

## Visible Light Nitrogen-doped TiO<sub>2</sub> Nanobelt Photocatalyst

Nianqiang Wu\*, Jin Wang,

Department of Mechanical and Aerospace Engineering,  
WVNano Initiative, West Virginia University,  
Morgantown, WV 26506-6106, USA

\*Corresponding author: Fax: +1-(304)-293-6689,

E-mail: [nick.wu@mail.wvu.edu](mailto:nick.wu@mail.wvu.edu)

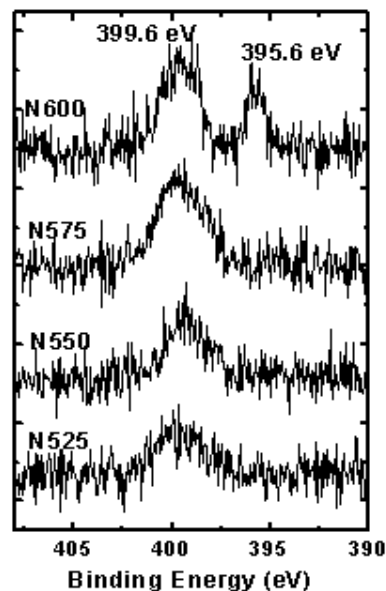
Extensive efforts have been made to study titanium dioxide photocatalyst due to its wide applications in environmental remediation and solar energy conversion. Unfortunately, the relatively large bandgap of TiO<sub>2</sub> (3.2 eV for the anatase phase) requires ultraviolet (UV) light for electron-hole separation, which is only 5% of the natural solar light. It is of significance to develop photocatalysts utilizing both UV irradiation (290-400 nm) and visible light (400-700 nm) to enhance the photocatalysis efficiency. One approach is to dope TiO<sub>2</sub> with anions such as N, C, S and B [1,2]. However, it is unclear whether the photocatalytic activity of highly N-doped TiO<sub>2</sub> different from that of a TiO<sub>2</sub> doped with low-concentrations of N. Based on the calculation by Asahi et al [2], bandgap narrowing will occur when a high-concentration of oxygen sites (6-12.5 at%) are substituted by nitrogen. Recently Okato et al [3] claimed that the N doping induced optical bandgap narrowing does not occur with increase in the N concentration. At low concentrations of N-substitution does not lead to the bandgap narrowing. When the N concentration in TiO<sub>2</sub> increased, it becomes saturated in the substitutional sites. Consequently the excessive N atoms are interstitially doped into the TiO<sub>2</sub> lattice, producing deep-level defects.

In the present work, pristine TiO<sub>2</sub> nanobelts were synthesized by hydrothermal processing. To dope nitrogen into the TiO<sub>2</sub> lattice, the TiO<sub>2</sub> nanobelts were heat-treated in NH<sub>3</sub> flow at different temperatures (525, 550, 575 and 600 °C). The nitrogen concentration in the TiO<sub>2</sub> nanobelts was controlled by modulating the heat-treatment temperature. The nanobelts were 60~400 nm wide and up to tens of micron long. X ray diffraction analysis (XRD) and transmission electron microscopy (TEM) measurements show that both the pristine and the N-doped TiO<sub>2</sub> nanobelts have a monolithic single-crystalline anatase structure. XPS measurement was performed on the N-doped TiO<sub>2</sub> nanobelts as shown in Figure 1. There is a peak at around 399.6 eV for all the N-doped samples. An additional peak appeared at 395.6 eV for Sample N600. The N 1s peak at 395.6 eV is characteristic of N<sup>3+</sup> that corresponds to TiN. The N 1s peak at around 399.6 eV is ascribed to Ti-O-N or Ti-N-O oxynitride. The N 1s peak at around 400 eV is assigned to interstitial nitrogen dopant while the peak at

around 396 eV is ascribed to substitutional nitrogen dopant. The nitrogen atoms tend to sit in the interstitial sites when the N content was below 1.2 at%. At relatively high temperature (600 °C), Substitutional nitrogen atoms are incorporated into the TiO<sub>2</sub> lattice besides the interstitial nitrogen atoms.

For the N-doped nanobelts, an add-on shoulder was imposed onto the cut-off edge of the UV-visible adsorption spectrum, which extended the absorption from 380 nm to 550 nm. The photocatalytic activities of the nanobelts were evaluated by monitoring the decomposition of methyl orange in an aqueous solution under the visible light. A trend in the photocatalytic activity has been observed in the following order: N550>N575>N525>pristine>N600. The photocatalytic activity upon the visible light irradiation increases with N content except for Sample N600. Nitrogen doping allows a visible-light-responsive photocatalytic activity but lowers the UV-light-responsive photocatalytic activity. The visible-light photocatalytic activity originates from the N 2p levels near the valence band.

This work is financially supported by a NSF grant (CBET-0834233), an ARTS grant from Eberly College of Arts and Sciences at West Virginia University and the Research Challenge Grant of West Virginia State (EPS08-01).



**Figure 1** XPS spectra of the N 1s core level obtained from the anatase TiO<sub>2</sub> nanobelts before and after heat-treatment in ammonia flow at different temperatures

### References

- [1] Sato, S. *Chem. Phys. Lett.* **1986**, *123*, 126.
- [2] Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- [3] Okato, T.; Sakano, T.; Obara, M. *Phys. Rev. B* **2005**, *72*, 115124.