Direct Observation of Charge Separation on Anatase TiO$_2$ Crystals with Selectively Etched {001} Facets

Xiaogang Liu, Guojun Dong, Shaopeng Li, Gongxuan Lu, and Yingpu Bi*

State Key Laboratory for Oxo Synthesis & Selective Oxidation, National Engineering Research Center for Fine Petrochemical Intermediates, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

S *Supporting Information*

ABSTRACT: Synchronous illumination X-ray photoelectron spectroscopy (SIXPS) was employed for the first time to directly identify the photogenerated charge separation and transfer on anatase TiO$_2$ single-crystals with selectively etched {001} facets. More specifically, for the TiO$_2$ crystals with intact {001} and {101} facets, most of photogenerated charge carriers rapidly recombined, and no evident electron–hole separation was detected. With selectively etching on {001} facets, high efficient charge separation via hole transfer to titanium and electron to oxygen was clearly observed. However, when the {001} facets were completely etched into a hollow structure, the recombination for photogenerated electron–hole pairs would dominate again. These demonstrations clearly reveal that the appropriate corrosion on {001} facets could facilitate more efficient electron–hole separation and transfer. As expected, the optimized TiO$_2$ microcrystals with etched {001} facets could achieve a hydrogen generation rate of 74.3 μmol/h/g, which is nearly 7 times higher than the intact-TiO$_2$ crystals.

Recently, the crystal facet controlled fabrication of semiconductor materials has attracted considerable attention because the photocatalytic and photoelectric properties can be further enhanced or optimized by tailoring the surface atomic configuration.[1−6] More specifically, the crystal facets with more undercoordinated atoms as well as high surface energy usually exhibit high reactivity in photocatalytic reactions. Among the numerous metal oxides, the anatase TiO$_2$ photocatalysts with defined {001} facets are generally considered to be more favorable for solar energy conversion.[7−15] Recently, Lu et al. first demonstrated the fabrication of high-quality anatase TiO$_2$ crystals with exposed 47% {001} facets by using HF as a capping agent.[16] Moreover, they reported that the {001} facets of anatase TiO$_2$ were much more reactive than the thermodynamically stable {101} facets for the hydrogen production reaction.[17] Since then, significant efforts have been devoted to the fabrication of nano- or microsized TiO$_2$ crystals with high percentages of {001} specific facets. For example, Yang et al.[18] improved the percentage of {001} facets up to 64% in micrometer-sized single crystal sheets by using 2-proponal as the capping agent. Furthermore, the percentage of {001} facets was reached up to 89% by Han et al.[19] Wen et al.[20] reported that the exposure percentage of {001} facets was further increased up to 98.7% by reacting TiF$_4$ powder with 1-butanol. Recently, Chen et al.[21]

synthesized the hierarchical anatase microspheres assembled from the high-surface-area nanosheets with nearly 100% {001} facets.

Although the exposure percentage of {001} facets has nearly reached its maximum value, there still remains an urgent need for thorough understanding of the facet effects on TiO$_2$ photocatalysts. Recently, Cheng et al.[22] demonstrated a distinct viewpoint about the high activity of {001} facets based on the investigation of various anatase crystals with predominant {001}, {101}, or {010} facets and revealed that the clean {001} facets exhibited a lower reactivity than {101} facets for hydrogen evolution. More recently, some studies demonstrated that the cooperative effect of different facets was the major factor for determining photocatalytic activity. For instance, Yu et al.[23] proposed a new "surface heterojunction" concept based on the density functional theory calculations to explain the difference in the photosynthetic activity of TiO$_2$ as a result of photogenerated electron and hole transfer to {101} and {001} facets, respectively. However, despite these efforts to understand the role of different facets in photocatalysis, the intrinsic causes leading to the different reactivity are still quite ambiguous. More importantly, the direct observation for the photoinduced charge separation on TiO$_2$ single crystals has been rarely reported.

Herein, we demonstrate the application of synchronous illumination X-ray photoelectron spectroscopy (SIXPS) for directly identifying the charge separation and transfer on the anatase TiO$_2$ single crystals with selectively etched {001} facets. The SIXPS results clearly reveal that the intact-TiO$_2$ crystals with coexposed {001} and {101} facets possesses a high recombination probability of the photogenerated electron–hole pairs. Interestingly, selective etching on the {001} facets could facilitate more efficient charge separation, and spatial transfer of hole to titanium atoms and electron to oxygen atoms was directly observed. However, when the {001} facets were completely etched into a hollow structure, the efficiency of charge separation was distinctly reduced. Furthermore, the photocatalytic results confirm that the TiO$_2$ microcrystals with appropriately etched {001} facets could yield a higher hydrogen generation rate (74.5 μmol·h^{-1}) than intact TiO$_2$ (11.4 μmol·h^{-1}) under the same conditions.

Figures 1A and S1A,B show the typical scanning electron microscopy (SEM) images of anatase TiO$_2$ single crystals with intact {001} surface and well-faceted truncated octahedra (denoted as intact-TiO$_2$), in which the two square surfaces and
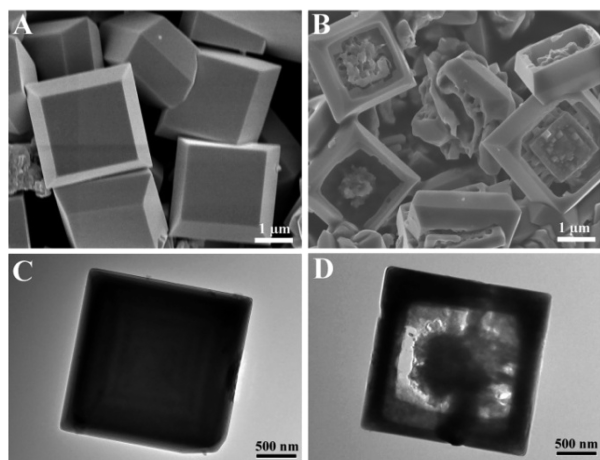
Figure 1. SEM images of anatase TiO_2 single crystals with (A) intact and (B) etched {001} facets; the corresponding TEM images of (C) intact- and (D) etched-TiO_2, respectively.

the other eight isosceles were confirmed to be {001} and {101} facets, respectively.[24,25] However, when slightly adjusting the HF concentrations, the etching phenomenon on the {001} surfaces of the anatase TiO_2 single crystal has been observed (Figures 1B and S2A,B, the sample denoted as etched-TiO_2).[26] Interestingly, no evident corrosion has been observed for the {101} facets, indicating that the {101} facets exhibit higher resistibility than {001} facets for the HF etching.[27] These crystals were further examined by transmission electron microscopy (TEM), and the typical TEM images were shown in Figures 1C,D, S1C,D, and S2C−E, respectively. It can be clearly seen that the intact-TiO_2 possesses perfectly regular surfaces (Figure 1C), while for the etched-TiO_2 (Figure 1D), a stamp-like structure was observed as a result of etching on the {001} facets. Moreover, by tailoring the HF concentrations, the etched degrees of {001} facets could be rationally controlled. As shown in Figures S3 and S4, the TiO_2 crystals with slightly and completely etched {001} facets could be obtained (denoted as slightly etched-TiO_2 and etched off-TiO_2, respectively). The corresponding HRTEM images clearly reveal that all the etched TiO_2 samples still remain the original single crystal structures, which are consistent with the previous reports.[12]

Furthermore, their crystalline structures have been measured by the X-ray diffraction as shown in Figure S5A. All the diffraction peaks of both intact and etched TiO_2 samples could be indexed to the body-centered cubic structure of anatase TiO_2 (JCPDS no. 73-1764). However, it is worth noting that obvious changes have been observed in the intensity of (004) diffraction peaks compared with other peaks, which give further support to the above SEM and TEM observation. More specifically, as a result of etching on the {001} planes, the intensity of (004) diffraction peaks in all the etched TiO_2 samples is much lower than that of the intact sample (shown in Figure S5A). Moreover, the ultraviolet−visible diffuse reflectance spectra (shown in Figure S5B) reveal that with increasing the corrosion degree on the {001} facets, the light absorption within both UV and visible light ranges has been slightly increased, and a weak red-shift in the absorption edge has been observed. However, when the {001} facets were completely etched, both light absorption intensity and absorption edges would be slightly reduced. Moreover, the calculated band gaps for the etched-, slightly etched-, etched off-, and intact-TiO_2 samples are 3.08, 3.12, 3.15, and 3.22 eV, respectively.[28−30]

It is well-known that the photoinduced charge transfer and separation process play a crucial role in determining the light-to-energy conversion efficiencies. However, despite the great efforts to understand this issue via various methods, the direct observation for the anisotropic photoinduced charge transfer on the surfaces of photocatalysts still remains a great challenge. Here, we have developed a powerful XPS technique combined with synchronous light illumination to directly extract this information. More specifically, as shown in Figure 2A, routine
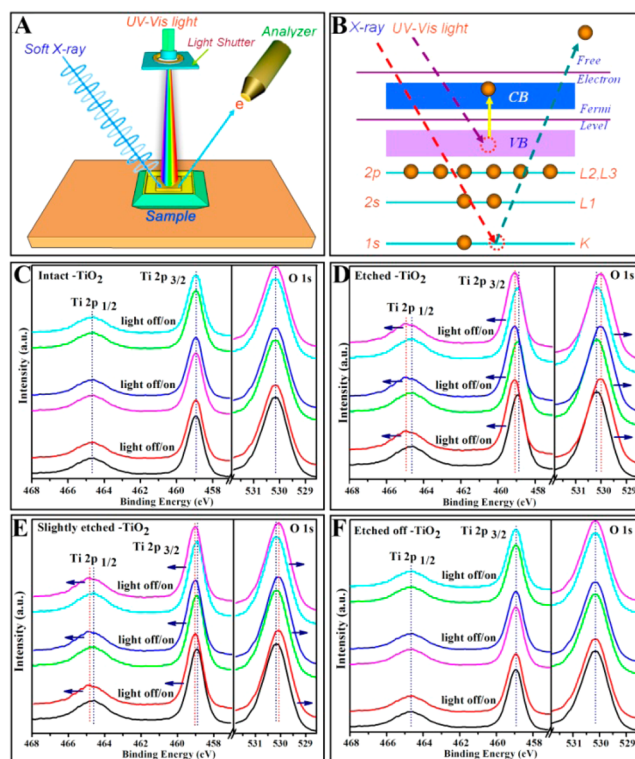

Figure 2. (A) Typical illustration of synchronous illumination XPS technique and (B) corresponding electron density variations. SIXPS spectra for (C) intact-, (D) etched-, (E) slightly etched-, and (F) etched off-TiO_2, respectively.

XPS spectra were first performed to obtain the chemical binding energy of each element in the ground state. Subsequently, the XPS measurements were repeated under synchronous light irradiation (imported by an optical fiber) to detect the peak shifts resulting from the electron density changes of various atoms in the excited state, which could directly reveal the separation efficiency and transfer direction of photoexcited charges. Figure 2B shows a schematic diagram to clarify the basic principle for this issue. In the case of semiconductors, the light irradiation could induce the physical shifts of binding energy of various elements due to the electron transfer from the valence band (VB) to the conduction band (CB) and holes left behind on the VB. More specifically, the VB and CB of semiconductors were composed of spin-orbits of various elements. Thereby, the charge transfer and electron density changes among various atoms could be well and truly detected by XPS spectra. In contrast, when light irradiation was removed, the excited electron on the CB would come back to the VB and recombine with holes, and all the binding energy peaks of various elements would shift to their original positions. Thus, by combining the synchronous illumination with XPS techniques, detailed information on the

charge separation as well as transfer among various elements in the semiconductors can be directly obtained.

Furthermore, the SIXPS technique has been employed to study the photoinduced charge separation and transfer on both intact- and etched-TiO_2 samples, and the related results are shown in Figure 2C,D. For routine XPS spectra, two peaks at 458.8 and 464.6 eV (Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks) and a peak at 530.16 eV (O 1s) could be detected in all the samples. Amazingly, under synchronous light irradiation, distinct changes on the binding energy shifts of both Ti 2p and O 1s peaks in the TiO_2 samples have been observed. More specifically, in the case of intact TiO_2, no evident shift of all peaks has been detected either under light or in dark (Figure 2C). However, for the etched TiO_2 sample under light irradiation, the bind energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ drastically shift to the high values, while the O 1s peak moved to the low binding energy (Figure 2D). Interestingly, all the peaks of both Ti 2p and O 1s could return to the original positions when synchronous light irradiation was removed. Moreover, as shown in Figure 2E, similar phenomenon could be observed in the slightly etched-TiO_2 sample, while their shifts were slightly smaller than that of etched TiO_2 samples. However, when the {001} facets were completely etched, no evident shift in the Ti 2p and O 1s peaks has been detected (Figure 2F). On the basis of above results, it could be concluded that appropriate etching on {001} facets could facilitate the more efficient charge separation and transfer of the TiO_2 crystals, and the separated electrons and holes are mostly transferred to O and Ti atoms, respectively.

On the basis of above SIXPS results, some possible reasons have been proposed to explain the distinct phenomena for the charge separation over TiO_2 crystals with selectively etched {001} facets. Figure 3A shows the bulk atomic structural model
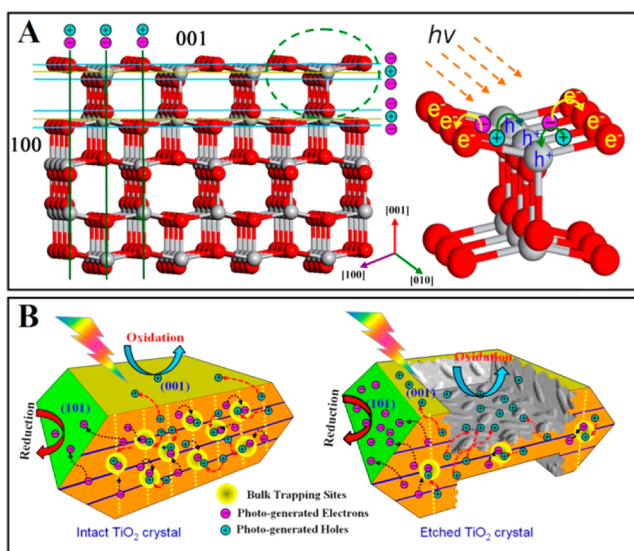

Figure 3. (A) The bulk atomic structural model of anatase TiO_2 crystal, and (B) the corresponding surface and bulk electron carrier trapping phenomenon for intact- and etched-TiO_2, respectively.

of anatase TiO_2, which is independent of the exposed facets. Two bulk planes, {001} and {100}, possess completely different titanium and oxygen atomic arrangements. More specifically, the O and Ti atoms are highly coplanar in the bulk {100} planes, which inevitably leads to the high recombination probabilities of electrons and holes during the photoexcitation as well as charge

transfer process. However, for the bulk {001} planes, the spatially separated O and Ti atomic layers could effectively facilitate the separation and transfer of photogenerated electron—hole pairs. Accordingly, in the intact-TiO_2 crystals, bulk {100} planes may serve as the recombination centers for the photoexcited electron—hole pairs owing to their unfavorable atomic arrangement, and only a small portion of electrons and holes transfer to the surface of TiO_2 crystals (Figure 3B). However, when the {001} planes have been selectively etched, the ratios of bulk {100} planes have also been reduced. Thus, the photoexcited electron and hole can efficiently migrate to the outer surface rather than recombine each other in the bulk {100} planes. However, in further etching of the {001} facet into a hollow structure, although the {100} recombination centers have been drastically decreased, the pathways for charge separation as well as transfer over {001} planes have also been blocked.

Furthermore, the photocatalytic behaviors for the hydrogen generation from splitting water were explored to verify the SIXPS results and correlative speculations. To the best of our knowledge, these etched-TiO_2 single crystals were used, for the first time, as the photocatalysts for the hydrogen generation reaction. As shown in Figure 4A, except for intact-TiO_2 catalysts,
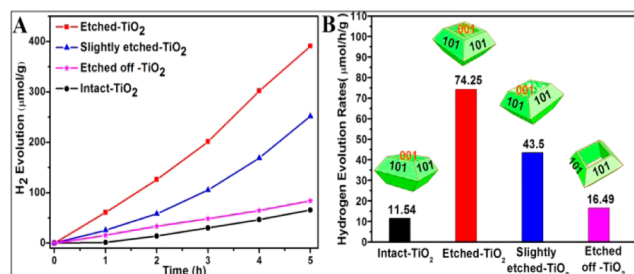

Figure 4. (A) Photocatalytic H_2 evolution tests of the 1 wt % Pt-loaded TiO_2 samples under UV light irradiation. (B) Comparative presentation of the hydrogen evolution rates.

all these etched-TiO_2 photocatalysts exhibited an improved photocatalytic activity for the hydrogen generation. Among them, the etched-TiO_2 sample (Figure 4B and Table S2) exhibited the highest photocatalytic activity, and the H_2 generation rate could be reached up to 74.25 μmol/h/g, which is nearly 7 times higher than that of intact-TiO_2 sample (11.54 μmol/h/g). The hydrogen evolution rate of slightly etched-TiO_2 samples is about 43.5 μmol/h/g. However, in the case of etched off-TiO_2 sample, the hydrogen evolution rate is only 16.49 μmol/h/g, which is slightly higher than that of the intact-TiO_2 samples. Moreover, all these TiO_2 samples could generally keep their original activities even after four cycles of photocatalytic reactions (Figure S11), indicating their relatively high stabilities. The photoelectrochemical properties have also been investigated, and the related results have been shown in Figures S13 and S14. Among them, the etched-TiO_2 sample exhibited much higher photocurrent intensity than intact-, slightly etched-, and etched off-TiO_2 samples, indicating the more efficient charge separation and transfer in this sample, which is identical with the photocatalytic results. Additionally, note that both photoreactivity and photoelectric order are highly consistent with the SIXPS observations for charge separation. Therefore, these demonstrations indicate that the selectively etching on {001} facets of anatase TiO_2 microcrystals could effectively enhance the photocatalytic performances of H_2 production, while the drastic corrosion would lead to a decrease of the photoreactivity.

In summary, SIXPS has been successfully applied in directly identifying the charge separation and transfer for the anatase TiO_2 single crystals with controllable etched {001} facets. The SIXPS results clearly reveal that the appropriate etching on the {001} facets could facilitate more efficient charge separation and transfer in the TiO_2 crystals, and the separated electrons and holes are mostly transferred to O and Ti species, respectively. Furthermore, the photocatalytic results confirm that the optimized TiO_2 single crystals with etched {001} facet could yield a higher photocatalytic hydrogen generation rate (74.5 μmol·h^{-1}) than intact-TiO_2 (11.4 μmol·h^{-1}) under the same conditions, which is highly consistent with the SIXPS results for charge separation. These findings may provide new insights for developing highly efficient TiO_2 photocatalysts in practical applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12521.

    Experimental details and data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*yingpubi@licp.cas.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Wen, C. Z.; Jiang, H. B.; Qiao, S. Z.; Yang, H. G.; Lu, G. Q. *J. Mater. Chem.* **2011**, *21*, 7052.

(2) Fang, W. Q.; Gong, X. Q.; Yang, H. G. *J. Phys. Chem. Lett.* **2011**, *2*, 725.

(3) Liu, G.; Yu, J. C.; Lu, G. Q.; Cheng, H.-M. *Chem. Commun.* **2011**, *47*, 6763.

(4) Marshall, M. S. J.; Castell, M. R. *Phys. Rev. Lett.* **2009**, *102*, 146102.

(5) Kennedy, R. J.; Stampe, P. A. *J. Cryst. Growth* **2003**, *252*, 333.

(6) Jeong, B. S.; Norton, D. P.; Budai, J. D.; Jellison, G. E. *Thin Solid Films* **2004**, *446*, 18.

(7) Roy, N.; Sohn, Y.; Pradhan, D. *ACS Nano* **2013**, *7*, 2532.

(8) Hu, C.; Zhang, X.; Li, W.; Yan, Y.; Xi, G.; Yang, H.; Li, J.; Bai, H. *J. Mater. Chem. A* **2014**, *2*, 2040.

(9) Wang, M.; Zhang, F.; Zhu, X.; Qi, Z.; Hong, B.; Ding, J.; Bao, J.; Sun, S.; Gao, C. *Langmuir* **2015**, *31*, 1730.

(10) Ma, X. Y.; Chen, Z. G.; Hartono, S. B.; Jiang, H. B.; Zou, J.; Qiao, S. Z.; Yang, H. G. *Chem. Commun.* **2010**, *46*, 6608.

(11) Zhu, J.; Wang, S.; Bian, Z.; Xie, S.; Cai, C.; Wang, J.; Yang, H.; Li, H. *CrystEngComm* **2010**, *12*, 2219.

(12) Fang, W. Q.; Zhou, J. Z.; Liu, J.; Chen, Z. G.; Yang, C.; Sun, C. H.; Qian, G. R.; Zou, J.; Qiao, S. Z.; Yang, H. G. *Chem. - Eur. J.* **2011**, *17*, 1423.

(13) Liu, G.; Yin, L.-C.; Pan, J.; Li, F.; Wen, L.; Zhen, C.; Cheng, H.-M. *Adv. Mater.* **2015**, *27*, 3507.

(14) De Angelis, F.; Vitillaro, G.; Kavan, L.; Nazeeruddin, M. K.; Graetzel, M. *J. Phys. Chem. C* **2012**, *116*, 18124.

(15) Wen, C. Z.; Hu, Q. H.; Guo, Y. N.; Gong, X. Q.; Qiao, S. Z.; Yang, H. G. *Chem. Commun.* **2011**, *47*, 6138.

(16) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. *Nature* **2008**, *453*, 638.

(17) Pan, J.; Liu, G.; Lu, G. Q.; Cheng, H. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2133.

(18) Yang, H. G.; Liu, G.; Qiao, S. Z.; Sun, C. H.; Jin, Y. G.; Smith, S. C.; Zou, J.; Cheng, H. M.; Lu, G. Q. *J. Am. Chem. Soc.* **2009**, *131*, 4078.

(19) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. *J. Am. Chem. Soc.* **2009**, *131*, 3152.

(20) Wen, C. Z.; Zhou, J. Z.; Jiang, H. B.; Hu, Q. H.; Qiao, S. Z.; Yang, H. G. *Chem. Commun.* **2011**, *47*, 4400.

(21) Chen, J. S.; Tan, Y. L.; Li, C. M.; Cheah, Y. L.; Luan, D.; Madhavi, S.; Boey, F. Y. C.; Archer, L. A.; Lou, X. W. *J. Am. Chem. Soc.* **2010**, *132*, 6124.

(22) Liu, G.; Yang, H.; Pan, J.; Yang, Y.; Lu, G.; Cheng, H. *Chem. Rev.* **2014**, *114*, 9559.

(23) Yu, J.; Low, J.; Xiao, W.; Zhou, P.; Jaroniec, M. *J. Am. Chem. Soc.* **2014**, *136*, 8839.

(24) Zhang, B.; Wei, F.; Wu, Q.; Piao, L.; Liu, M.; Jin, Z. *J. Phys. Chem. C* **2015**, *119*, 6094.

(25) Zhang, D. Q.; Li, G. S.; Yu, J. C. *Chem. Commun.* **2009**, *29*, 4381.

(26) Yang, X. H.; Yang, H. G.; Li, C. Z. *Chem. - Eur. J.* **2011**, *17*, 6615.

(27) Wang, Y.; Zhang, H.; Han, Y.; Liu, P.; Yao, X.; Zhao, H. *Chem. Commun.* **2011**, *47*, 2829.

(28) Liu, G.; Sun, C.; Yang, H. G.; Smith, S. C.; Wang, L.; Lu, G. Q.; Cheng, H.-M. *Chem. Commun.* **2010**, *46*, 755.

(29) Zheng, Z.; Huang, B.; Lu, J.; Qin, X.; Zhang, X.; Dai, Y. *Chem. - Eur. J.* **2011**, *17*, 15032.

(30) Sakai, N.; Ebina, Y.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2004**, *126*, 5851.