agreement with the preferential transfer of hot electrons generated upon the SPR excitation of the Au NPs to the TiO_2 conduction band (relative to adsorbed O_2 molecules), that hampers the O_2 activation steps and thus the PATP to DMAB oxidation.[21]

After the TiO_2-Au NPs were exposed to UV illumination, the appearance of a band located at 1336 cm^{-1} could be clearly observed, and its intensity increased as a function of

time (Figure S1b). This band was assigned to *p*-nitrothiophenol (PNTP), indicating that, while the PATP oxidation on Au NPs leads to the formation of DMAB, the use of TiO_2-Au for the PATP oxidation under UV exposure leads to PNTP.[24,25] To confirm that this signal indeed originated from the formation of PNTP, the SERS spectra of TiO_2-Au NPs that had been functionalized with PATP (black trace) and PNTP (red trace) are shown in Figure S2. The SERS spectrum of PNTP is dominated by a prominent peak at 1336 cm^{-1} corresponding to a NO_2 symmetric stretching vibration, and four peaks at 1076, 1107, 1174, and 1568 cm^{-1} were assigned to the benzene ring vibrations.[24,25]

These results show that the UV exposure and the nature of the catalyst (Au or TiO_2-Au NPs) made it possible to control the nature of the product from PATP oxidation. This control over product formation can be explained as summarized in Figure 3 and Figure S3. For Au NPs (Figure 3a), either with or without UV exposure, SPR excitation by visible light leads to the formation of hot electrons that are transferred to adsorbed O_2 molecules, generating $^3O_2$ that subsequently can participate in the oxidation of PATP to DMAB (the actual size of Au NPs is much larger than that of azobenzene molecules, so there is no geometric constrain for the formation of azobenzene on the same particle). The SPR excitation and UV illumination of TiO_2-Au NPs (Figure 3b) makes possible the transfer of electrons from the UV-excited TiO_2 to the Au NPs. Therefore, it is plausible that both the UV-excited electrons from TiO_2 and the hot electrons from Au SPR excitation can participate in the O_2 activation step. Here, rather than oxidizing PATP to DMAB, this process leads to the formation of PNTP. The oxidation of PATP to PNTP (rather than to DMAB) may be related to the larger number of electrons available to participate in the O_2 activation step (hot electrons + electrons from excited TiO_2). Therefore, electrons injected from TiO_2 into Au can be employed to maneuver the selectivity of the PATP oxidation mediated by the SPR excitation.

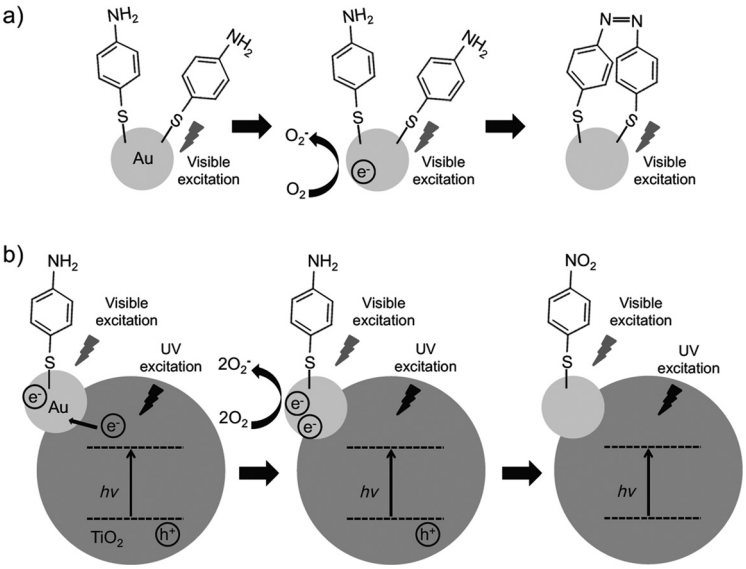

Figure 3. Proposed mechanism for a) the oxidation of PATP to DMAB over Au NPs and b) the oxidation of PATP to PNTP over TiO_2-Au NPs. a) In Au NPs, SPR-excited hot electrons were transferred to adsorbed O_2 molecules, generating $^3O_2$ that participated in the PATP oxidation to DMAB. b) When the TiO_2-Au NPs were excited both by the SPR and UV light, SPR-excited hot electrons and electrons transferred from TiO_2 to Au contributed to the O_2 activation step, leading to the formation of PNTP rather than DMAB.

The increase in the PNTP formation as a function of time observed for the TiO_2-Au material (Figure S1b) can be fitted according to the Poisson's equation, $I = A + B\exp(-t/\tau)$, to give the $\tau = 1.96$ minutes time constant when the UV illumination was on.[23,24] The observed exponential increase in this signal with time can be assigned to the spatial redistribution and re-trapping of photocarriers.[26,27]

Interestingly, the nature of the product obtained from TiO_2-Au NPs as catalysts can be further manipulated by switching the UV exposure on and off as shown in Figure 4. For instance, after the formation of PNTP from TiO_2-Au NPs under SPR excitation and UV exposure (bottom and middle traces), the reduction of PNTP to DMAB was detected when the UV exposure was turned off (top trace) within 5 s. This process was reversible up to three times. Figure S4 shows the SERS spectra of Au NPs that had been functionalized with PNTP as a function of the laser power, confirming that DMAB can be formed from PNTP upon SPR excitation,[24,25]

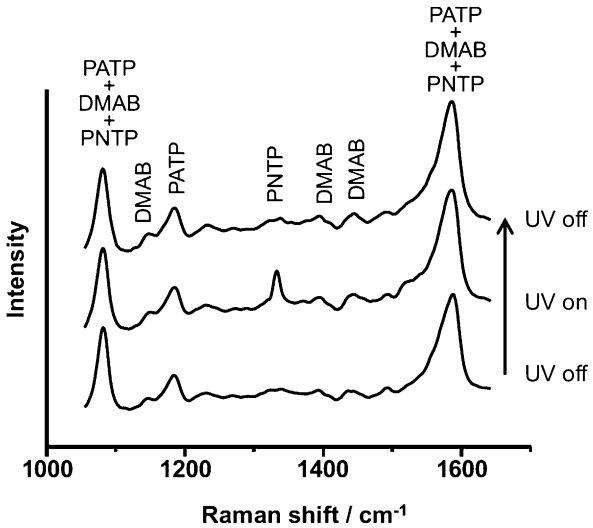

Figure 4. SERS spectra recorded for TiO_2-Au NPs that had been functionalized with PATP: before UV illumination (bottom trace), under UV illumination (middle trace), and after the UV illumination was turned off (top trace). Before UV excitation, only peaks assigned to PATP were detected (DMAB peaks displayed very low intensities). Under UV exposure for 5 minutes, the formation of PNTP was detected. PNTP could be further reduced to DMAB as the UV illumination was removed (red trace). All spectra employed 1 mW and 1 mW cm^{-2} as the laser and UV illumination power, respectively.

in agreement with the results obtained from TiO_2-Au after the UV exposure was turned off. The increase in the product formation as a function of the laser power is in agreement with a SPR-mediated mechanism.[17] The mechanism for the

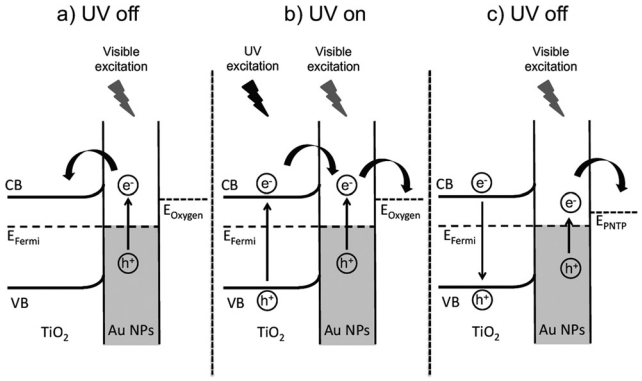

Figure 5. Energy level diagrams for the TiO_2-Au NPs: a) Hot electrons from SPR-excited Au NPs were transferred to TiO_2 when UV exposure was not employed. b) Under UV illumination, both hot electrons from SPR-excited Au NPs and electrons transferred from excited TiO_2 participated in the O_2 activation step. c) As the UV exposure was turned off, SPR-excited hot electrons were transferred to PNTP as its energy level is lower relative to O_2, leading to its reduction to DMAB.

formation of DMAB from PNTP is illustrated in Figure 5. Initially (UV off, Figure 5a), most of the hot electrons generated from the SPR excitation of Au NPs were transferred to TiO_2, and only PATP peaks could be observed in the SERS spectrum (DMAB peaks were present at very low intensities). As the UV exposure was turned on, electrons excited from TiO_2 could be transferred to Au and participate to the O_2 activation step together with the hot electrons produced from SPR excitation of Au to yield PNTP. As the UV exposure was turned off (Figure 5c), hot electrons from Au NPs were transferred to PNTP molecules, driving its reduction to DMAB. This process takes place because of the lower energy level of PNTP relative to that of adsorbed O_2 molecules.[15]

In summary, we demonstrated that the selectivity of the SPR-mediated oxidation of PATP employing Au NPs as catalysts can be effectively controlled by the choice of catalysts (Au or TiO_2-Au NPs) and by maneuvering the charge transfer in the TiO_2-Au hybrid materials. When individual Au NPs were employed as catalyst, the SPR-mediated oxidation of PATP yielded DMAB. When TiO_2-Au NPs were employed as catalysts, the oxidation of PATP was not observed, as SPR-excited hot electrons from Au NPs were transferred to TiO_2. However, when UV illumination was employed together with SPR excitation, the PATP oxidation led to the formation of PNTP rather than DMAB in a single step. Interestingly, the produced PNTP molecules could also be reduced to DMAB after the UV illumination was removed, in which the SPR-excited hot electrons from Au NPs were transferred to PNTP. These results show that charge-transfer processes may play an important role for the control of product formation and selectivity in plasmon-enhanced or mediated catalytic processes.

Keywords: catalysis · nanoparticles · oxidation · photochemistry · surface plasmon resonances

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[1] F. Zaera, *Catal. Lett.* **2012**, *142*, 501 – 516.
[2] G. Somorjai, C. Kliewer, *React. Kinet. Catal. Lett.* **2009**, *96*, 191 – 208.
[3] A. Grirrane, A. Corma, H. García, *Science* **2008**, *322*, 1661 – 1664.
[4] A. Corma, P. Serna, *Science* **2006**, *313*, 332 – 334.
[5] S. Gontier, A. Tuel, *Appl. Catal. A* **1994**, *118*, 173 – 186.
[6] S. Sarina, H. Y. Zhu, E. Jaatinen, Q. Xiao, H. W. Liu, J. F. Jia, C. Chen, J. Zhao, *J. Am. Chem. Soc.* **2013**, *135*, 5793 – 5801.
[7] M. J. Kale, T. Avanesian, P. Christopher, *ACS Catal.* **2014**, *4*, 116 – 128.
[8] G. Baffoua, R. Quidant, *Chem. Soc. Rev.* **2014**, *43*, 3898 – 3907.
[9] M. A. Fox, *Acc. Chem. Res.* **1983**, *16*, 314 – 321.
[10] M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341 – 357.
[11] Y. F. Huang, H. P. Zhu, G. K. Liu, D. Y. Wu, B. Ren, Z. Q. Tian, *J. Am. Chem. Soc.* **2010**, *132*, 9244 – 9246.
[12] Y.-F. Huang, M. Zhang, L.-B. Zhao, J.-M. Feng, D.-Y. Wu, B. Ren, Z.-Q. Tian, *Angew. Chem. Int. Ed.* **2014**, *53*, 2353 – 2357; *Angew. Chem.* **2014**, *126*, 2385 – 2389.
[13] P. Xu, L. L. Kang, N. H. Mack, K. S. Schanze, X. J. Han, H.-L. Wang, *Sci. Rep.* **2013**, *3*, 2997.
[14] Z. G. Dai, X. H. Xiao, Y. P. Zhang, F. Ren, W. Wu, S. F. Zhang, J. Zhou, F. Mei, C. Z. Jiang, *Nanotechnology* **2012**, *23*, 335701.
[15] L.-B. Zhao, M. Zhang, Y.-F. Huang, C. T. Williams, D.-Y. Wu, B. Ren, Z.-Q. Tian, *J. Phys. Chem. Lett.* **2014**, *5*, 1259 – 1266.
[16] Y. Fang, Y. Li, H. Xu, M. Sun, *Langmuir* **2010**, *26*, 7737 – 7746.
[17] J. L. Wang, R. A. Ando, P. H. C. Camargo, *ACS Catal.* **2014**, *4*, 3815 – 3819.
[18] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, N. J. Halas, *Nano Lett.* **2013**, *13*, 240 – 247.
[19] S. M. Kim, S. J. Lee, S. H. Kim, S. Kwon, K. J. Yee, H. Song, G. A. Somorjai, J. Y. Park, *Nano Lett.* **2013**, *13*, 1352 – 1358.
[20] Y. K. Lee, C. H. Jung, J. Park, H. Seo, G. A. Somorjai, J. Y. Park, *Nano Lett.* **2011**, *11*, 4251 – 4255.
[21] R. Long, K. K. Mao, M. Gong, S. Zhou, J. H. Hu, M. Zhi, Y. You, S. Bai, J. Jiang, Q. Zhang, X. J. Wu, Y. J. Xiong, *Angew. Chem. Int. Ed.* **2014**, *53*, 3205 – 3209; *Angew. Chem.* **2014**, *126*, 3269 – 3273.
[22] G. Williams, B. Seger, P. V. Kamat, *ACS Nano* **2008**, *2*, 1487 – 1491.
[23] T. C. Damato, C. C. S. de Oliveira, R. A. Ando, P. H. C. Camargo, *Langmuir* **2013**, *29*, 1642 – 1649.
[24] M. T. Sun, H. X. Xu, *Small* **2012**, *8*, 2777 – 2786.
[25] L. L. Kang, P. Xu, B. Zhang, H. Tsai, X. J. Han, H.-L. Wang, *Chem. Commun.* **2013**, *49*, 3389 – 3391.
[26] J. L. Wang, B. Vilquin, N. Barrett, *Appl. Phys. Lett.* **2012**, *101*, 092902.
[27] R. Shao, M. P. Nikiforov, D. A. Bonnell, *Appl. Phys. Lett.* **2006**, *89*, 112904.

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