Window Cleaning
aka
Visible-Light Photocatalysis

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“Environmental” Programs

- WC nanoparticles as an alternate automobile catalyst.

  EPA STAR

- Ge-TiO_2 Quantum Dot Nanocomposite for broad band solar cells

  NSF ACT

- Simultaneous Adsorption and Reduction on TiO_2 nanoparticles

  NSF INT Egypt

- Visible light photocatalysis with nano-TiO_2

  NSF NIRT

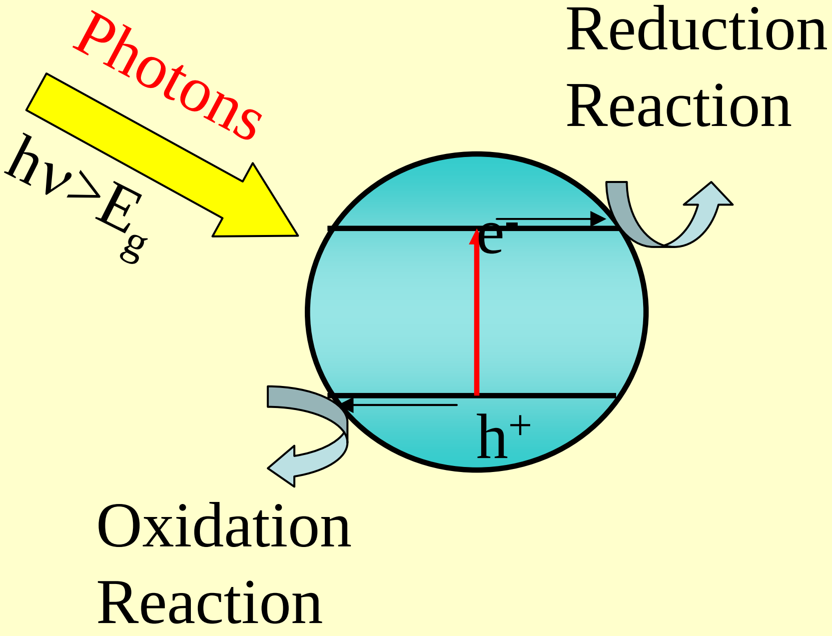
Photocatalysis

- The aim of semiconductor photocatalysis is to effectively detoxify organic pollutants.
- A photon is used to create electron hole pairs in the semiconductor.

  $$e^- + O_2 \rightarrow O_2^-$$

  $$h^+ + OH^- \rightarrow OH\bullet$$

- Radicals then react with organic pollutants completely oxidizing to CO_2, H_2O



Photons

$h\nu > E_g$

Reduction Reaction

e^-

h^+

Oxidation Reaction

Types of Photocatalysts

TiO_2 (E_g = 3.2eV)

ZnO (E_g = 3.2eV)
ZnS (E_g = 3.6eV)
α-Fe_2O_3 (E_g = 2.8eV)

- Unstable
- Corrodes or subject to poisoning

WO_3 (E_g = 2.8eV)
$SrTiO_3$ (E_g = 3.2eV)

- Expensive
- Difficult to produce

Why TiO_2?

- Chemically and Biologically Inert (?)
- Inexpensive
- Reusable
- Redox potential of $H_2O/OH^{\bullet}$ lies within the bandgap

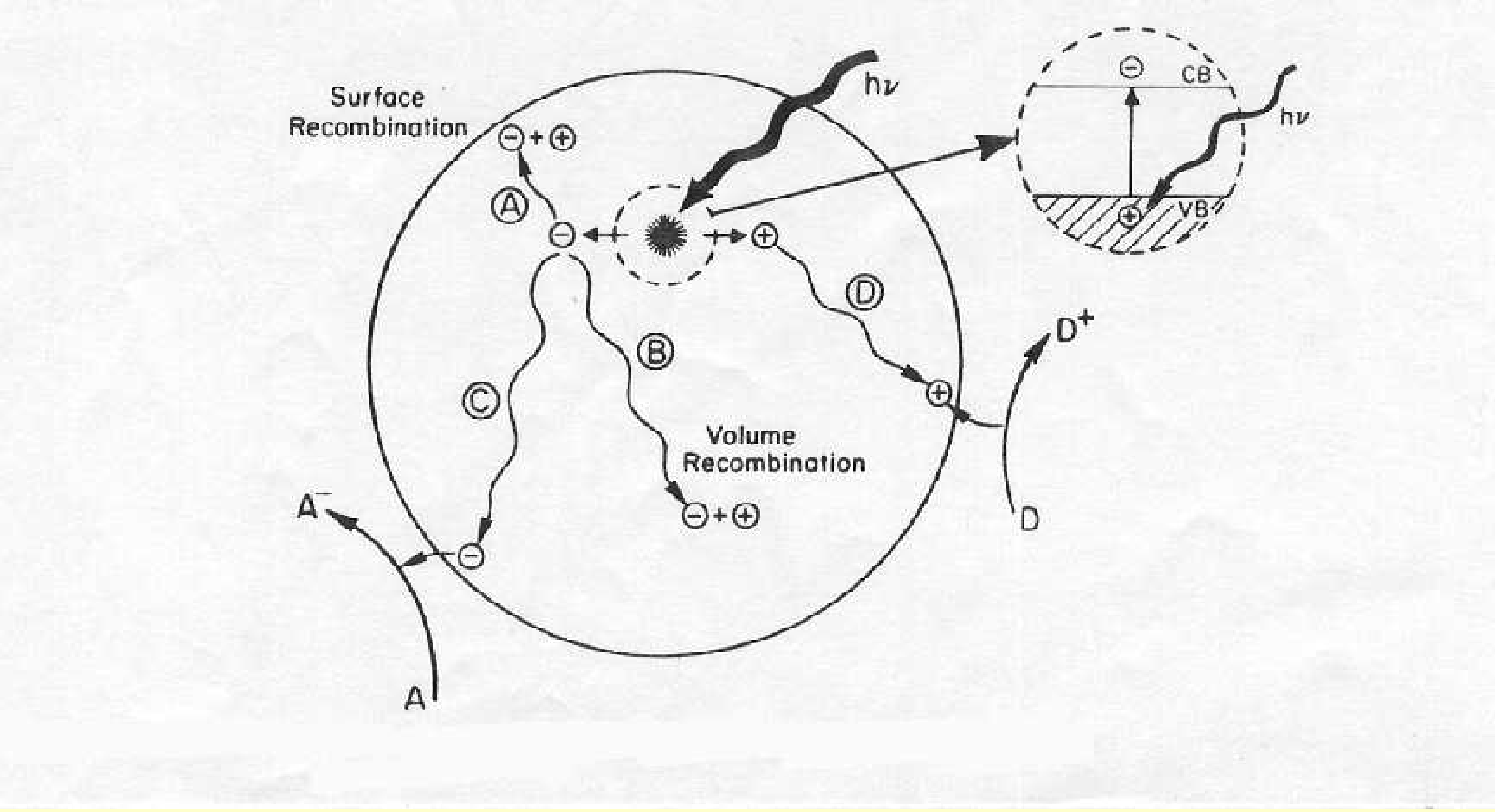
Exciton Recombination

- Excitons in pure/bulk TiO_2 have a very short lifetime (~10ps) because of charge recombination

$$e^- + h^+ = h\nu \text{ (heat or light)}$$

- Therefore, it is important to prevent hole-electron recombination before a designated chemical reaction occurs on the TiO_2 surface

Exciton Recombination



A. Linsebigler et al., *Chem. Rev.*, **95**, 735, 1995

Volume Recombination

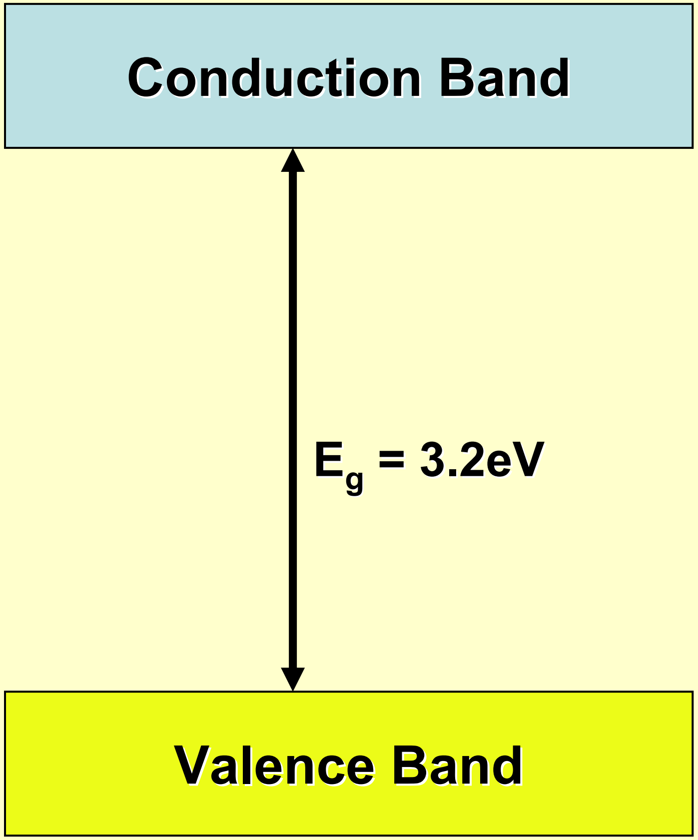
- In order to reduce volume recombination it is necessary to minimize the volume of the particle
- Use Nanoparticles
- Nanoparticles have a high surface/volume ratio therefore surface recombination is probable
- Therefore particle size optimization is necessary.

Reducing Recombination

- Doping the catalyst decreases recombination by introducing trapping sites
- The trapping of electrons/holes at these sites effectively increases their lifetime and probability that they will participate in the desired photocatalysis reaction

Band Gap Reduction of TiO_2

- TiO_2 is a large band gap semiconductor (~3.2 eV)
- Absorption edge is in UV region, which is only 5-8% of the solar light.
- This absorption edge needs to be extended to the visible range



Conduction Band

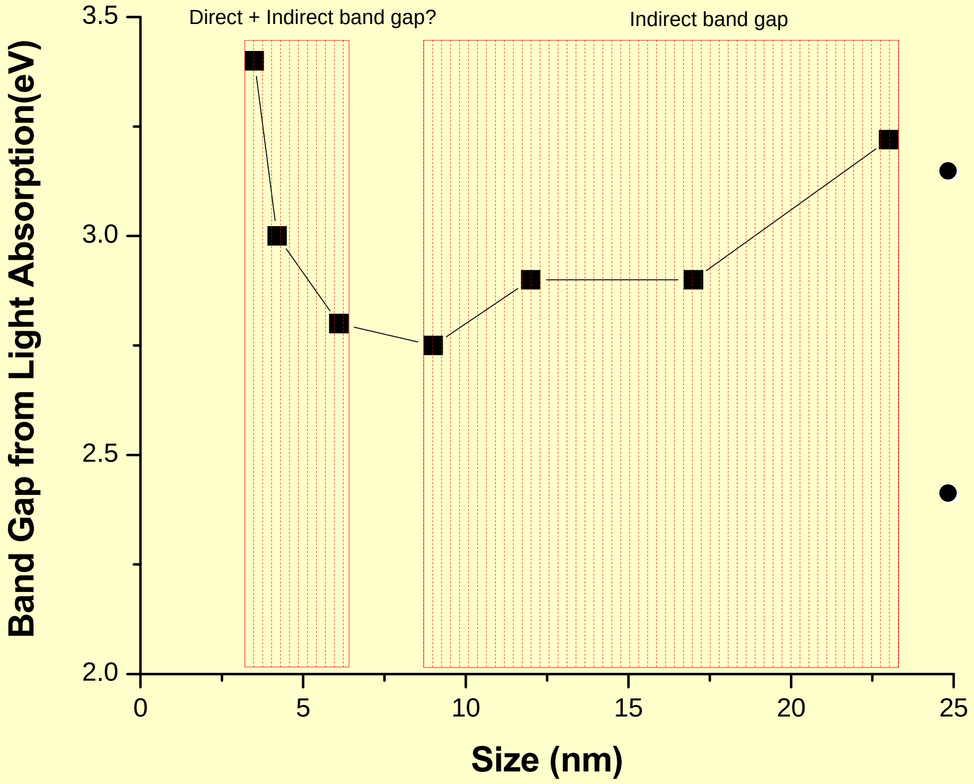
$E_g = 3.2eV$

Valence Band

Band Gap Tailoring

1. Reduce Particle Size
    - W. Li and C. Ni, H. Lin and C. P. Huang, S. Ismat Shah, J Appl. Phys. 96, 6663 (2004)
2. Cation Doping
    - Nd, Pd, Pt, Co, Nb, Sc, etc.
        - Shah, et al J. Appl. Phys. Lett. 83, 4143 (2003)
        - Shah et al, Phys Rev B, Psotion of Nd Accepted (2005)
        - M. A. Barakat, G. Hayes, and S. Ismat Shah, Catalysis 10, 1 (2005)
        - M.A. Barakat, H. Schaeffer, G. Hayes, S. Ismat Shah, Applied Catalysis B: Environ 57, 23 (2004)
        - W. Li and C. Ni, H. Lin and C. P. Huang, S. Ismat Shah, J Appl. Phys. 96, 6663 (2004)
        - W. Li, A. I. Frenkel, J. C. Woicik, C. Ni, S. Ismat Shah, Submitted to Phys. Rev. B. March (2005)
        - W. Li, S. Ismat Shah, Y. Wang, H. Lin, C. P. Huang, J. G. Chen, J. McCormick, D. J. Doren and M.A. Barteau, Appl. Phys. Lett. 83, 4143 (2003)
        - Andrew Burns, W. Li, E. Peng, J. Hirvonen and S.Ismat Shah, Mat. Sci. Engin. B. (2004)
        - W. Li, S. Ismat Shah, C.-P. Huang, O. Jung, and C. Ni, Proc. National Academy of Science, 99, 6482 (2002)
3. Anion Doping
    - C, S, N

Particle Size Variation

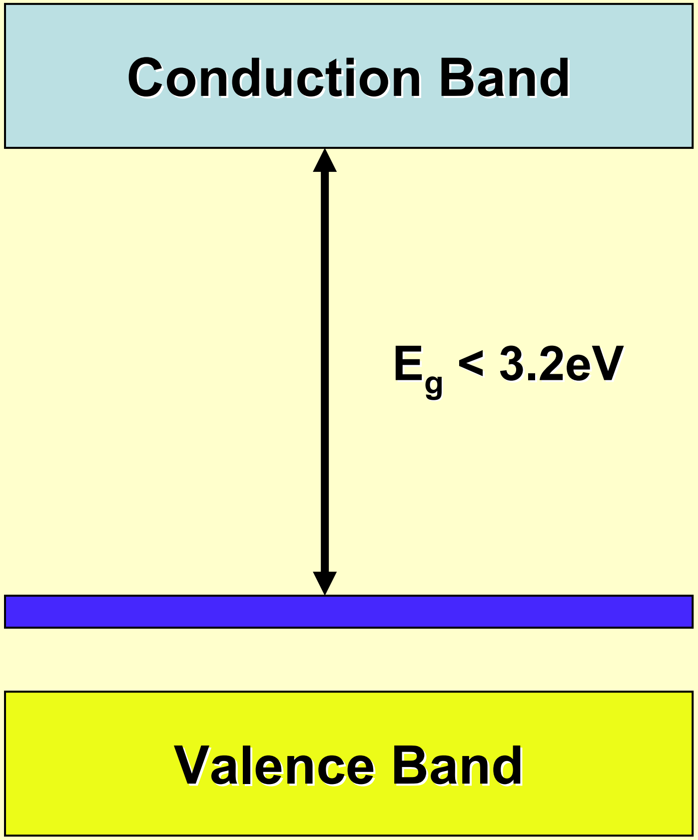


- Band gap decreases with particle size till exciton Bohr radius is reached
- Quantum confinement effect first proposed Efros and Efros (1982 *Sov. Phys. Semicond.)*
- The confinement effect on the band gap of a nanosolid of radius *R* was expressed as:

$$E_G(R) = E_G(\infty) + \frac{\hbar^2\pi^2}{2\mu R^2}$$

Band Gap Reduction of TiO_2

- New molecular orbitals may form as a result of doping
- Effectively narrowing the band gap
- Lowering the absorption edge into to the visible-light region



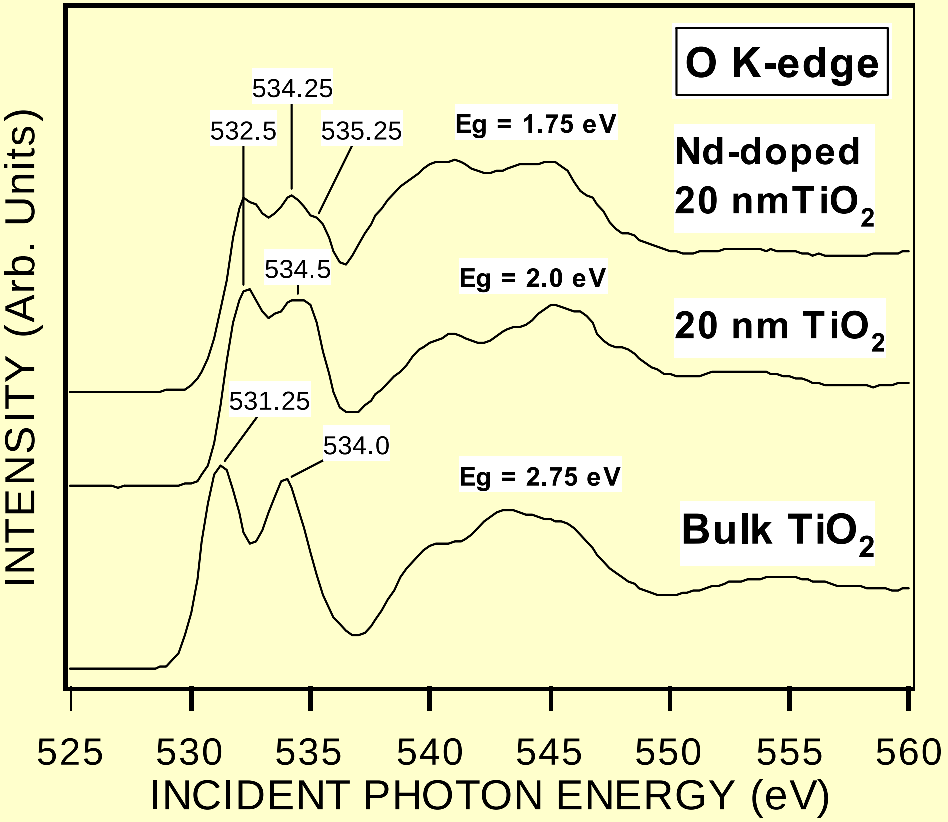
Conduction Band

$E_g < 3.2\text{eV}$

Valence Band

Near Edge X-ray Absorption Fine Structure for Band Gap Measurements

Nd doped TiO_2



- NEXAFS reveals LUMO and HOMO states (related to Eg) of TiO_2.
- The band gap narrowing of doped TiO_2 is consistent with that from light absorption measurements.
- Figure is for 1%Nd doped TiO_2 and the band gap decreased by ~0.3 eV.
- The Eg value from NEXAFS is typically 80-90% of that from optical measurements because of the different excitation mechanisms

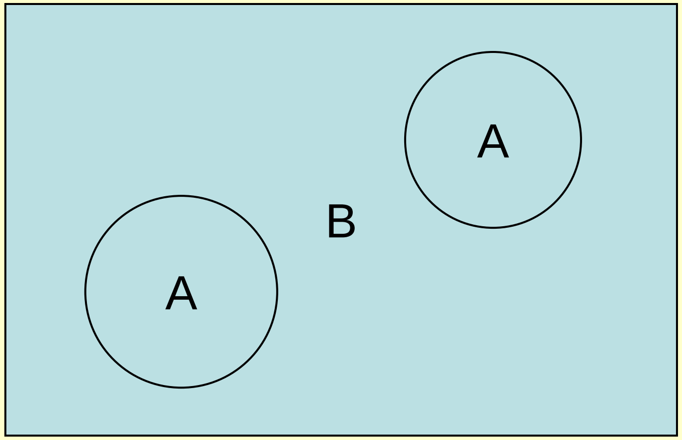
LAPW : Linearized Augmented Plane Wave

A procedure for solving the Kohn–Sham equation for the ground state density, total energy, and energy bands

Unit cell is divided into two types of regions

(A) non – overlapping atomic spheres (atomic cores)

(B) interstitial region



Basis sets are adapted to these two regions.

$$\phi_{kn} = \sum_{\ell m} \left[A_{\ell m,kn} u_\ell (r, E_\ell) + B_{\ell m,kn} \dot{u}_\ell (r, E_\ell) \right] Y_{\ell m}$$

In core region (A),

where u_l is a numerical solution of the radial

Schrodinger equation for energy E_l and ù$_l$ is the

energy derivative of u_l.

$$\phi_{kn} = e^{iknr}$$

In interstitial region (B), a plane wave expansion is used

Solutions are matched at the boundary

LAPW Calculations: Anatase TiO_2

Tetragonal Anatase Structure.

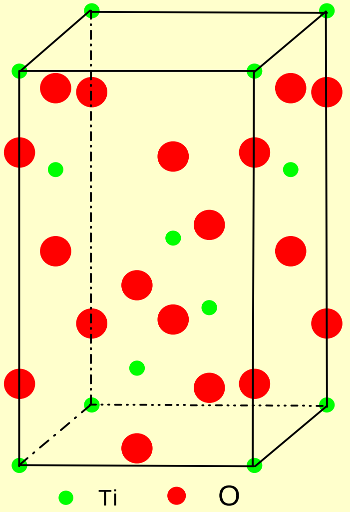


Fig1., the crystal structure of the unit cell of TiO_2

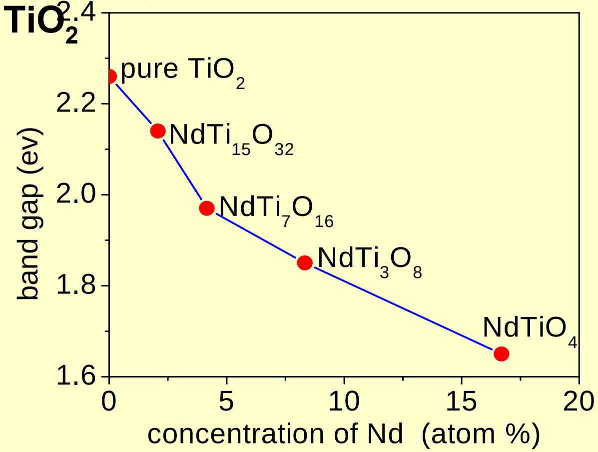


Fig3. the relationship between the band gap and the amount of the doped Nd

The density of states (DOS) of Nd – doped TiO_2 are shown as Fig 2.

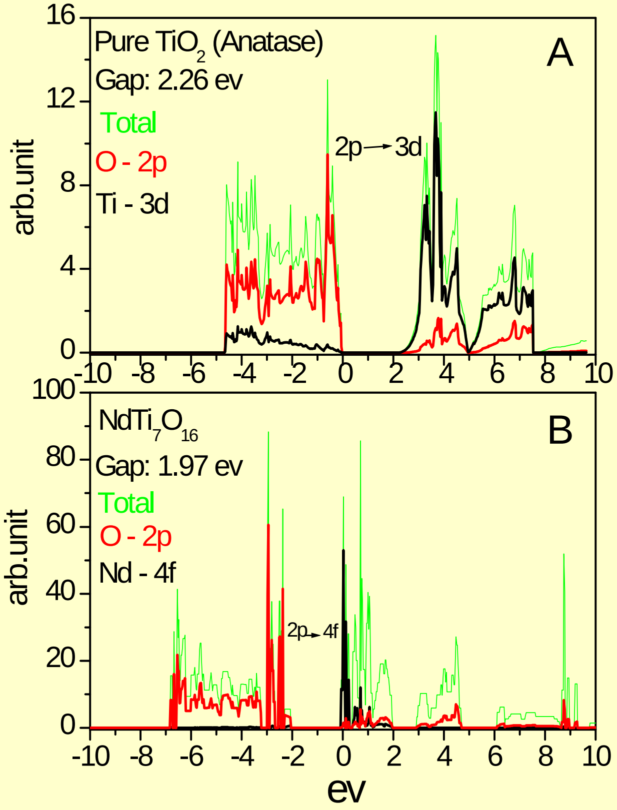
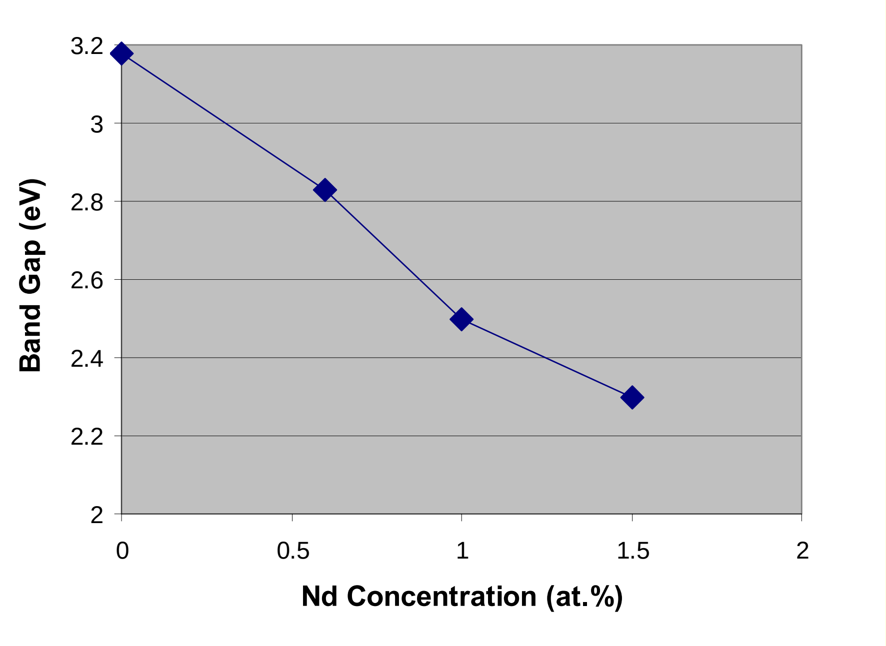
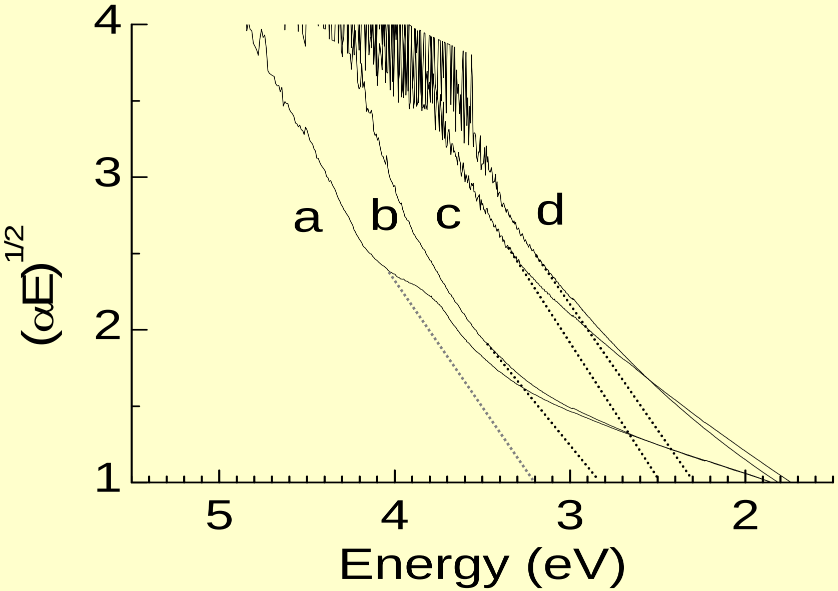


Fig2. in A are total DOS (green) of the pure TiO_2 , and the partial DOSs of O – 2p (red), Ti – 3d (black); in B, total DOS (green) of NdTi7O16 are represented , with the partial DOSs O – 2p (red), and Nd – 4f (bl

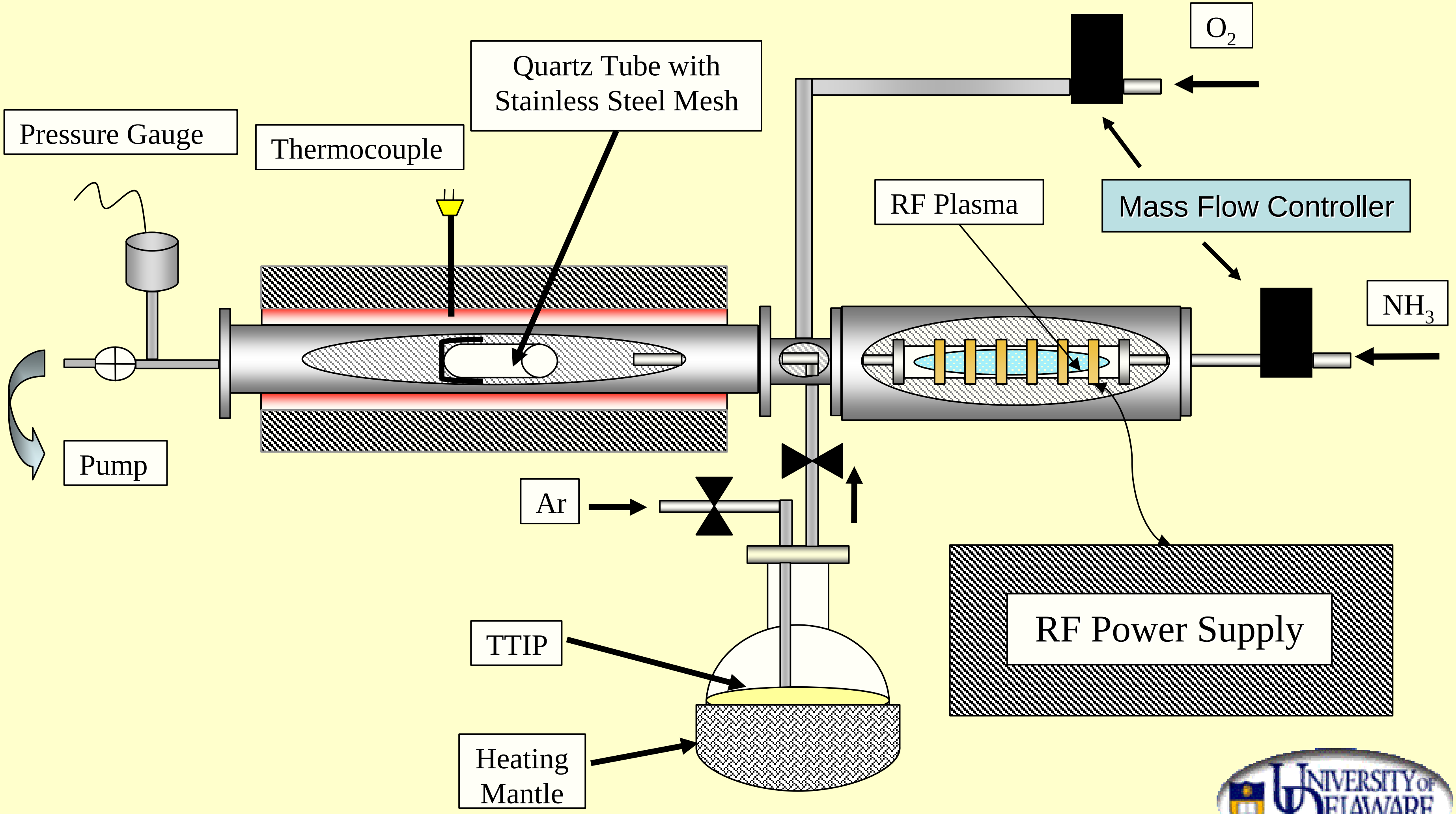
Band Gap Variation with Nd Concentration





N-Doped TiO_2 Synthesis & Characterization

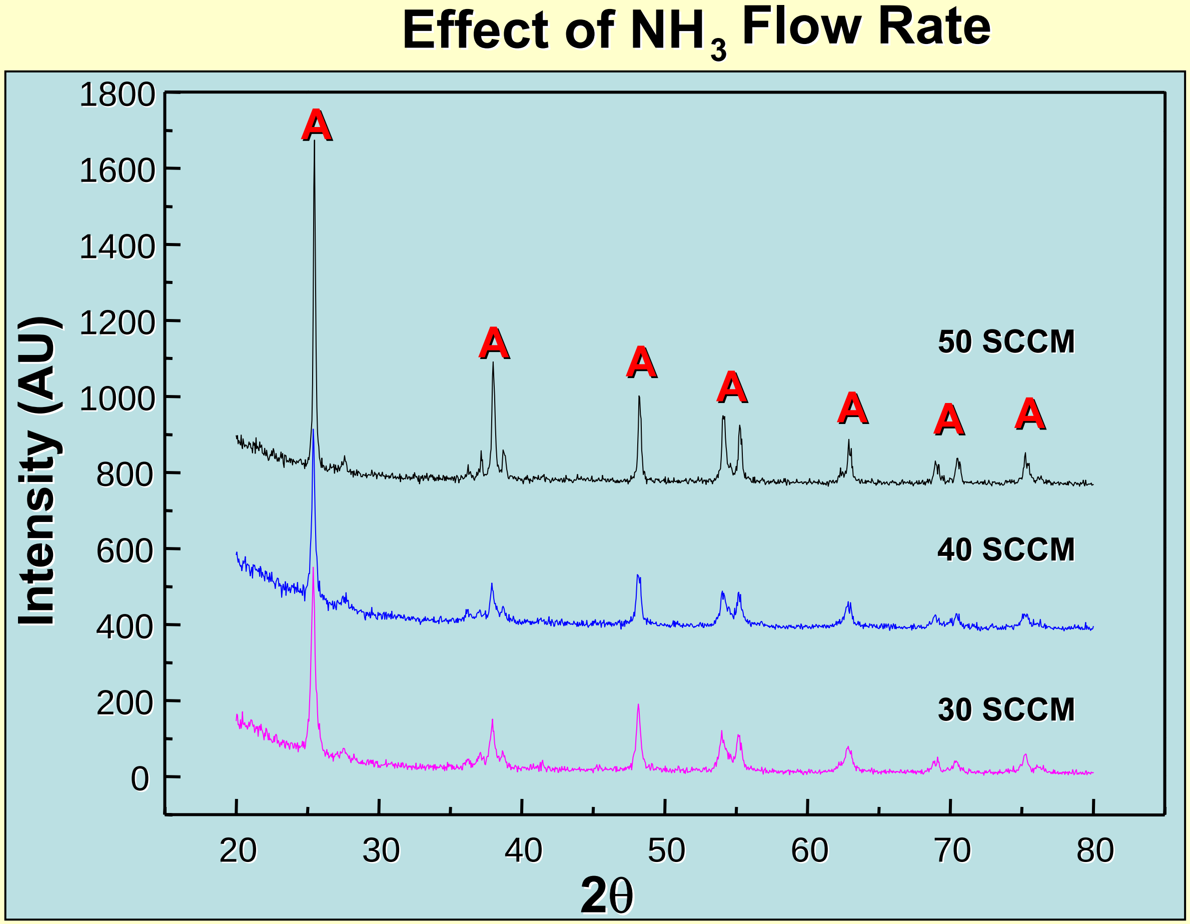
PA-MOCVD System



Experimental Parameters

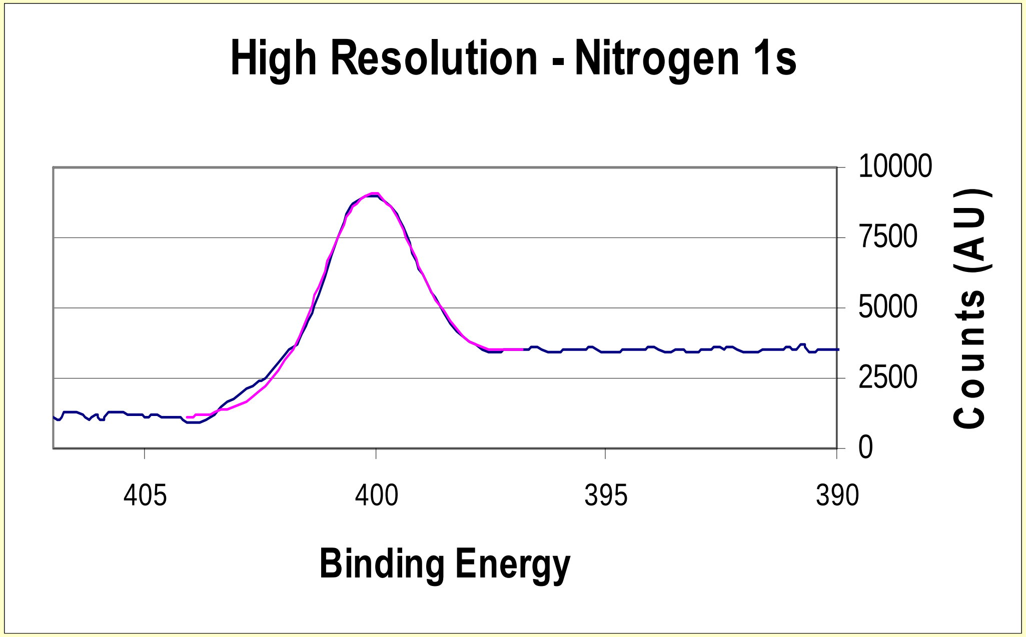
- Titanium Tetraisopropoxide (TTIP)
- Ammonia Gas ionized by 100W RF Plasma
- Gas Pressures:
  - O_2 – 3 Torr @ 35 SCCM
  - Ar/TTIP – 1 Torr
  - NH_3 – 0.5 Torr @ 30, 40 and 50 SCCM
  - Total Pressure – 4.5 Torr
- Reaction Temperature – 600^{o}C for 4 hours

XRD Characterization



- All samples were anatase phase
- No separate dopant related phases present (ex. TiN, TiON)

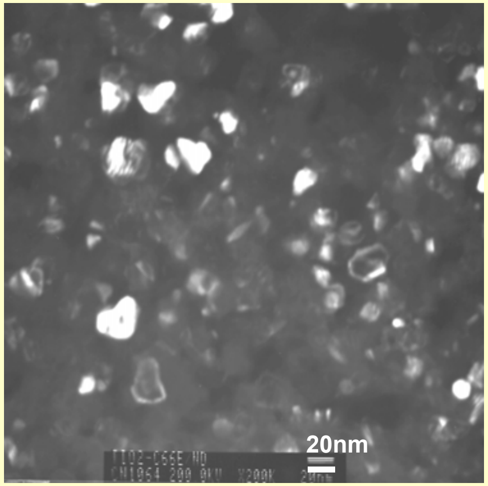
XPS Analysis



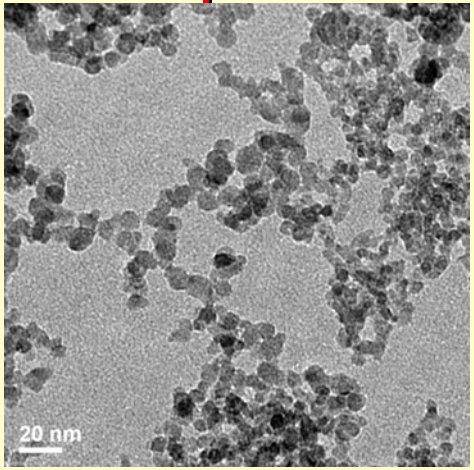
- Elemental analysis shows N concentrations 0 – 1.5 at%
- N1s peak for substituted nitrides (ex. TiN) usually is a sharp peak at 397eV
- However N1s peak for N-doped TiO_2 ($TiO_{2-x}N_x$) is a broad peak centered at 401.3eV extending from 397.4 to 403.7eV

X. Chen, Y Lou, A. Samia, C. Burda, J. Gole, *Adv. Funct. Mater.* 2005, 15, 41

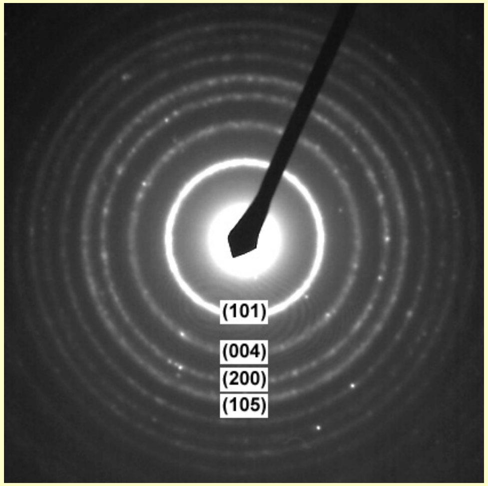
TEM Observation of N-doped TiO_2 Nanoparticles



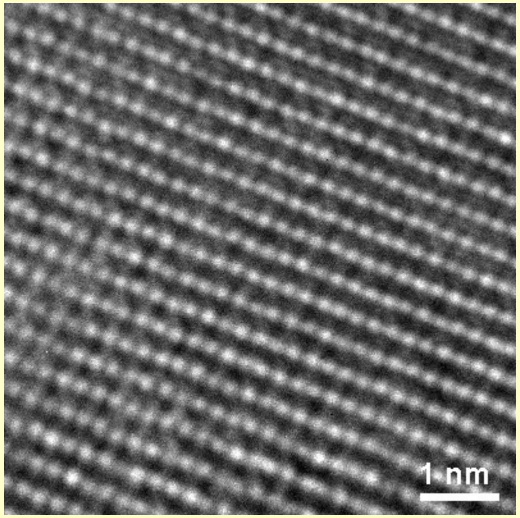
(a) dark field image



(b) bright field image



(c) diffraction patterns

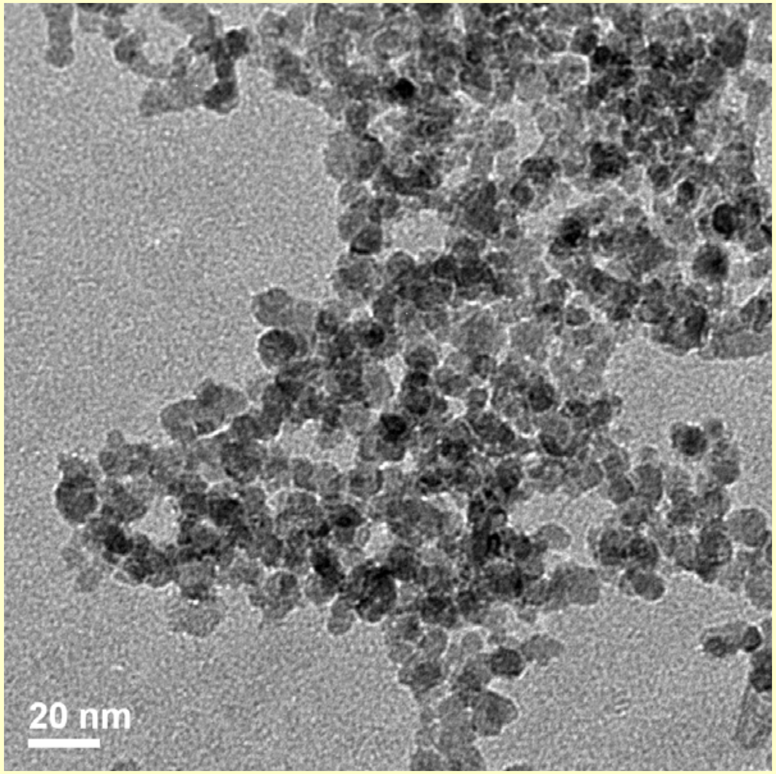


(d) Lattice image

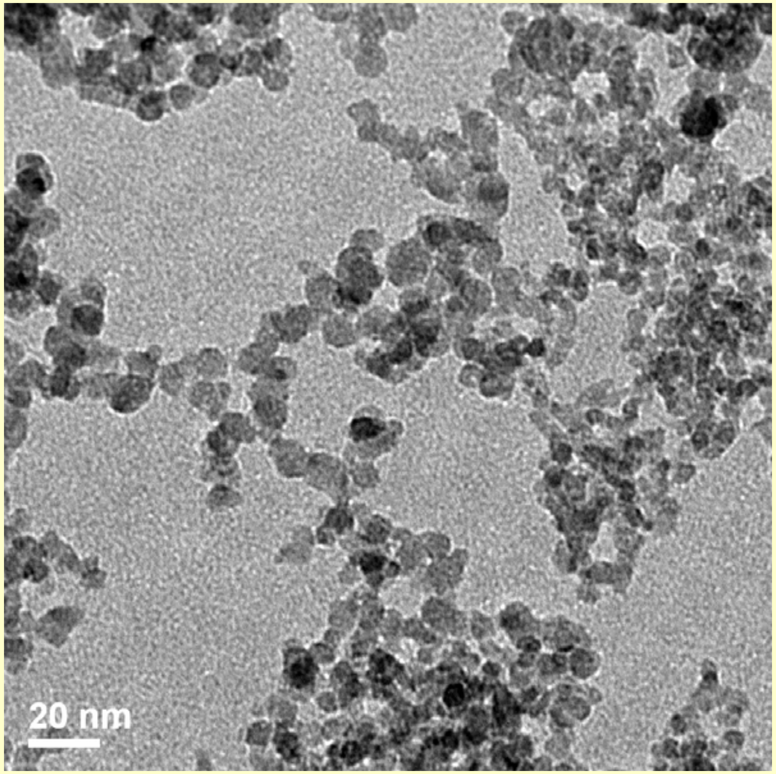
- The structure of all samples is anatase with no separate dopant related phase.
- The particle sizes from TEM are ~10 nm for doped TiO_2 nanoparticles.

Transmission Electron Microscopy

0.5 at% N



1.5 at% N



- uniform nanoparticles
- Particle size ~10nm

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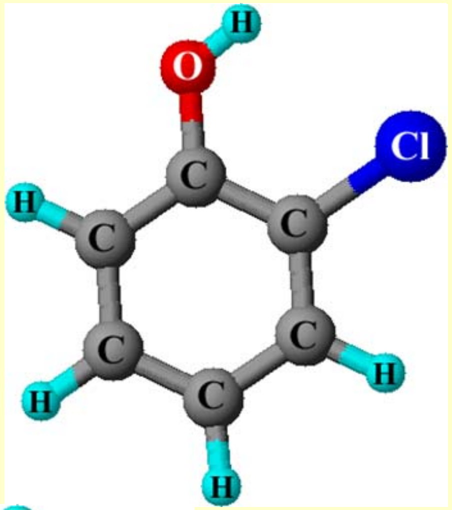
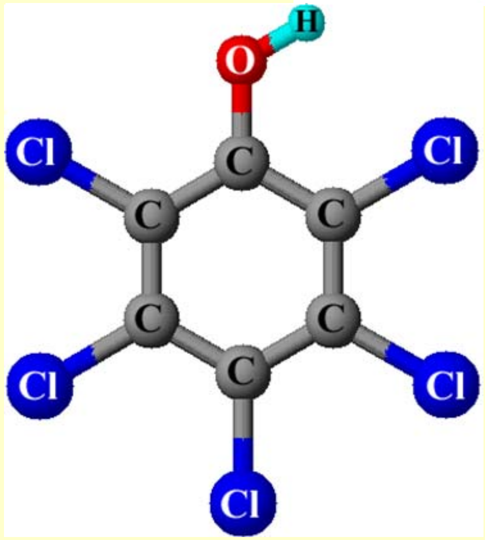
Common Organic Contaminants

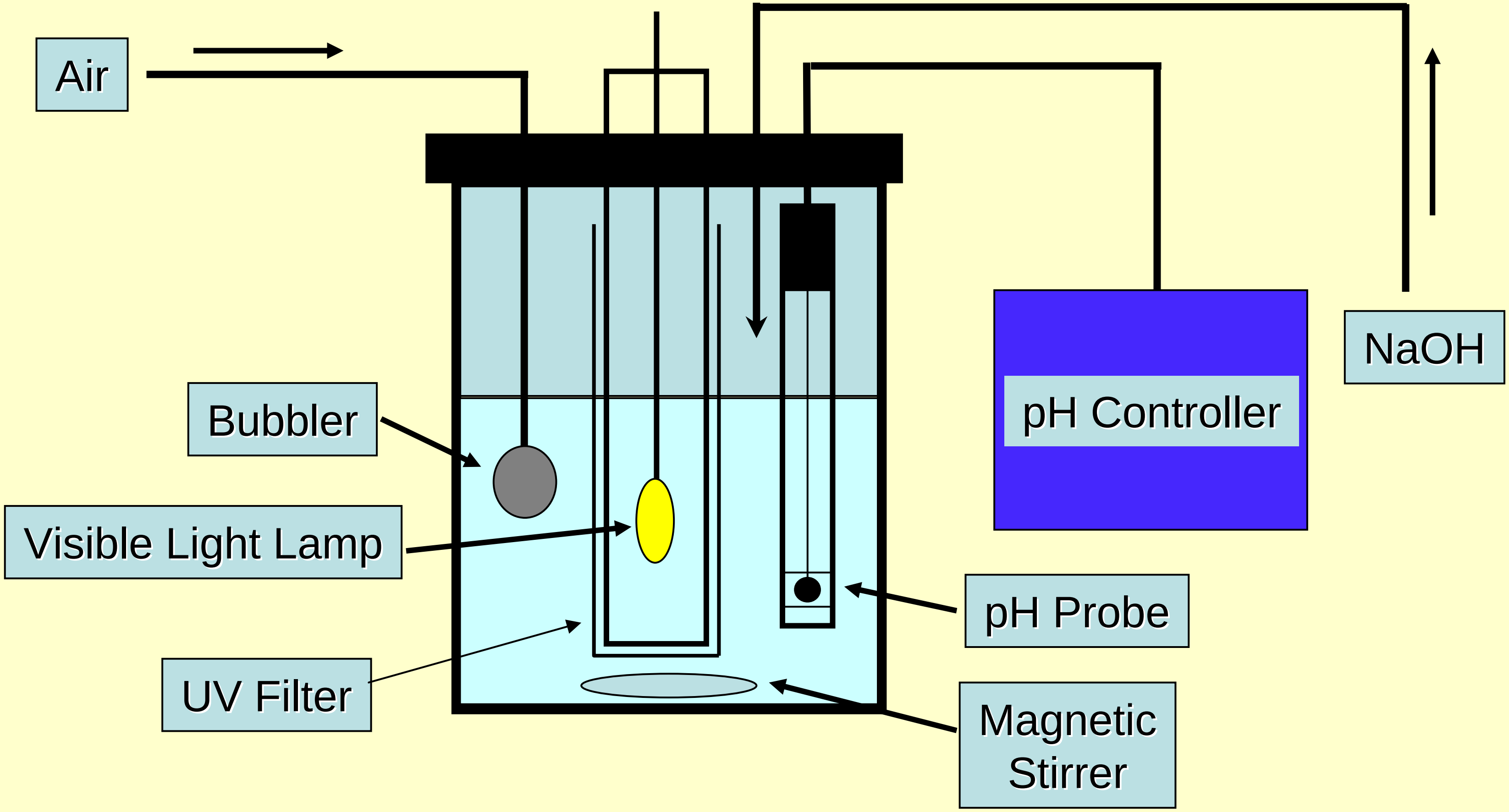


2-chlorophenol
(high water solubility)



penta-chlorophenol
(low water solubility)

Photodegradation Cell



Air

Bubbler

Visible Light Lamp

UV Filter

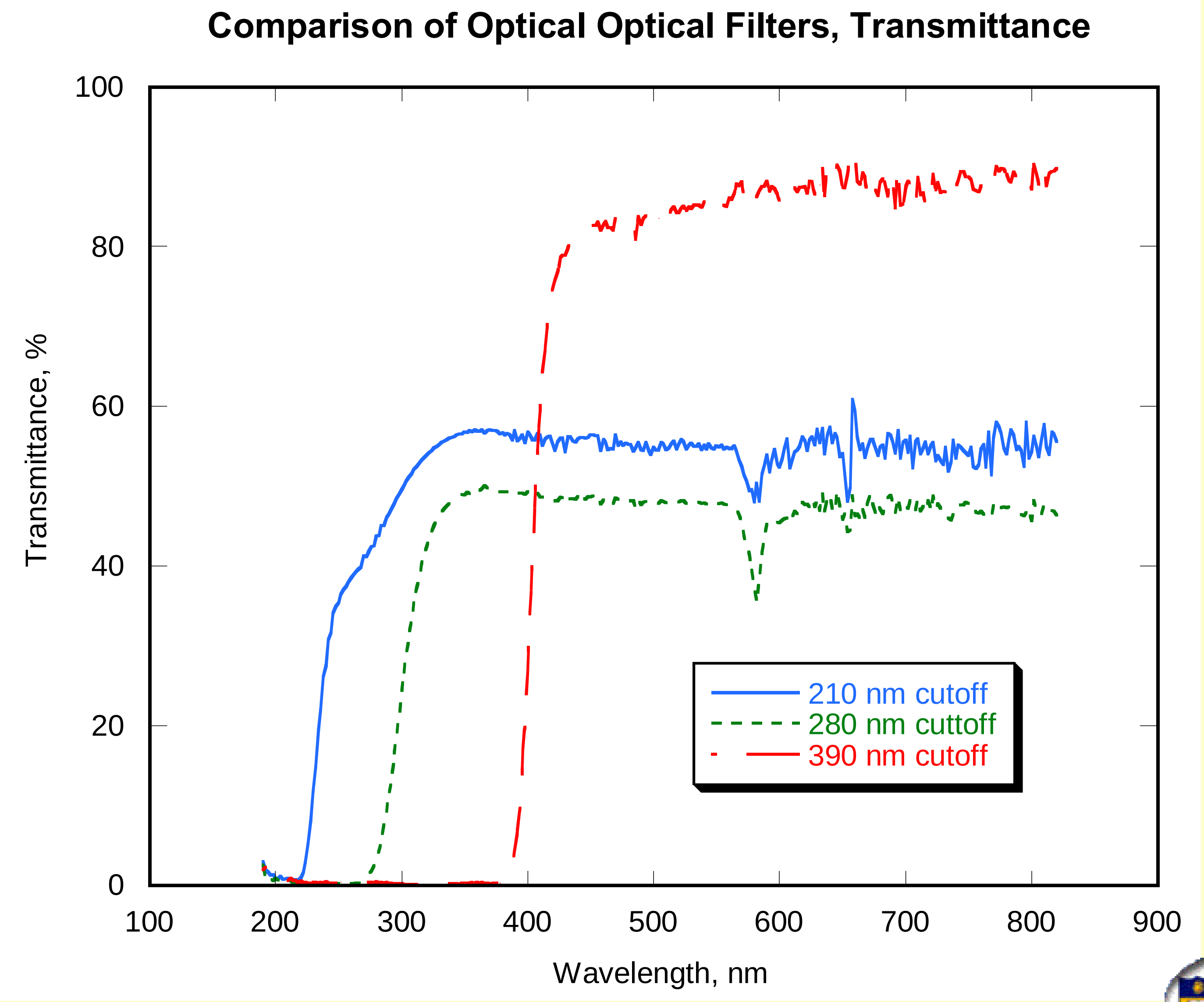
pH Controller

NaOH

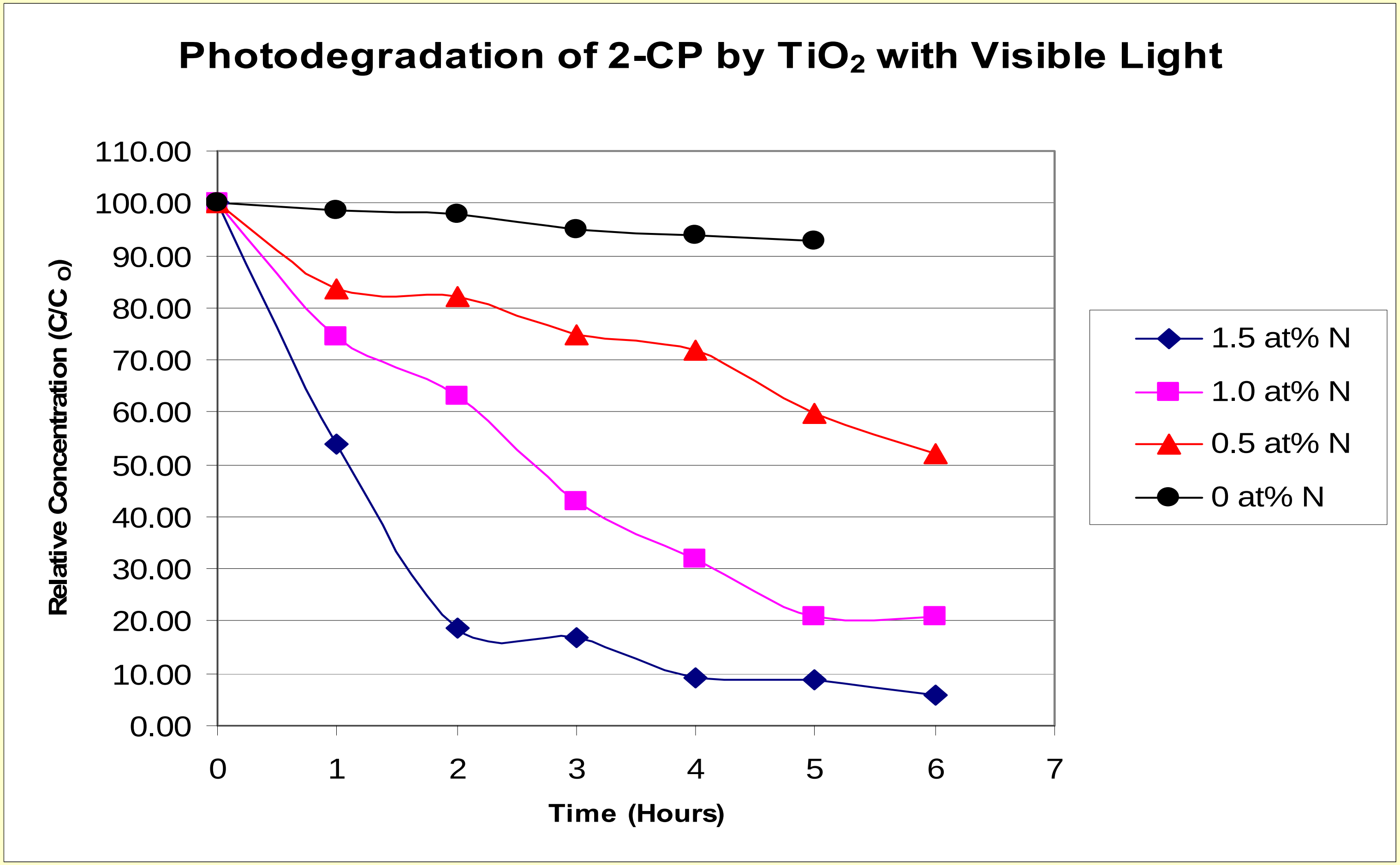
pH Probe

Magnetic Stirrer

UV Filter Cut-off

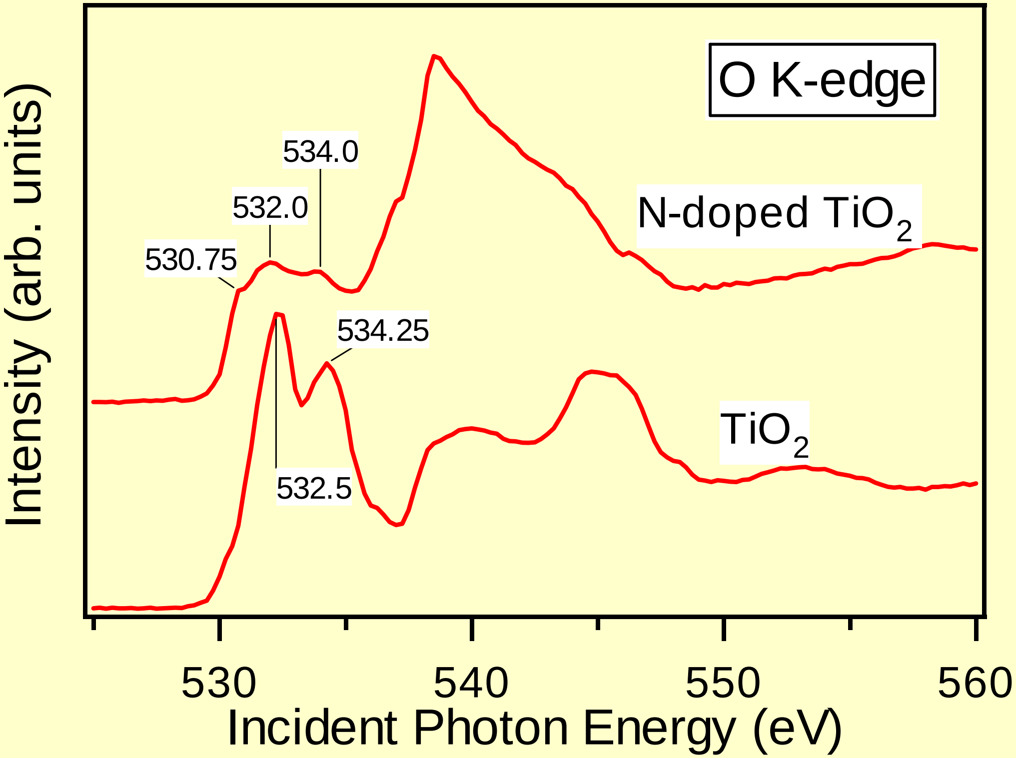


2-CP Degradation with Visible Light



NEXAFS Characterization

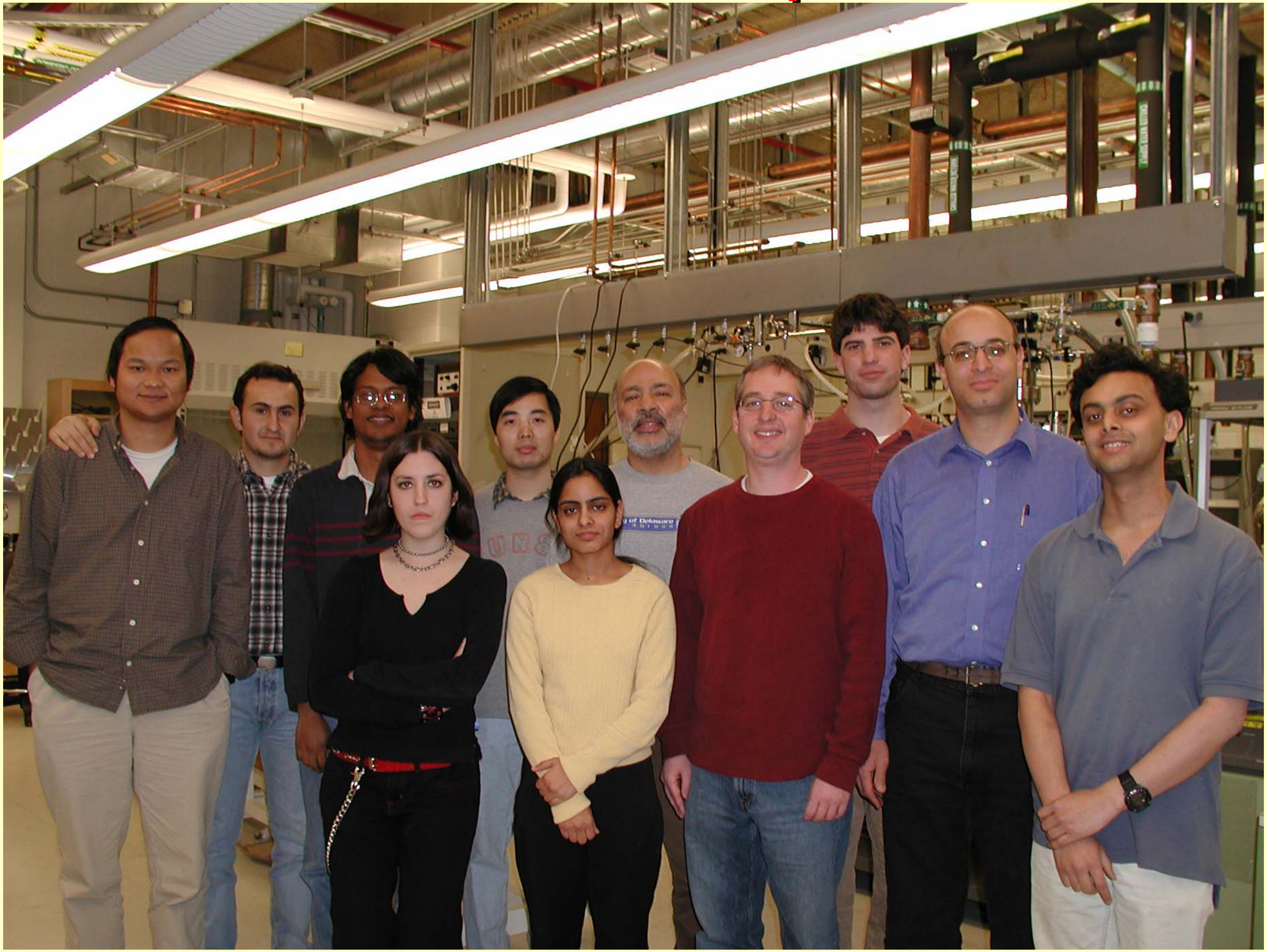
- **Undoped TiO_2, two relatively sharp O K-edge features are observed at 532.5 and 534.25 eV.**
- **Origin: dipole transition of O 1s electrons to the t_{2g} and e_g states, respectively.**
- **N-doped TiO_2 has new features appearing at 530.75, 532, and 534 eV.**



Conclusions

- TiO_2 Band gap tailoring is possible with cations as well as anion doping.
- N-doped TiO_2 with N concentration as high as 1.5% have been prepared.
- Nitrogen doping led to a increase in the visible light photocatalytic activity
- Removal efficiency is comparable to un-doped samples in UV light
- N leads to the formation of additional states within the band gap for effective band gap reduction.

The Group



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