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Reply to "Comment on "Photoelectron Spectroscopic Investigation of Nitrogen-Doped Titania Nanoparticles""

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As in the responses of other authors to Gopinath's previous comments,^{1,2} we argue that also this comment by Gopinath is based on a misunderstanding of the addressed paper.^{3,4} It is unfortunate that the meaning of the shorthand notation, N- Ti- O, in the recent letter,⁵ referred to above, has been misunderstood.⁶ Such confusion should, however, have not arisen as the meaning of this nomenclature and more extended results have also been published by our team⁷⁻⁹ nine months or more before submission of the comment and the recent manuscript co-authored by Gopinath.¹⁰ Also others have used this nomenclature in the past.¹¹ In ref 5, we describe a minimal structure fragment within the TiO₂ lattice in which nitrogen is likely connected in some manner to Ti, and, as well to other atoms (Ti or O) to complete its valency. The nomenclature used is, of course, *not* meant to be an isolated triatomic molecular species with an unoxidized nitrogen. The extensive experimental data and discussions already in the literature^{7-9,11} are well correlated to and in agreement with related work before and after the publication of the photoelectron studies in ref 5, which are the subject of the above comment. The data and discussion presented in ref 6 have already been discussed and previously correlated with several other measurement techniques.^{8,9} We regret that it was not clear from the shorthand notation that N, Ti, and O should be assumed to be bound to next neighbor atoms (Ti or O) in the TiO₂ lattice. We were surprised by this misinterpretation because it was chemically obvious to us and others.¹¹ In addition, there are numerous misrepresentations of the results presented in refs 12-22 given in the comment by Gopinath.¹²⁻²² Moreover, we note that in several instances the above comment presents essentially the same arguments as to the attribution of our XPS data as discussed in much greater detail in our prior publications.⁷⁻⁹ In the full papers,⁷⁻⁹ one also finds cross correlations to additional IR, Raman, EPR, and XRD data. However, while the discussions and references in the comment⁶ closely follow our previous work,⁷⁻⁹ references to this work^{8,9} are missing in the comment. The comment rephrases the apparent discrepancy in the XPS data in refs 13-20 but does not take into account that the data are taken under vastly different conditions ranging across distinct entities including films^{11,16} and undoped nanoparticles,¹⁴ and including both anatase and rutile structures.¹⁷ Needless to say, each species was prepared in a completely different way and this and the consequences have been extensively discussed by us previously⁷⁻⁹ under the assumption that doped TiO₂ lattice structures were present. We have clearly stated⁷⁻⁹ that we are discussing a

minimal structure fragment within a doped TiO₂ lattice (characterized by NO sites), and, of course, *not* species where the nitrogen is not oxidized. We have previously outlined a reaction mechanism that could possibly lead to substantial nitrogen incorporation.⁸ This mechanism was presented in the form of a working scientific hypothesis for which we are performing a thorough evaluation. The comment states "... It is suggested from the XPS results that there is N- Ti- O bond formation due to nitrogen doping, and no oxidized nitrogen is present".⁶ This statement misinterprets our study and appears to derive from the misconception that N, Ti, and O are isolated from their TiO₂ anatase environment. In fact, the XPS results in ref 5 clearly demonstrate that nitrogen is partially oxidized and the neighboring Ti is reduced relative to Ti in pure TiO₂, as discussed in refs 5, 8, and 9. A discussion concerning the valencies of the nitrogen already attributes the □401 eV peak to an NO site.^{8,9} The precise location of the NO site within the titania lattice requires further study.

A further scientific issue raised by the comment suggests possible surface contamination without additional experimental evidence. Our previous extensive range of studies⁷⁻⁹ with samples prepared under vacuum demonstrates no evidence for hydrocarbon impurities, although the possibility of carbon residues cannot be ruled out unequivocally.⁷ While nanoscale catalysts can show high activities, great care in their preparation is required for reproducibility. We have found experimentally that most common impurities lower or quench and do not increase the photocatalytic activity.⁷⁻⁹ To obtain enhanced activity at the nanoscale requires that the purity of the synthesis reagents used, and each synthesis step, face a scrutiny that must exceed that at the micro and larger scales. There is no new work in the comment⁶ which demonstrates that impurities are present in our samples; however, this must be the source of concern in all experiments. We have taken into account the expansion of the lattice as doping occurs due to the higher doping levels we have observed at the nanoscale. This factor, already discussed previously,⁷ does not manifest a change in the crystallinity of the doped anatase oxynitride. Furthermore, the high doping levels can well be explained by nucleophilic substitution chemistry, as pointed out by us previously.⁸ Further study of these factors is underway in our laboratories. The doping level on the nanoscale, especially with porous materials, can of course be higher than the □1% demonstrated previously.¹³

The photoionization cross sections, in contrast to the statement in the comment,⁶ were explicitly taken into account in all of the XPS data analyses we have previously presented.

The comment concludes: "A very careful XPS analysis of well-characterized N- TiO₂ could throw some light on the ... state of nitrogen atoms in N- TiO₂". In fact, such a collection of data has already been carefully compiled and was available in the literature⁷⁻⁹ nine months before the comment was submitted. In conclusion, the comment on our work addresses one issue, surface contamination, for which no evidence is presented. The remainder of the comment addresses issues that have already been discussed in the literature.

The present comment by Gopinath has undergone three iterative cycles, each of which absorbed our replies and consequently changed its focus and arguments. However, in its third version, we argue, the comment is still in its core a misunderstanding of our work.

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References and Notes

- (1) Gopinath, C. S.; Raja, T. *J. Phys. Chem. B* **2001**, *105*, 12427.
- (2) Gopinath, C. S.; Subramanian, S. *Phys. Rev. B* **1992**, *45*, 7513.
- (3) Itti, R.; Ikeda, K.; Koshizuka, N.; Tanaka, S. *Phys. Rev. B* **1992**, *45*, 7515.
- (4) Balikdjian, J. P.; Davidson, A.; Launay, S.; Eckert, H.; Che, M. *J. Phys. Chem. B* **2001**, *105*, 12429.
- (5) Chen, X.; Burda, C. *J. Phys. Chem. B* **2004**, *108*, 15446.
- (6) Gopinath, C. S. *J. Phys. Chem. B* **2006**, *110*, 7079.
- (7) Gole, J. L.; Stout, J.; Burda, C.; Lou, Y.; Chen, X. *J. Phys. Chem. B* **2004**, *108*, 1230.
- (8) Chen, X.; Lou, Y.; Samia, A. C. S.; Burda, C.; Gole, J. L. *Adv. Funct. Mater.* **2005**, *15*, 41.
- (9) Prokes, S. M.; Gole, J. L.; Chen, X.; Burda, C.; Carlos, W. E. *Adv. Funct. Mater.* **2005**, *15*, 161.
- (10) Sathish, M.; Viswanathan, B.; Viswanath, R. P.; Gopinath, C. S. *Chem. Mater.* **2005**, *17*, 6349.
- (11) Irie, H.; Watanabe, Y.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 5483.
- (12) Sato, S. *Chem. Phys. Lett.* **1986**, *123*, 126.
- (13) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- (14) (a) Grätzel, M. *Nature* **2001**, *414*, 338. (b) Yu, J. C.; Yu, J. G.; Ho, W. K.; Jiang, Z. T.; Zhang, L. *Z. Chem. Mater.* **2002**, *14*, 3808.
- (15) Sakthivel, S.; Kisch, H. *Chem. Phys. Chem.* **2003**, *4*, 487.
- (16) Sano, T.; Negishi, N.; Koike, K.; Takeuchi, K.; Matsuzawa, S. *J. Mater. Chem.* **2004**, *14*, 380.
- (17) (a) Diwald, O.; Thompson, T. L.; Goralski, E. G.; Walck, S. D.; Yates, J. T., Jr. *J. Phys. Chem. B* **2004**, *108*, 52. (b) Diwald, O.; Thompson, T. L.; Zubkov, T.; Goralski, E. G.; Walck, S. D.; Yates, J. T., Jr. *J. Phys. Chem. B* **2004**, *108*, 6004.
- (18) Di Valentin, C.; Pacchioni, G.; Selloni, A.; Livraghi, S.; Giamello, E. *J. Phys. Chem. B* **2005**, *109*, 11414.
- (19) Nakamura, R.; Tanaka, T.; Nakato, Y. *J. Phys. Chem. B* **2004**, *108*, 10617.
- (20) Saha, N. C.; Tomkins, H. G. *J. Appl. Phys.* **1992**, *72*, 3072.
- (21) Rodriguez, J. A.; Jirsak, T.; Dvorak, J.; Sambasivan, S.; Fischer, D. *J. Phys. Chem. B* **2000**, *104*, 319.
- (22) Gyorgy, E.; Perez del Pino, A.; Serra, P.; Morenza, J. L. *Surf. Coat. Technol.* **2003**, *173*, 265.