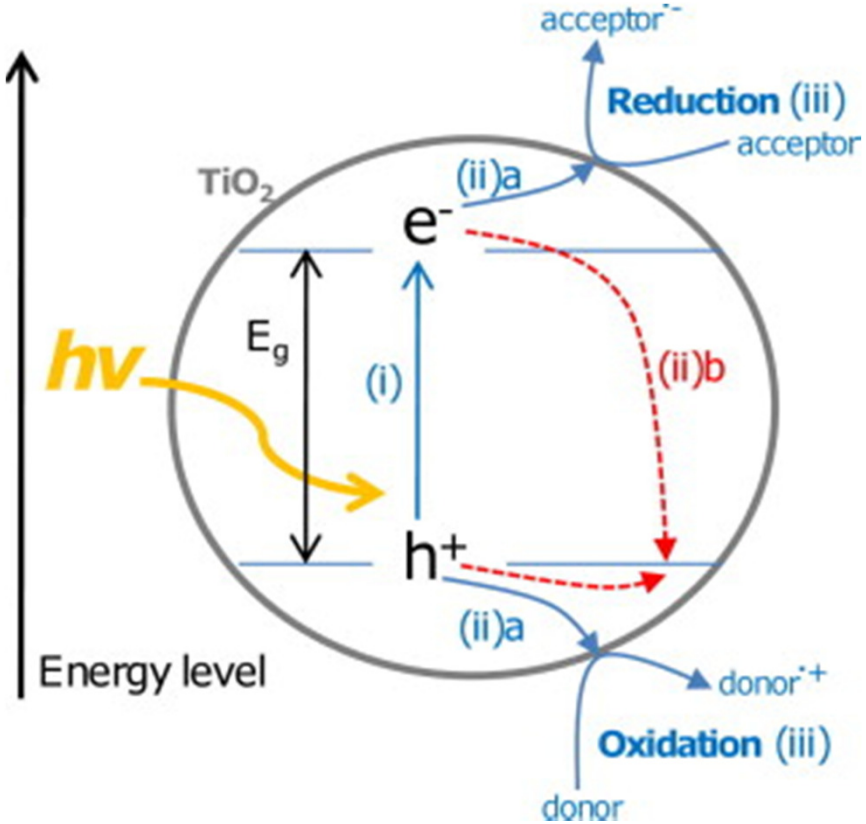
"Study of photo catalytic activity and antibacterial activity of Ag/B/N co-doped TiO_2/CNT composites films"

M. Nizam Uddin, PhD
Department of Chemistry
Shahjalal University of Science and Technology
Sylhet, Bangladesh

4th International Conference on
Nanotek & Expo
San Francisco, USA

Background

TiO_2 (titania): inexpensive, biocompatible, non-toxic, strong oxidizing and reducing power, and excellent photo-stability



Main processes in semiconductor photo-catalysis:

(i) Photon absorption (UV) and electron–hole pair generation.

(ii) Charge separation and migration;
a) to surface reaction sites or
b) to recombination sites.

(iii) Surface chemical reaction (oxidation or reduction) at active sites.

Ref.: CARBON 49 (2011) 741–772

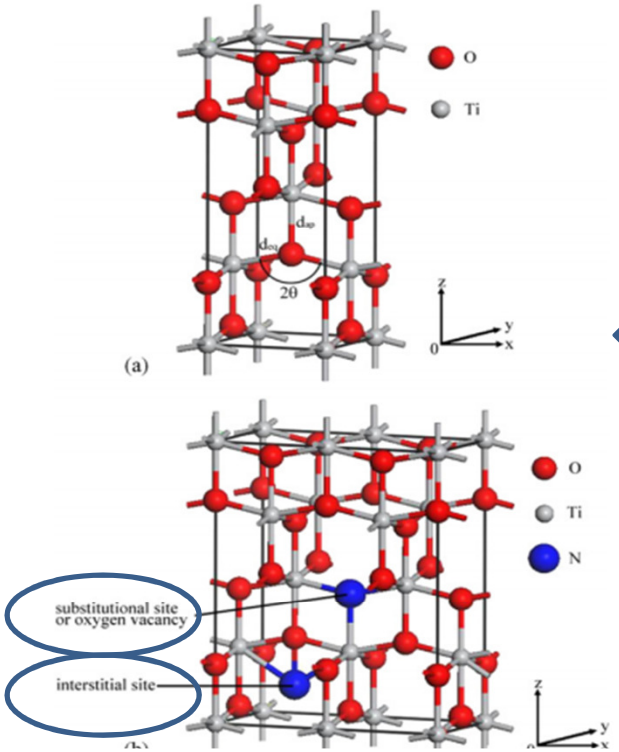
Application of TiO_2 in environmental pollution control

Typical drawbacks

…large band-gap (Eg=3.2 eV), can not be used as responsive catalysts in visible light.

...difficulties in separation of TiO_2 particles (powder) from the wastes and re-use.

…low rate of electron transfer to oxygen and a high rate of recombination between excited electron–hole pairs of TiO_2.



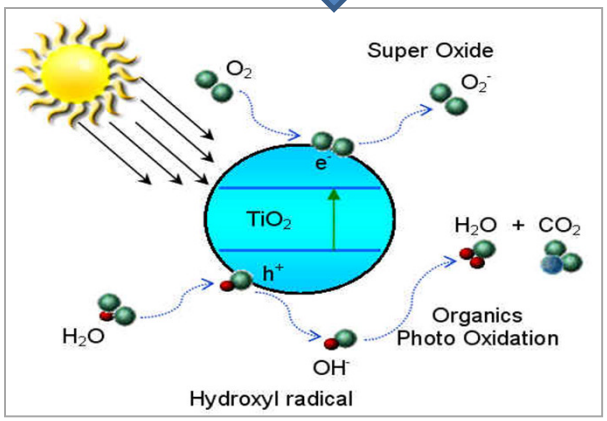
a) A primitive unit cell of TiO_2 in the anatase structure
b) A supercell model showing the sites of nitrogen doping

Z. Zhao et al., J. Phys. D: Appl. Phys. 41 (2008) 025105

Solutions

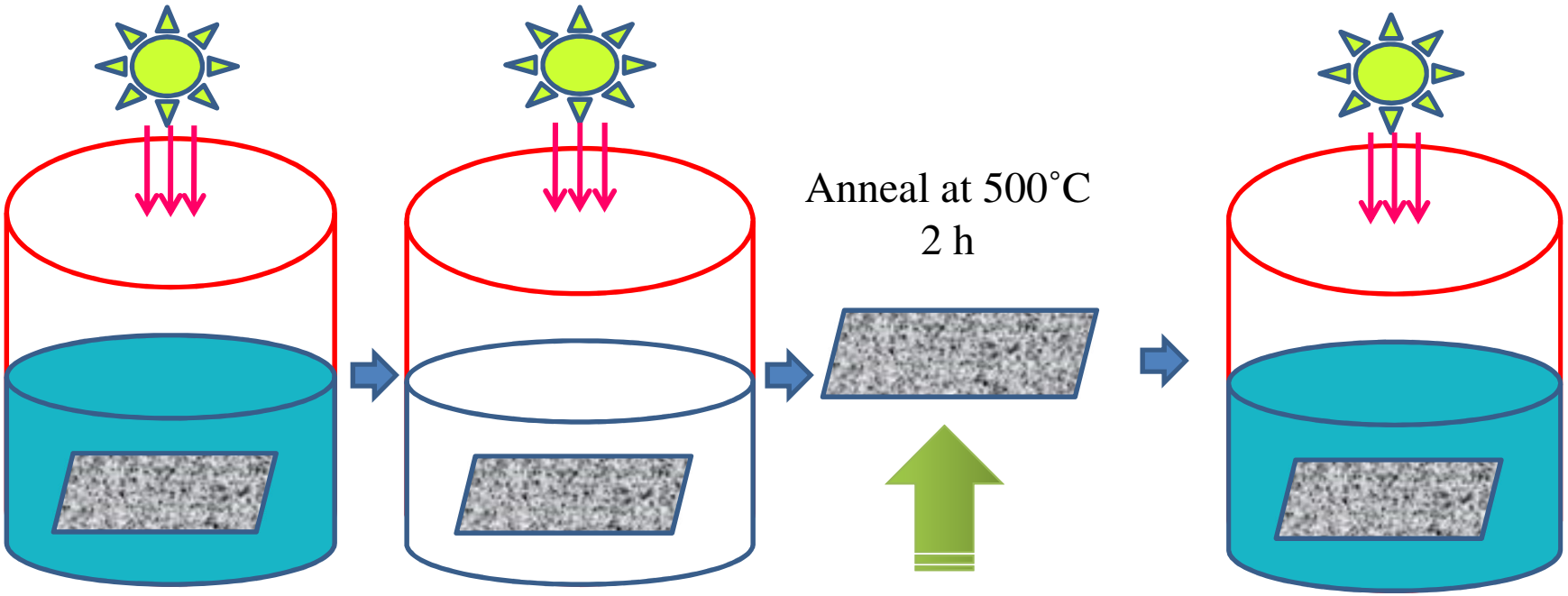
• using nano-crystalline TiO_2 thin films; no separation required and easy to reuse.

•red shift in the optical response of TiO_2 and effect on photocatalytic efficiency due to doping (metal or nonmetal.



K. Hashimoto, H. Irie , A. Fujishima, *Japan. J. Appl. Phy.*, 44, 2005, 8269–8285.

Advantages of thin film (schematically)



Reusability is the main advantage of photo-catalysis in the thin film form…

Some interesting applications:

Applications

TiO_2 coated tiles in an hospital environment showed that the surface bacteria on the wall surfaces were reduced to zero, plus airborne bacteria counts were reduced.

Titanium Dioxide can be coated on many building materials. These films exhibit a self cleaning effect due to the strong oxidizing properties.

Pollutant degradation

Decomposition of various environmentally hazardous compounds (organic, inorganic and biological materials), found in both gaseous and liquid phases.

Ref.: CARBON 49 (2011) 741–772

http://www.titaniumart.com/photocatalysis-ti02.html

-:Summarizing the Objectives of this project:-

•New challenge to use thin film forms of TiO_2 for its comfortable and effective re-use ability.

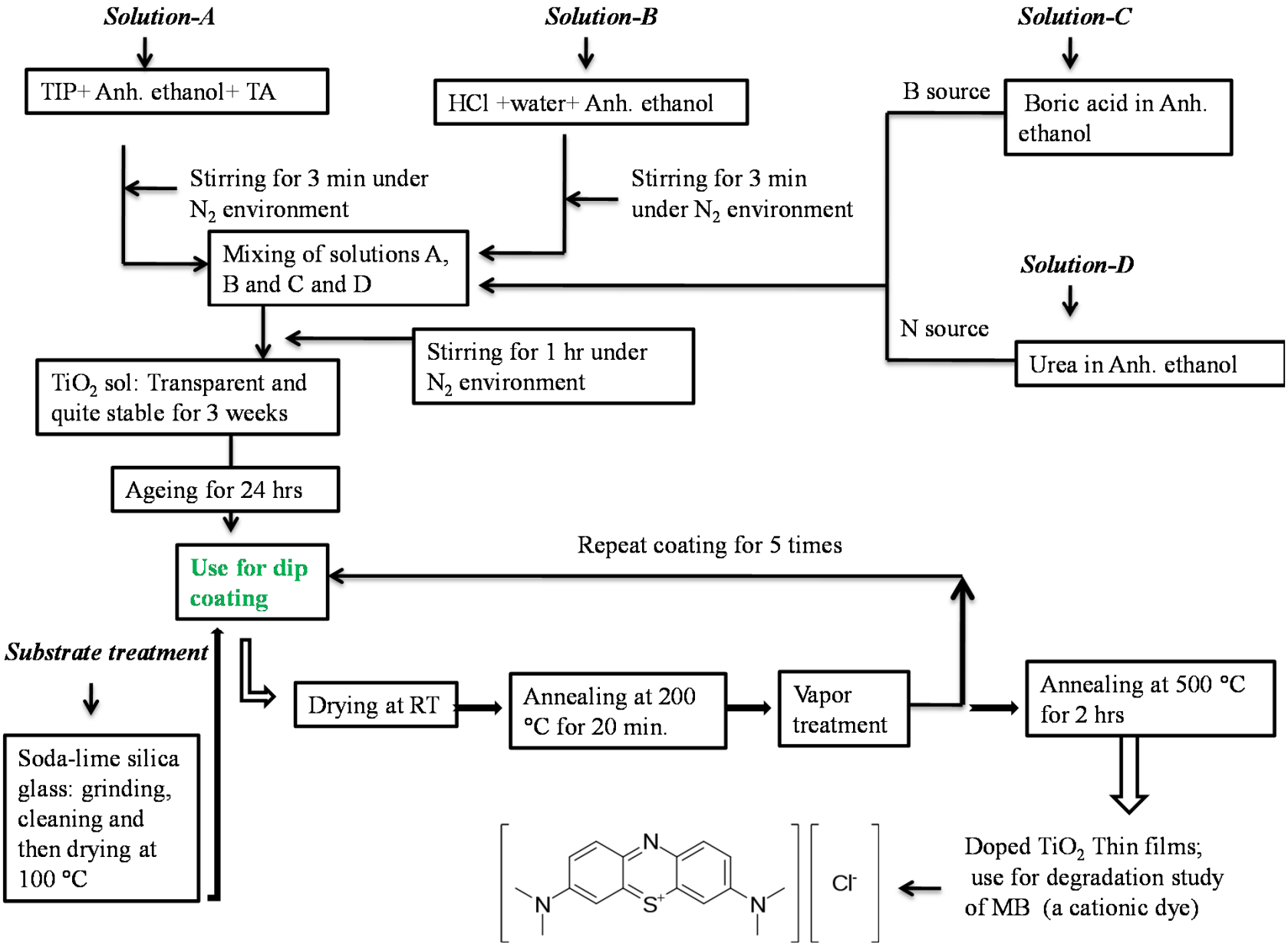
•Modification of TiO_2 by doping with metal and non-metal to extend its spectral response to visible region to promote 'efficient use of solar energy' for 'photodegradation of different dyes'. The aim is to use the modified TiO_2 for the treatment of industrial effluent and to clean polluted water.

•Target to use carbon nanotubes (CNT) with large surface area for better adsorption ability of organic dye .

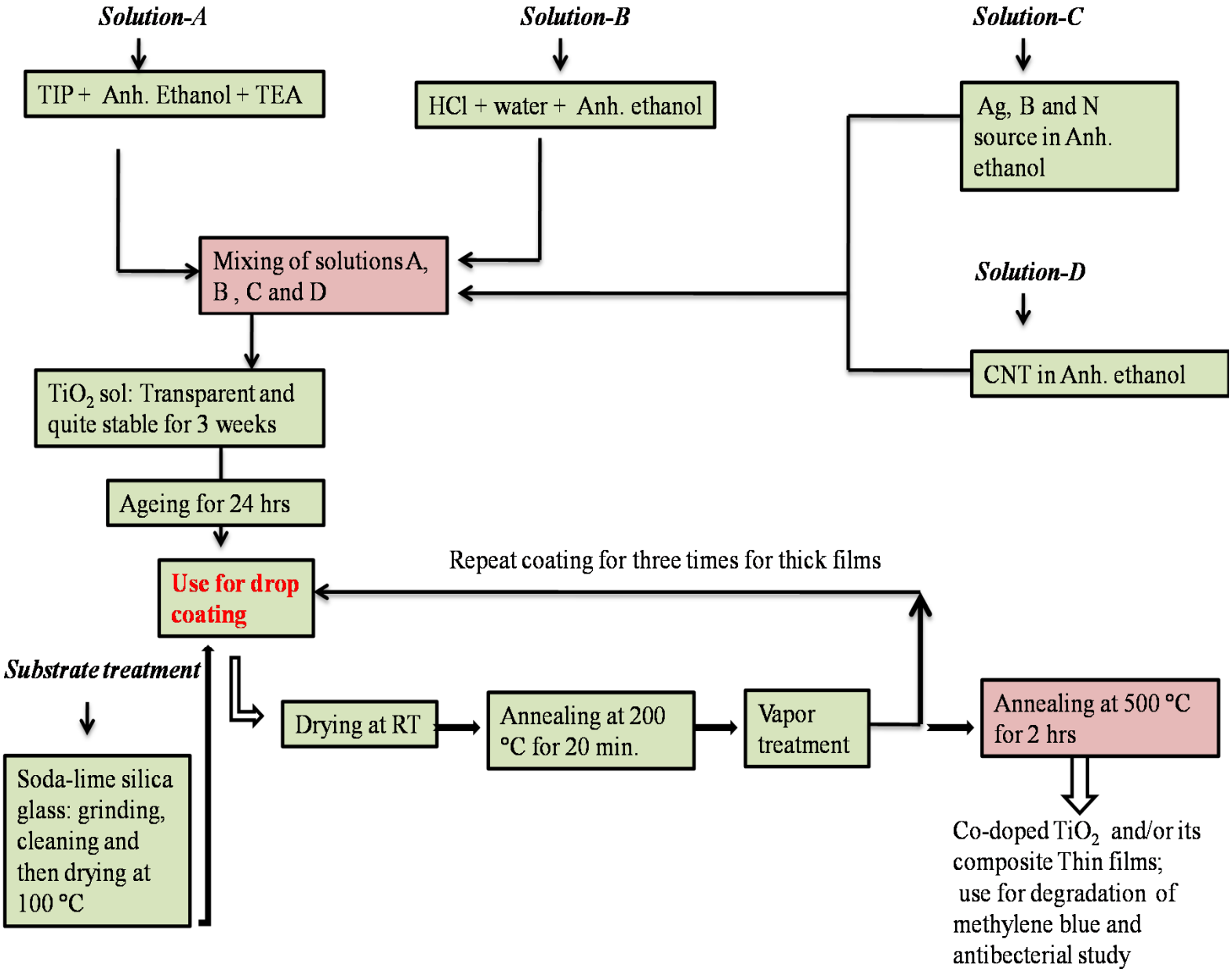
•Aiming to decrease the fast recombination rate of photo-generated election-hole pairs in TiO_2 matrix using co-doping and CNT which is supposed to increase photo-catalytic degradation efficiency.

Experimental Details

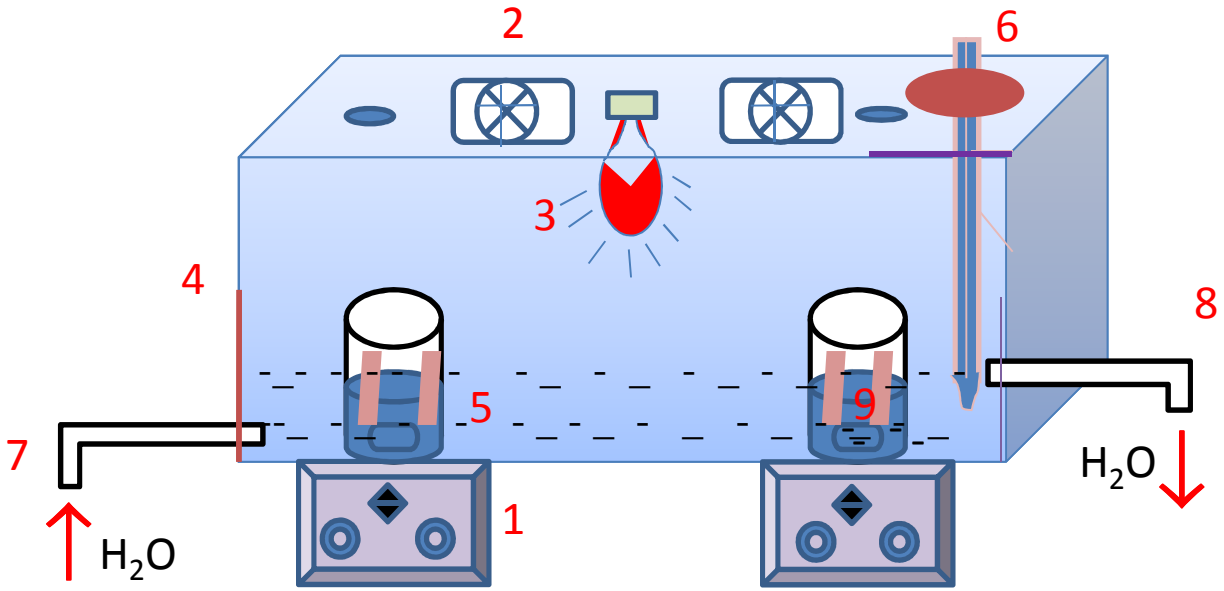
a) Non-metals co-doped TiO_2 as thin film form



b) Metal/non-metal co-doped TiO_2 -CNT composites as thin film forms



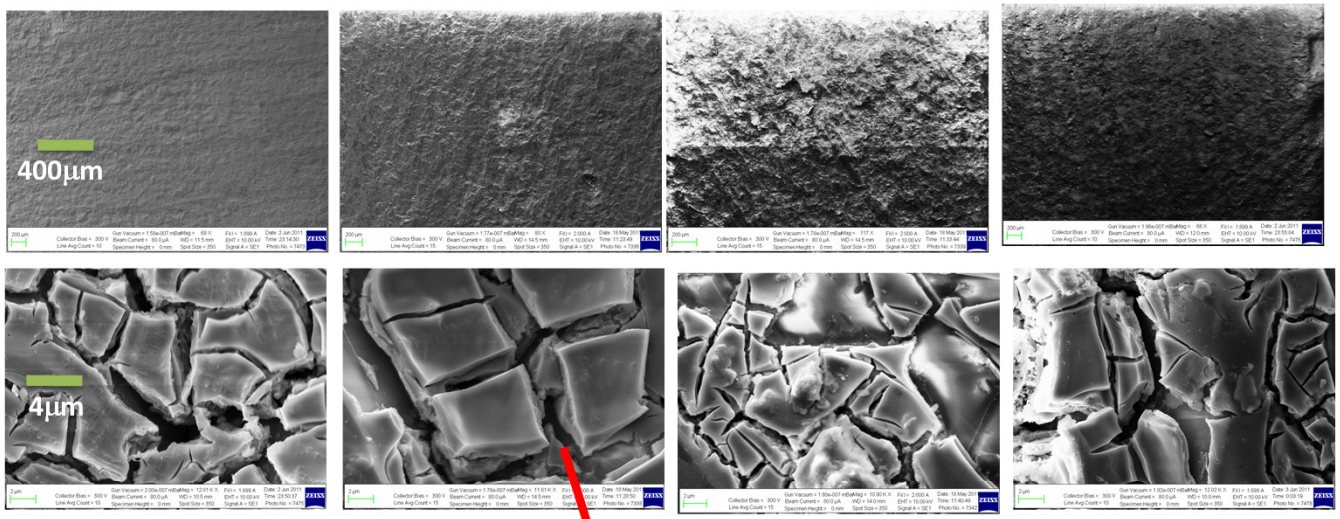
Degradation facilities



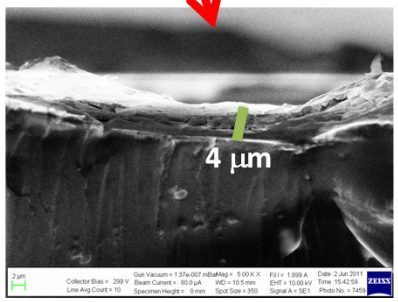
1. Magnetic stirrer
2. Cooling fan
3. Tungsten lamp
4. Glass box covered by Aluminum foil
5. MB solution
6. Thermometer
7. Circulating Water inlet
8. Circulating Water outlet
9. Thin film photo catalyst

(a)

An experimental and first-principles study of the effect of B/N doping in TiO_2thin films for visible light photo-catalysis



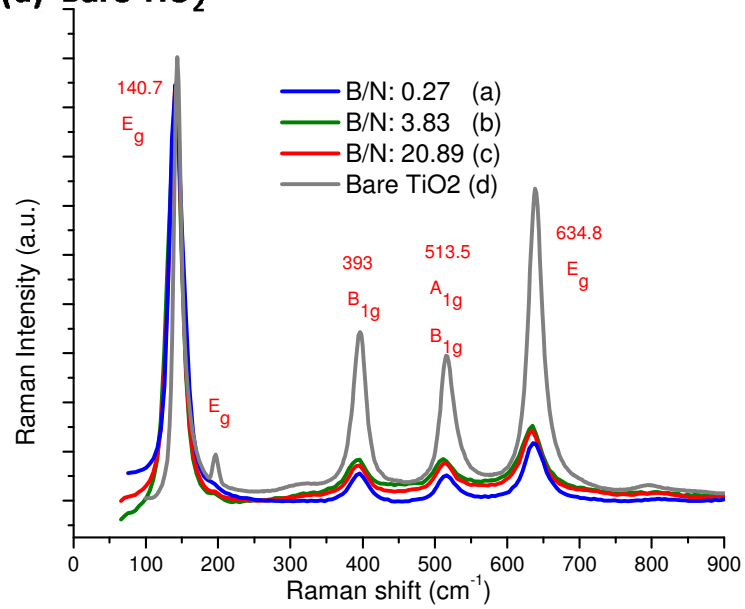
(a) B/N: 0.27 (b) B/N: 3.83 (c) B/N: 20.89 (d) Bare TiO_2



(e) Typical cross section view of films from (b)

SEM images:

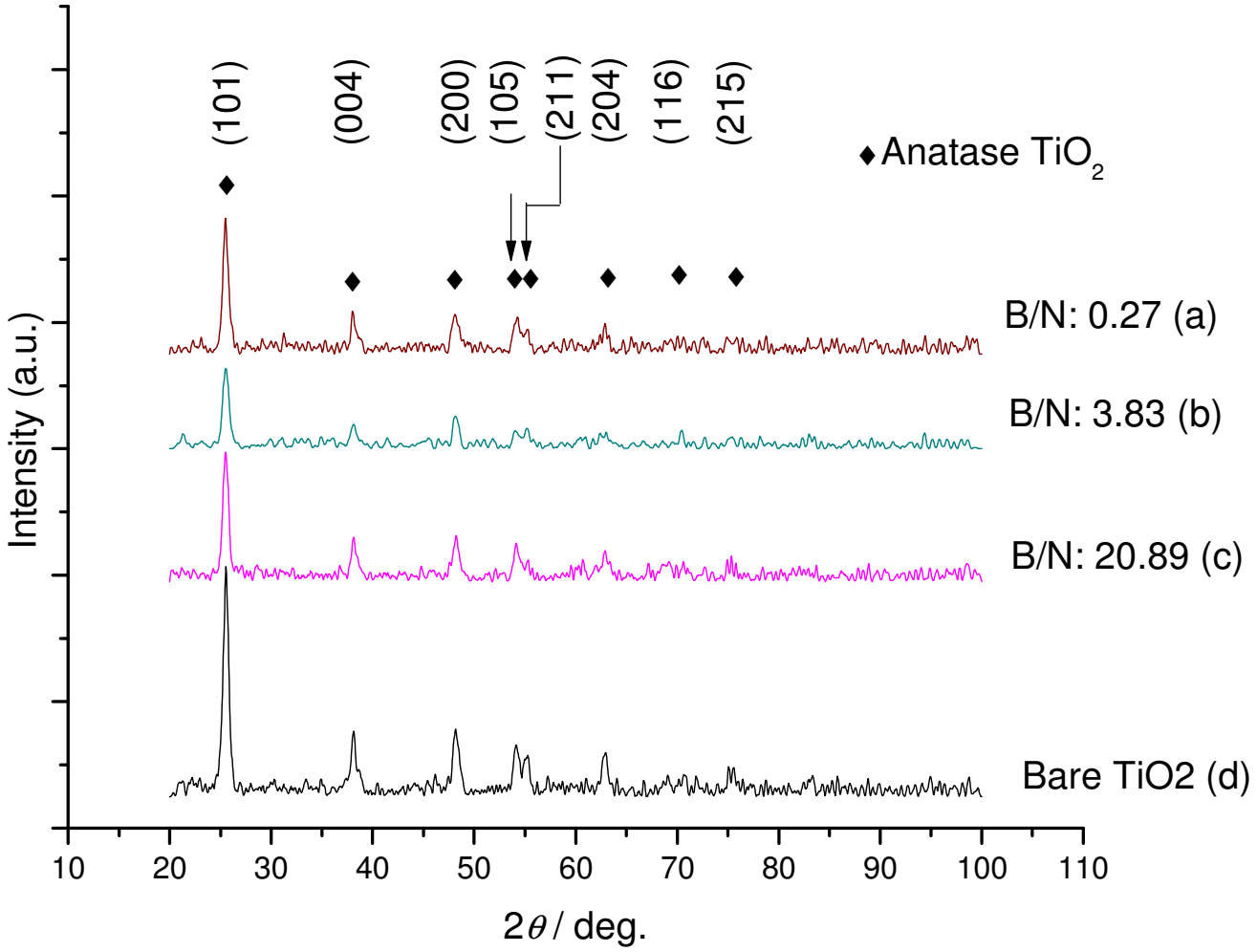
Observed significant cracking on the surface of all films.



Raman spectra:

Showed anatase TiO_2 bands

XRD:

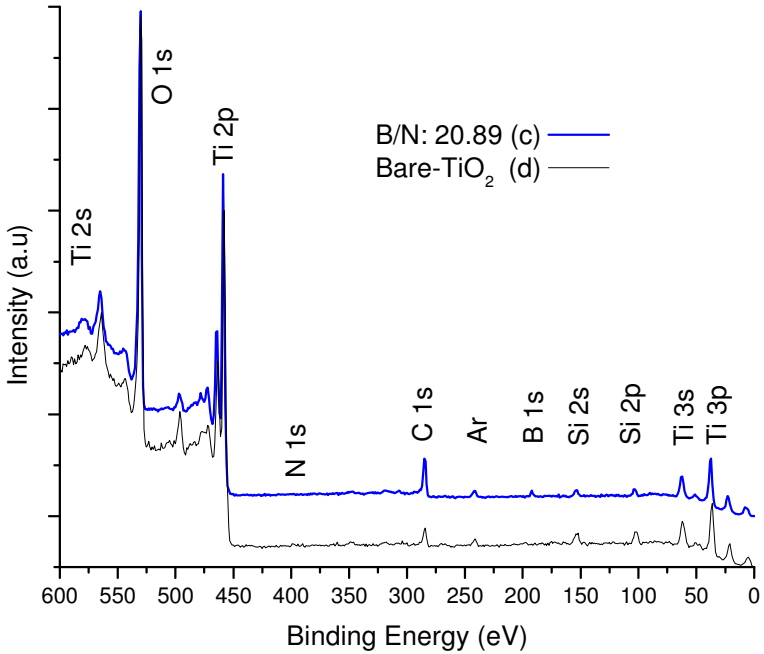


Anatase phase of TiO_2

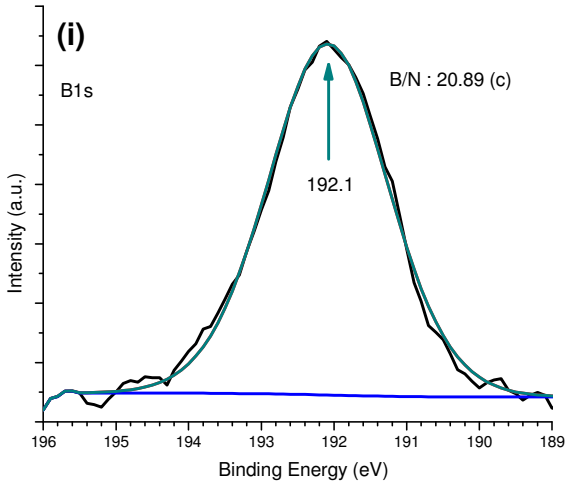
No B- and N- derived peaks due to other oxides and nitrides:

Indication of B and N as dopant in TiO_2 ; no tendency to segregate and/or precipitate in different phases during the synthetic process

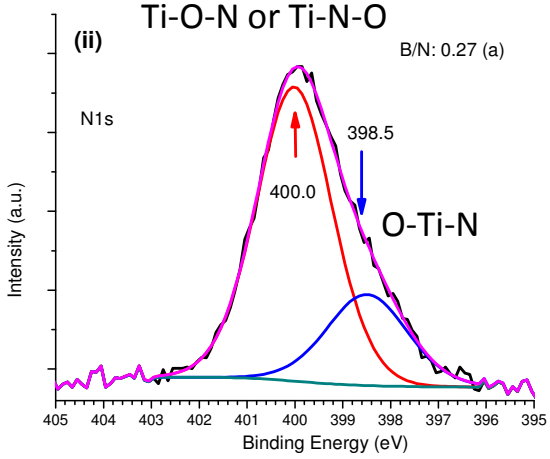
XPS



Ti-O-B or Ti-B-O or O-Ti-B



Ti-O-N or Ti-N-O

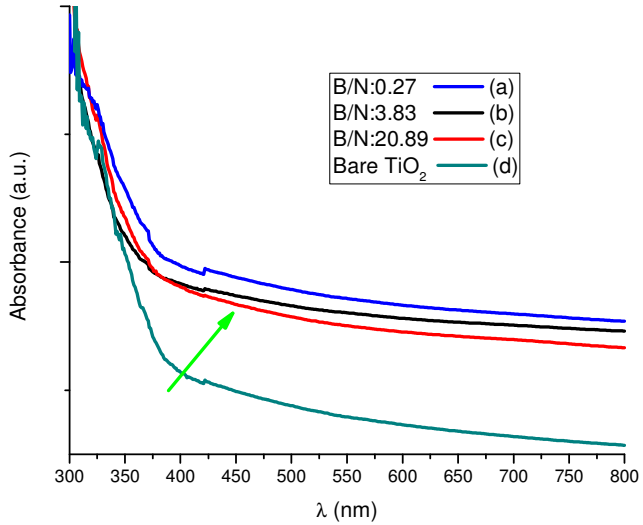


O-Ti-N linkages might be responsible for visible light photo-catalysis…

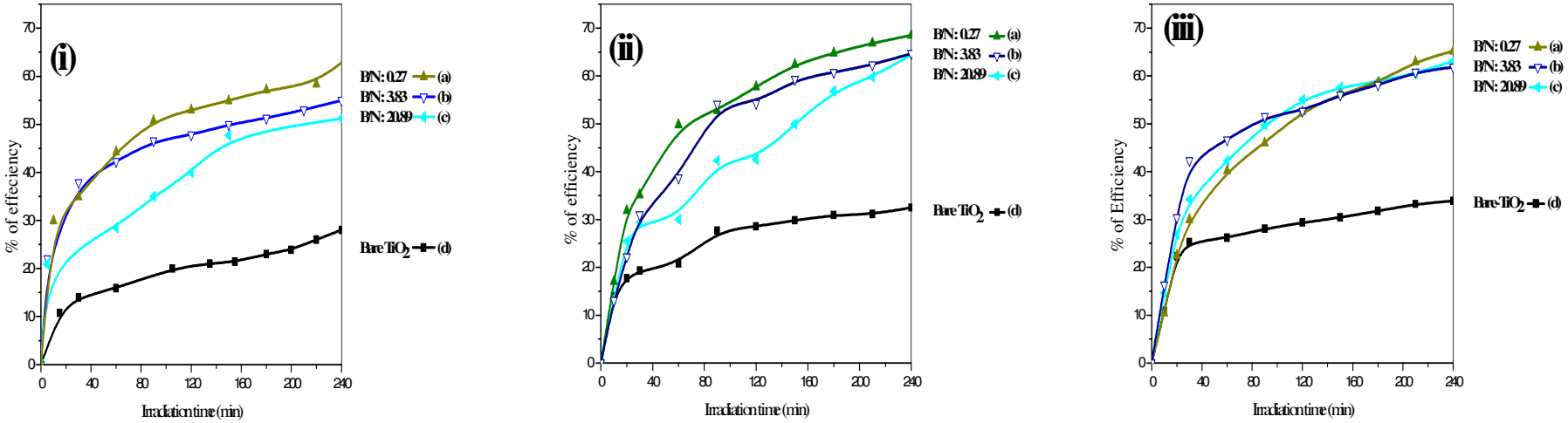
B1s XPS spectrum with the highest atomic percentage of B

N1s XPS spectrum with the highest atomic percentage of N

UV-Vis:



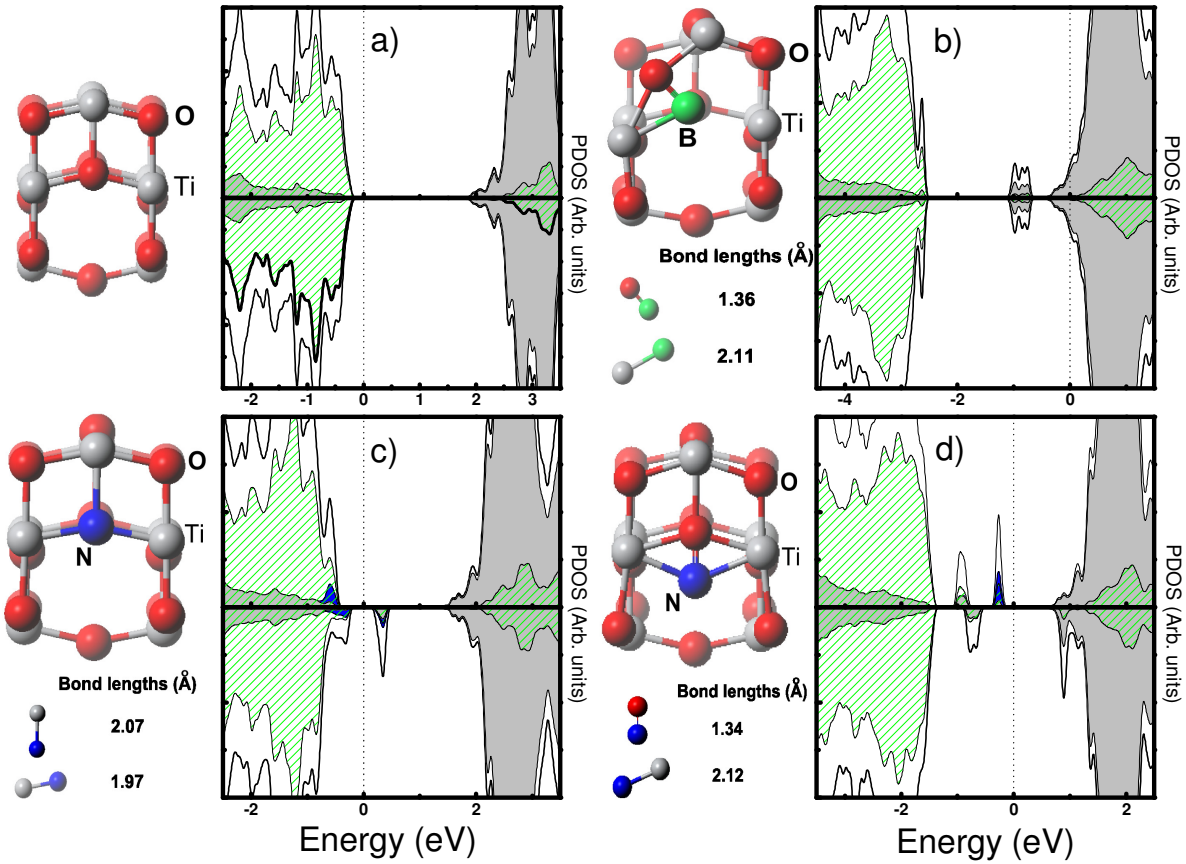
Clear red-shift in UV-Vis spectra; revealing the visible light absorption with B/N co-doped TiO_2



Percentage of degradation efficiency ; (i) 1° cycle, (ii) 2° cycle and (iii) 3° cycle

Density functional theory calculation (single doping)

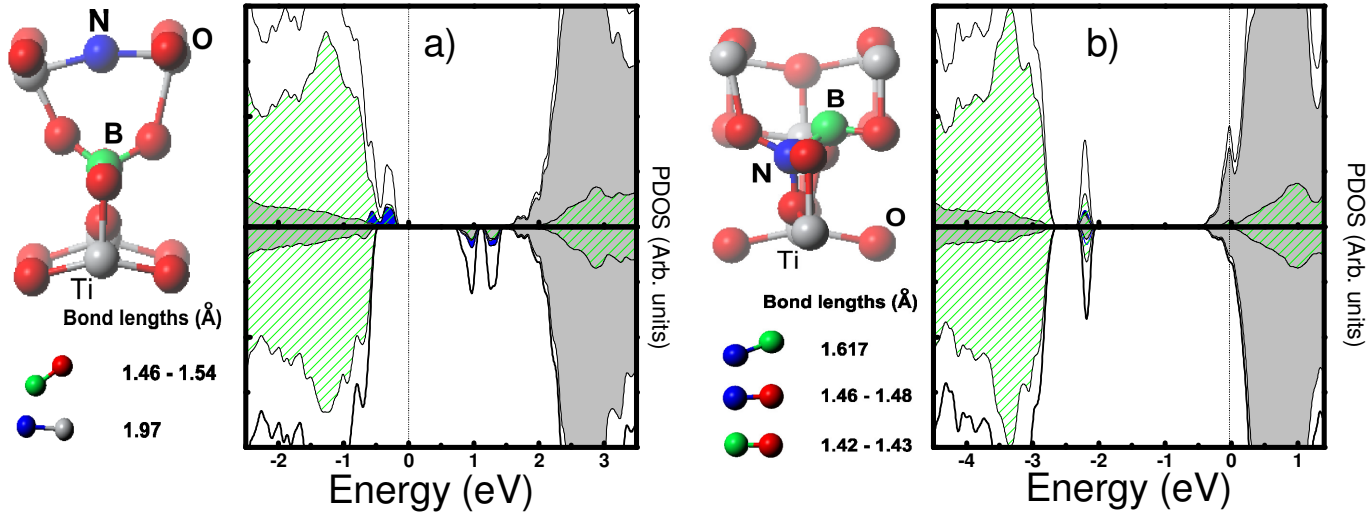
Mid-gap energy states



Relaxed structures and partial density of states (PDOS) of a) pure anatase, b) B- doped O-, c) N- doped O- and d) N interstitial models. Energies are shifted such that Fermi levels are matched with zero of energy. The bond lengths between doped atoms and first neighbors are indicated. Solid lines, gray shaded, green shaded and blue shaded areas represent the total DOS, PDOS of Ti3d, O2p and N2p states, respectively.

Density functional theory calculation (co-doping)

Mid-gap energy states



Co-doping of anatase: a) B atom replaced with Ti and N atom replaced with O and b) N atom replaced with Ti, and B atom replaced with O. Solid lines, gray shaded, green shaded and blue shaded areas represent the total DOS, PDOS of Ti3d, O2p and N2p states, respectively.

Summary

i. band gap narrowing leads to the red shift of the absorbance spectra to the visible light region.

Ii. the appearance of midgap states could be responsible for the enhancement of the photo-catalytic activity either by improving the absorbance or avoiding the recombination of electron-hole pairs.

(b)

SYNTHESIS, CHARACTERIZATION, PHOTO CATALYTIC AND ANTIBACTERIAL ACTIVITY OF Ag/B/N CO-DOPED TiO_2 / CNT COMPOSITE FILMS

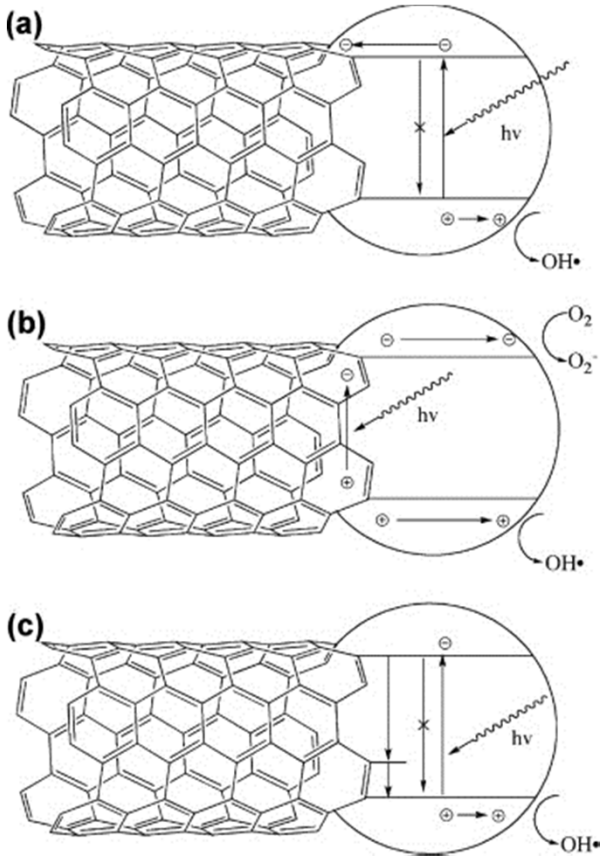
Effect of CNT on photo-catalytic activity of TiO_2 as Sensitizer…..

i. high-surface area and high quality active sites

ii. retardation of electron–hole recombination (a)

iii. UV to visible light catalysis by moadification of band-gap and / or sensitization(b)

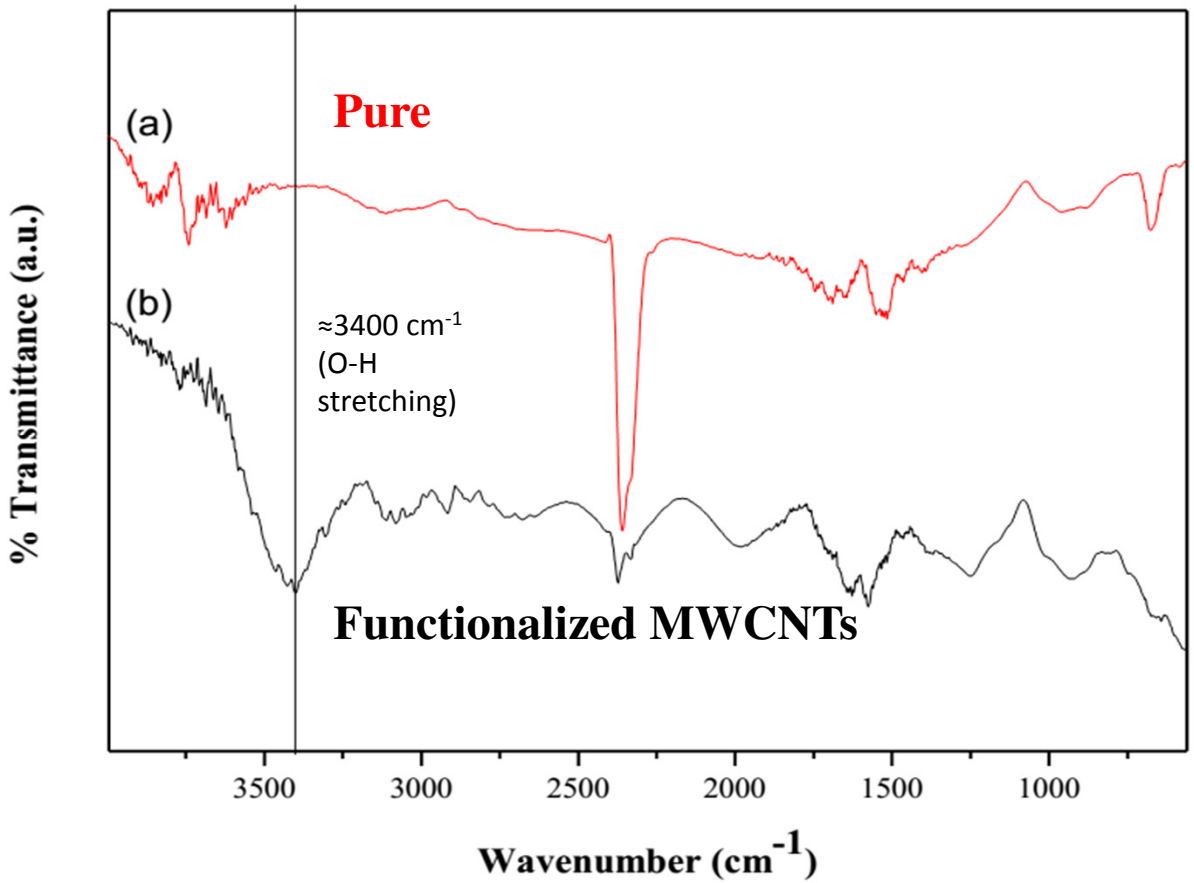
iv. C-O-Ti bond formation like carbon doped TiO_2; enhanced UV to VIS absorption (c)



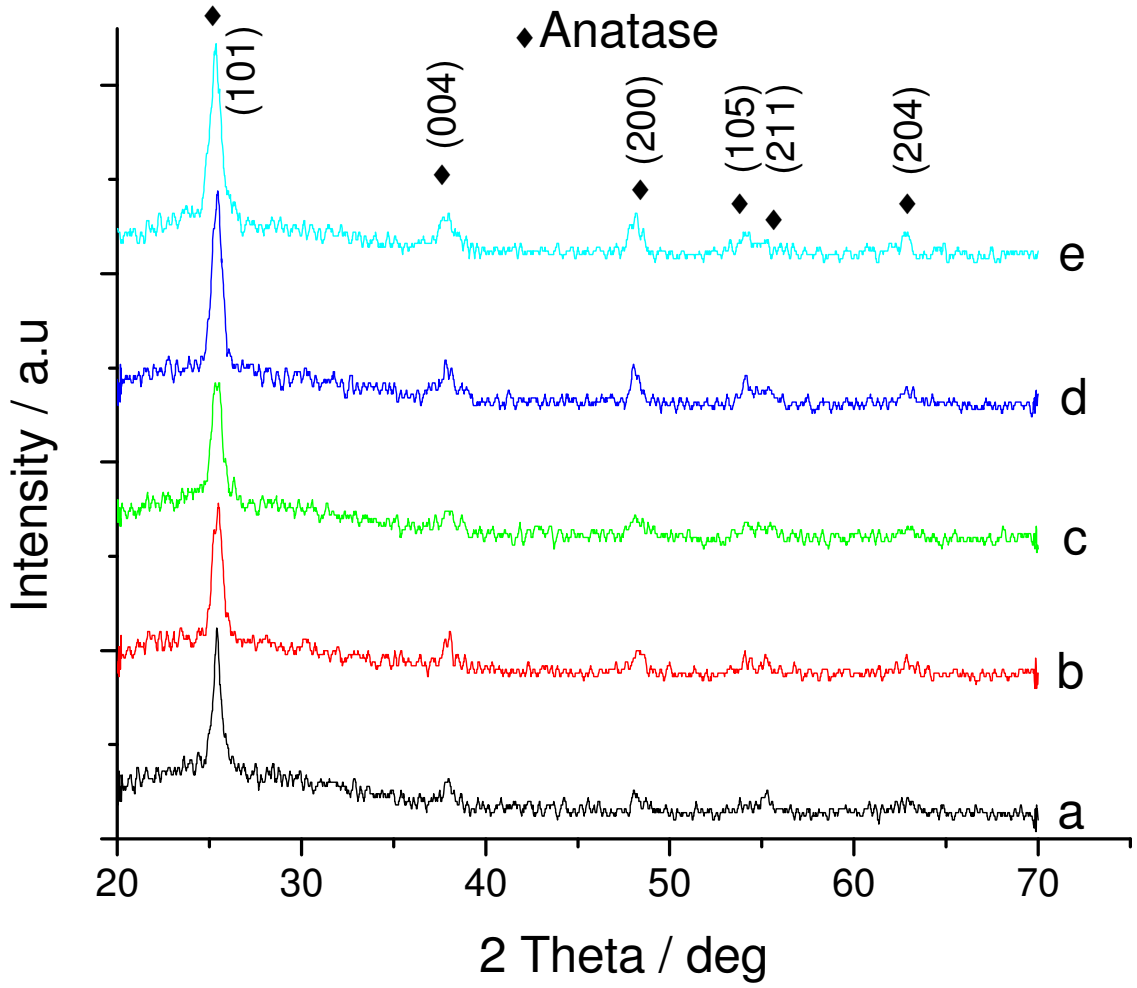
Proposed mechanisms of synergistic enhancement in TiO_2–CNT composites. (a) CNTs inhibit recombination by acting as sinks for photogenerated electrons in TiO_2. (b) Photosensitizing mechanism based on electron–hole pair generation in the CNT. Depending on the relevant positions of the bands, the electron or hole may be transfered into the TiO_2, from CNT generating O2- or OH species . (c) CNTs act as impurities through the Ti–O–C bonds .

Ref.: Woan et al., Adv Mater 2009;21(21):2233–9.
R. Leary, A. Westwood, *Carbon,* 49, 2011, 741–772.

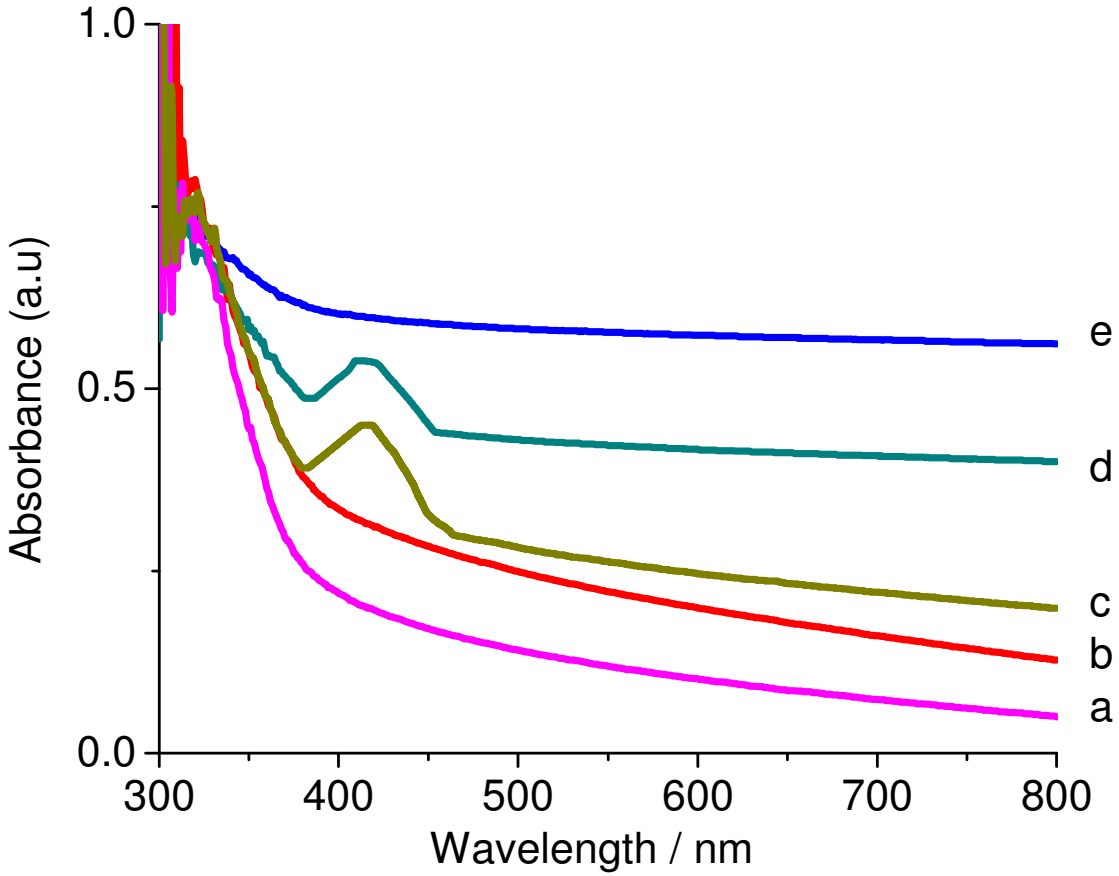
FTIR spectra of (a) Pure and (b) Functionalized MWCNTs



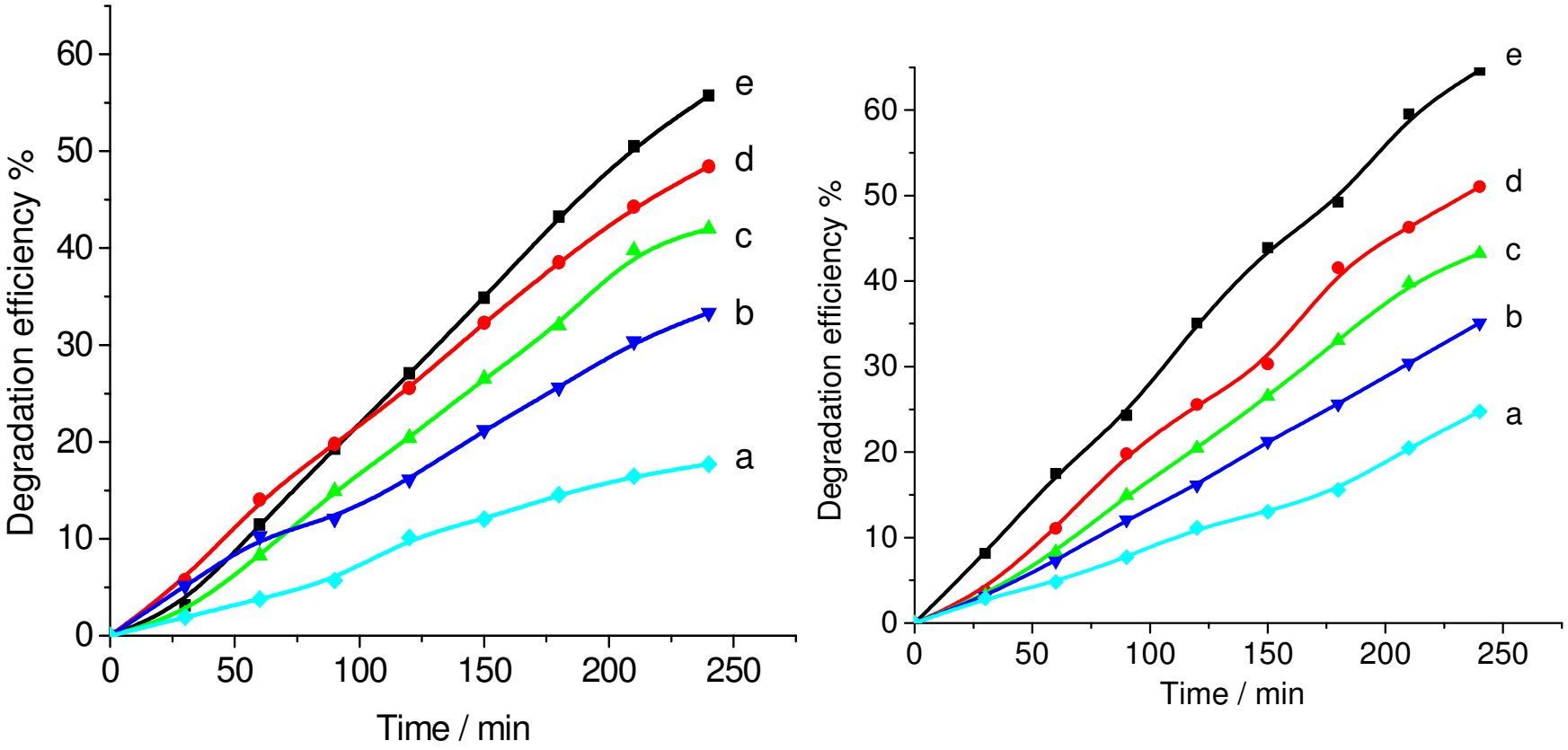
XRD spectra of (a) TiO_2, (b) CNT-TiO_2 (c) 2%Ag-TiO_2, (d) 2%B 5%N 2%Ag -CNT-TiO_2 and (e) 2%B 5%N-CNT-TiO_2 composite thin films calcinated at 500°C.



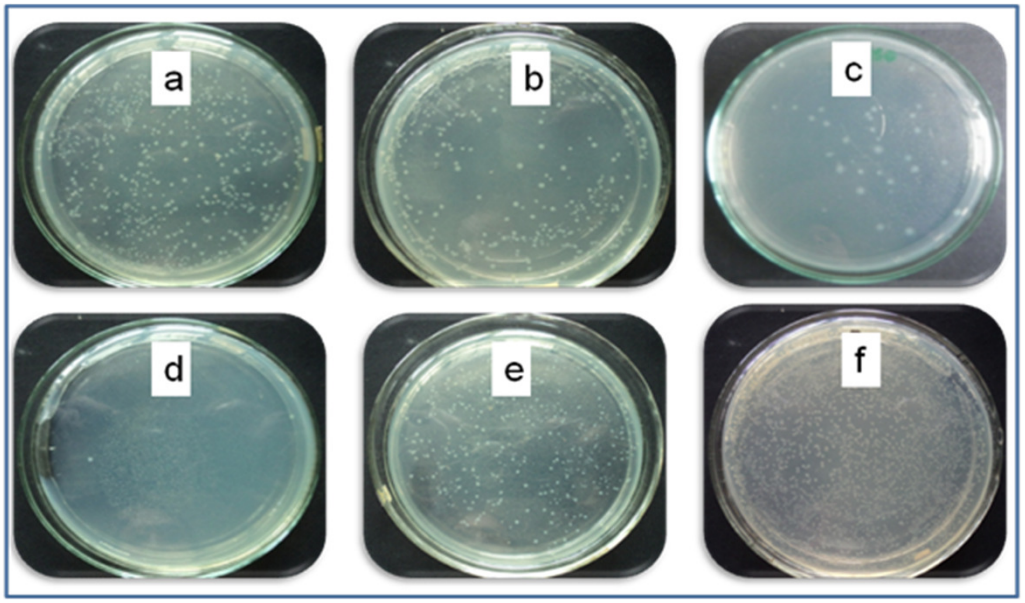
UV–Visible absorption spectra of (a) TiO_2, (b) CNT-TiO_2 (c) 2%Ag-TiO_2, (d) 2%B 5%N 2%Ag -CNT-TiO_2 and (e) 2%B 5%N-CNT-TiO_2 composite thin films calcinated at 500° C.



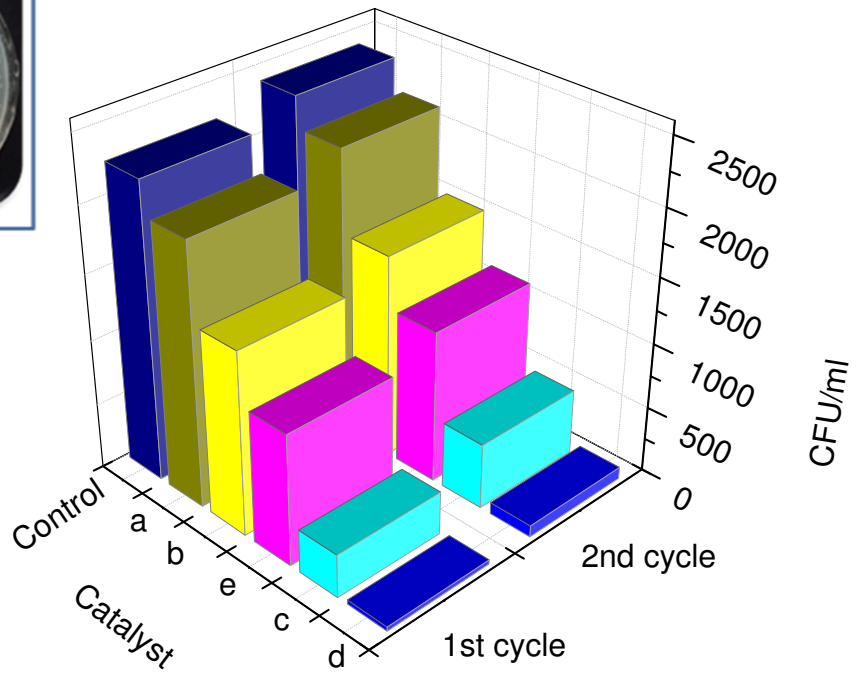
Percentage of degradation efficiency of (a) TiO_2, (b) CNT-TiO_2 (c) 2%Ag-TiO_2, (d) 2%B 5%N 2%Ag -CNT-TiO_2 and (e) 2%B 5%N-CNT-TiO_2 films (i) in cycle number 1 (1°cycle), (ii) in cycle number 2 (2° cycle).



Antibacterial activity :
Against the E. coli bacteria based on the so-called antibacterial drop-test in the laminar air flow chamber



Colony forming unit (CFU) of *E-coli* after visible light irradiation for 60 min in presence of (a) TiO_2, (b) CNT-TiO_2 (c) 2%Ag-TiO_2, (d) 2%B 5%N 2%Ag -CNT-TiO_2 and (e) 2%B 5%N-CNT-TiO_2 and without film (control) in 1° cycle and 2° cycle.



Antibacterial efficiency of (a) TiO_2, (b) CNT-TiO_2 (c) 2%Ag-TiO_2, (d) 2%B 5%N 2%Ag -CNT-TiO_2 (e) 2%B 5%N-CNT-TiO_2 composite thin films and (f) without film (control).

Conclusions

First Phase

•Co-doped TiO_2 thin films with B and N have been successfully synthesized by simple sol-gel dip coating method.

•The B/N co-doped TiO_2 films demonstrated up to 40% higher photo-catalytic activities than bare-TiO_2 films under visible light irradiation.

•The absorption edges for the doped films were found to be shifted toward the visible region.

•The film with the B/N atomic ratio of 0.27 displayed the highest degradation rate among all doped films.

•The doped films retained their superior catalytic activity for extended periods (Re-usability).

•Computational calculation findings supported experimental data by indicating the possible routes that can be responsible for the improvement of the photo-catalytic activity in TiO_2 due to B and N doping.

•It is revealed that B/N doped TiO_2 films could be a potential candidate for scaling up for industrial applications.

Second Phase

•Co-doped TiO_2 and CNT composite thin films with silver, boron and nitrogen have been successfully synthesized by newly developed simple **sol-gel drop coating** method.

•The 2%B 5%N-CNT-TiO_2 composite film demonstrated 58% photo-catalytic efficiency and 2%B 5%N 2%Ag -CNT-TiO_2 composite film showed 99% bacteria killing efficiency under visible light irradiation.

•The absorption edges for the doped films were found to be shifted toward the visible region, while the overall absorption remarkably increased.

•The doped composite films retained their superior catalytic activity for extended periods. It can also be concluded that silver acted as a very effective metal antibacterial agent as well as a kind of doping metal with boron, nitrogen in TiO_2 composite films.

Acknowledgement

E. Bengu, Rasim Ovali, Oguz Gulseren : Bilkent University, Turkey

M. M. R. Mazumder, M. S. Islam , Sayed Ul Alam Shibly , Saiful Islam , Md. Motiur Rahaman Mazumder , Md. Saidul Islam, M. Jasim Uddin , D. R. Sarker, Z. Rahman, M. A. Hossain, and M. Elias,:
Shahjalal University of Science and Technology, Bangladesh

Recent related journal publications of my research group

Md. Nizam. Uddin* et al *J. Photochem. Photobiol. A: Chem.*, 254 (2013) 25-34.

M. J. Uddin, Md. Nizam Uddin et al, *International Nano Letter,* 3 (2013) 16.

Submitted: **M. N. Uddin*** et al under review at ***J. Crystal Growth***, 2014.
M. N. Uddin* et al under review at ***J. Appl. Surface Science***, 2014.

This research was funded by the following projects

i. The world Academy of Sciences, Italy (Undertaken by UNESCO)

ii. University Grant Commission of Bangladesh,

iii. Research Center, Shahjalal University of Science and Technology,

iv. Ministry of Science and Technology, Bangladesh, and

v. Bilkent University via Ministry of Defense, Turkey.


Thank you very much for your attention!
National Parliament House of Bangladesh
EGASIA'11

SUST, my job place with Photo

Entrance way to SUST campus

Liberation War Memorial *'71 at SUST*

Mascots made by the Architecture students of SUST for a national festival

Students' Hall

Academic building of SUST

University Central Library