# Study of $TiO_2$ Nanotube-based Photocatalysts

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*Sham*'s group. April 15, 2013

1. Formation of ordered $TiO_2$ NTs array

2. Quantum dots sensitized $TiO_2$ NTs

3. Nanotube-based newly $TiO_2$ NP

4. $TiO_2$ NTs template for Nanowire growth

# Formation of ordered $TiO_2$ NTs array(part one)



Electrolyte: 0.3wt%$NH_4F$+2vol%$H_2O$+EG (80ml)

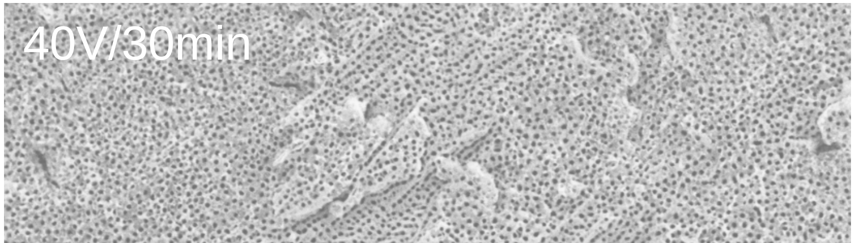
A two-step electrochemical anodization method:

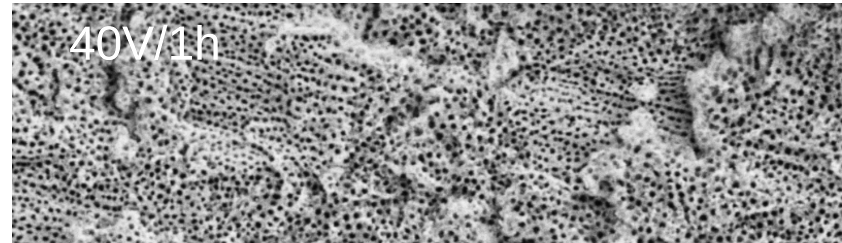
Ti foil was first anodized at 50V for 4h, then ultrasonically rinsed in 1M HCl to peel off the first layer. Subsequently, a second anodization of Ti substrate was performed at 50V for 1h

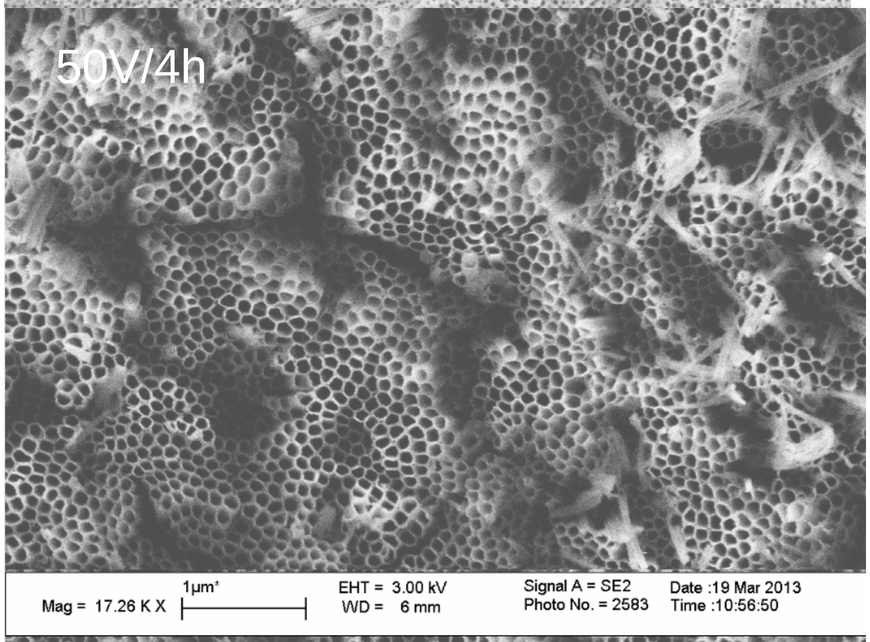
# Formation of ordered $TiO_2$ NTs array(part one)

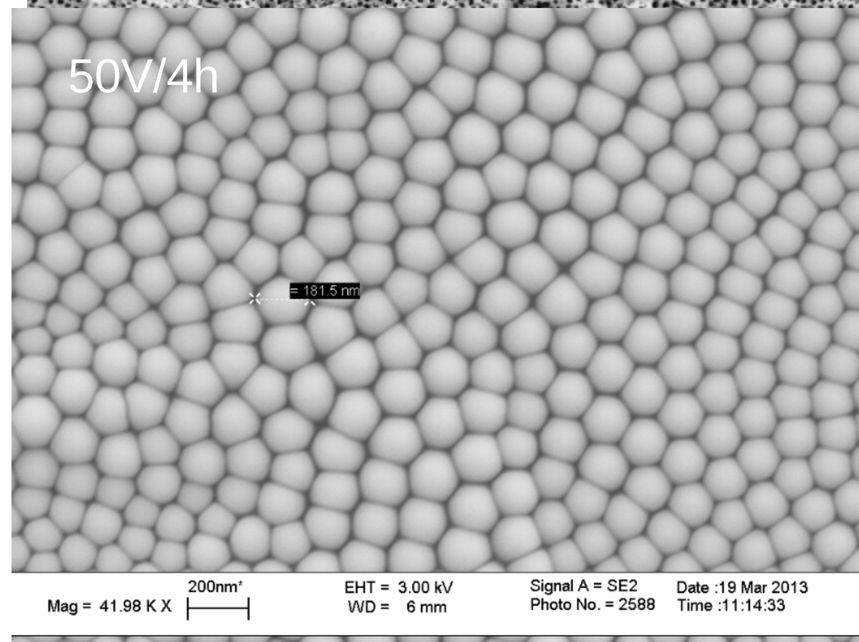
## Frist Layer

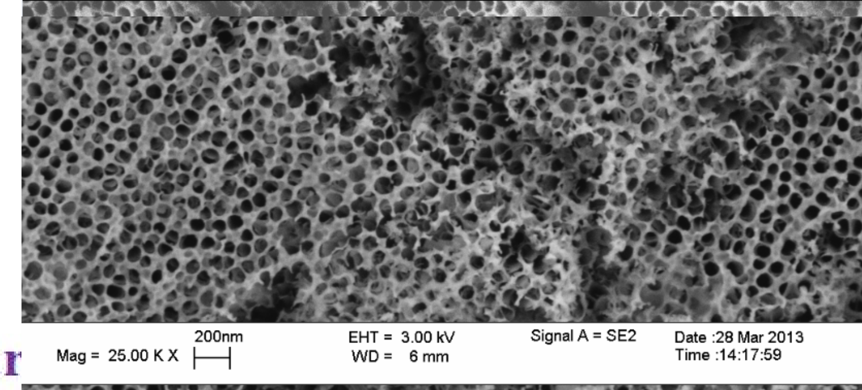


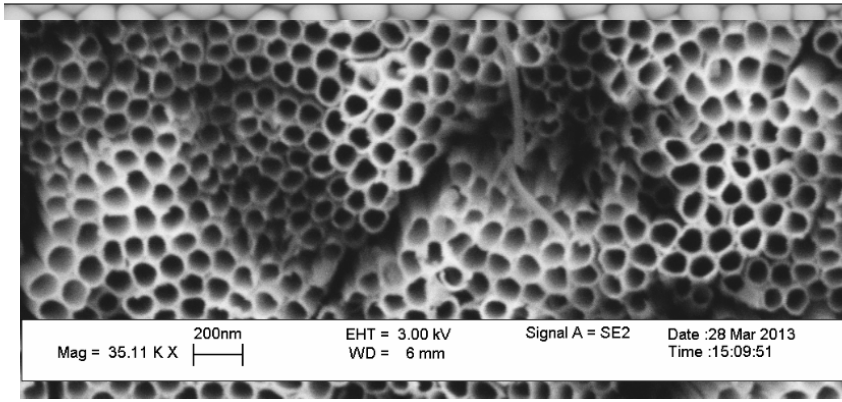


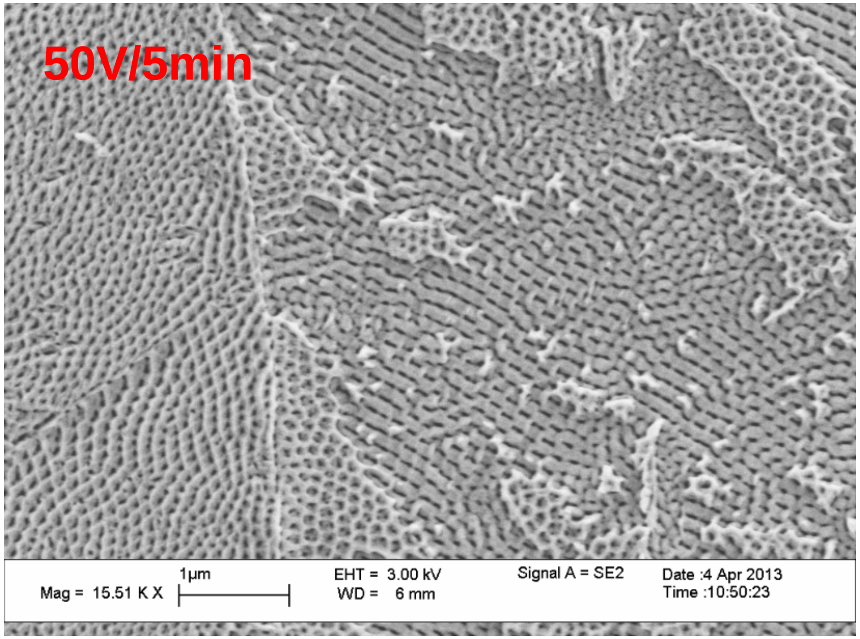



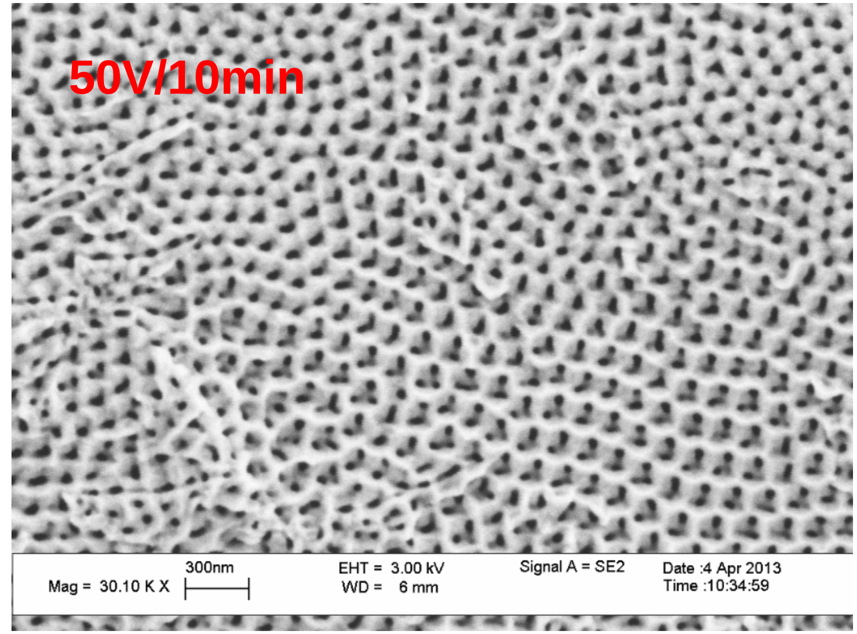



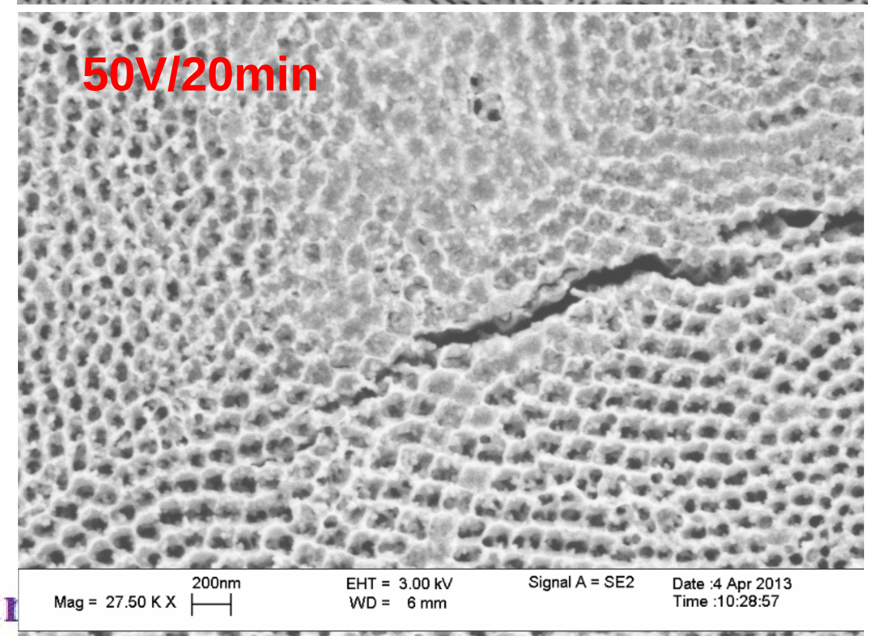



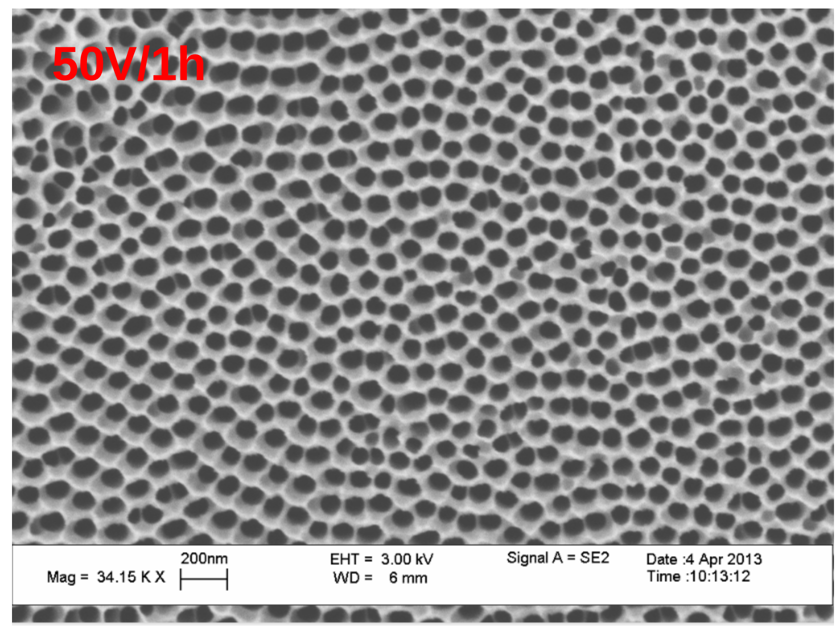
# Formation of ordered $TiO_2$ NTs array(part one) Second Layer





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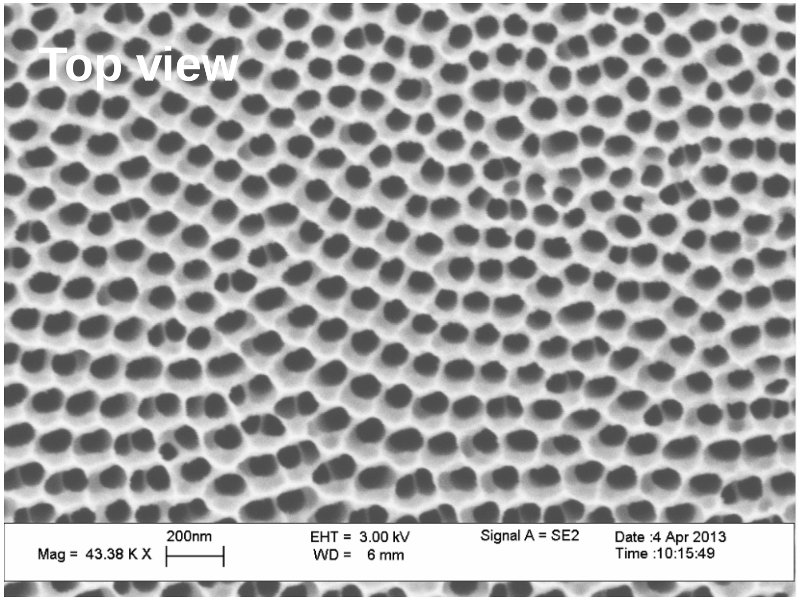
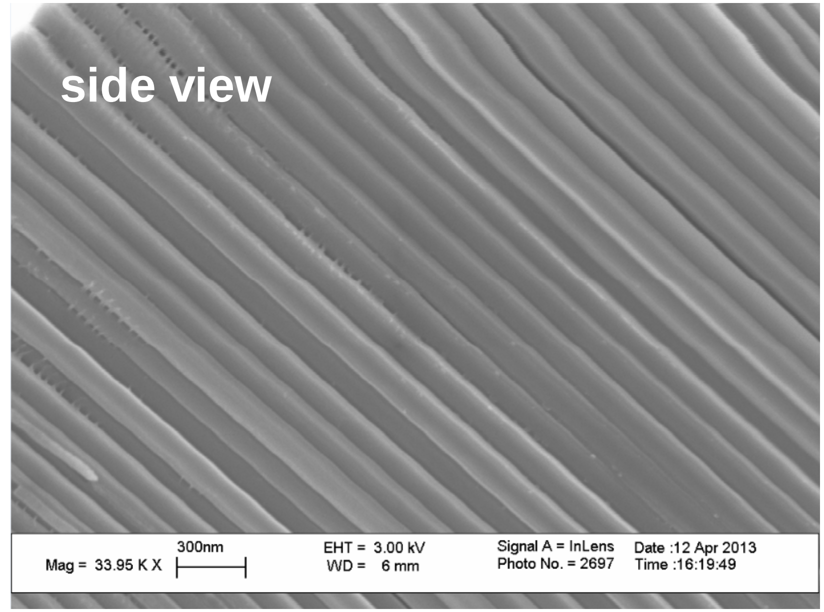
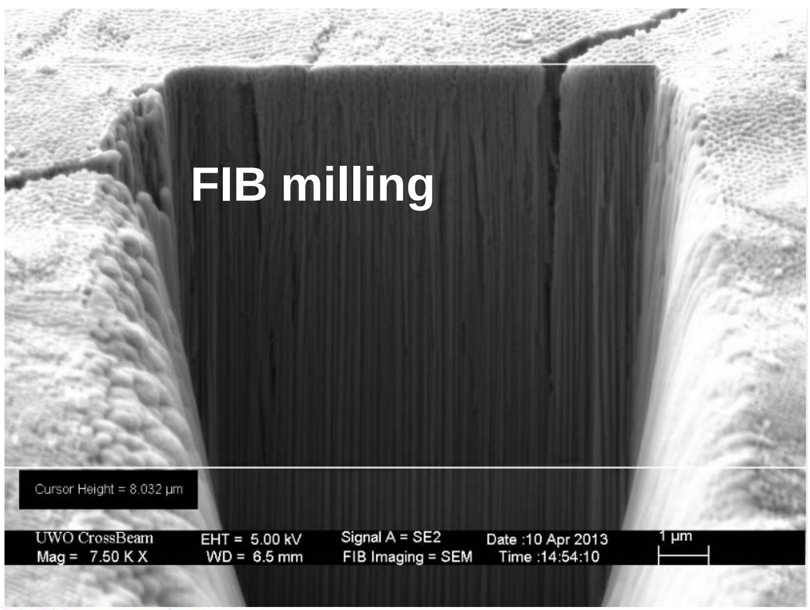
# Formation of ordered $TiO_2$ NTs array(part one)

## Second Layer






Average growth rate:134nm/min

## Quantum dots sensitized $TiO_2$ NTs(part two)

## Palladium Quantum Dots basic idea

Fermi level: Pd<$TiO_2$

⇩

$TiO_2$ —photoexcited $e^-$→ Pd particles

⇩

reducing electron-hole recombination
effecient charge separation
greater photocatalytic reactions

P25: 25%anatase+75%rutile

High photocatalytical property of P25 is due to the mixed-phase $TiO_2$, which provides unique charge transfer pathways

What's the best annealing temperature for highly ordered $TiO_2$ NTs which is best for Pd coating in order to reduce electron-hole recombination and get a better photocatalytic property

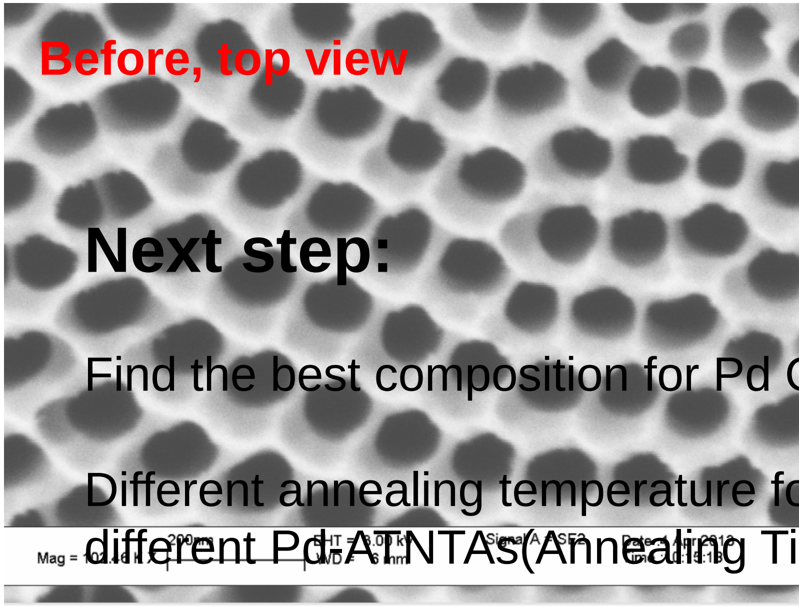
Different annealing temperature leads to different crystal composition of $TiO_2$

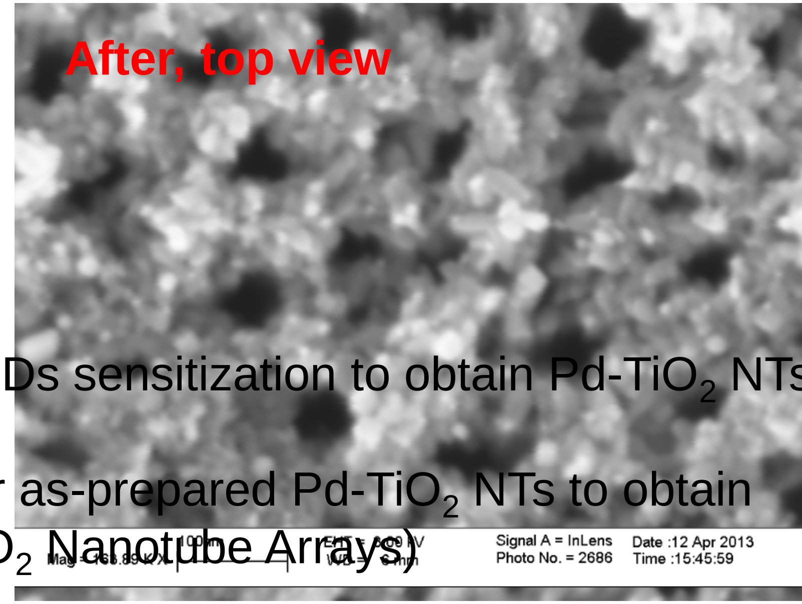
# Quantum dots sensitized $TiO_2$ NTs(part two)

## Palladium Quantum Dots coating



Hydrothermal method: orderly $TiO_2$ NTs+PVP+NaI+$PdCl_2$

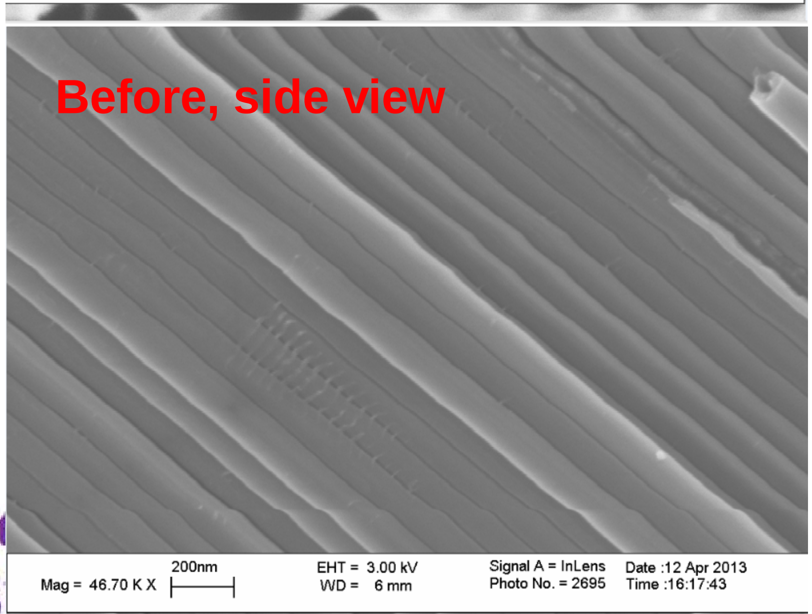


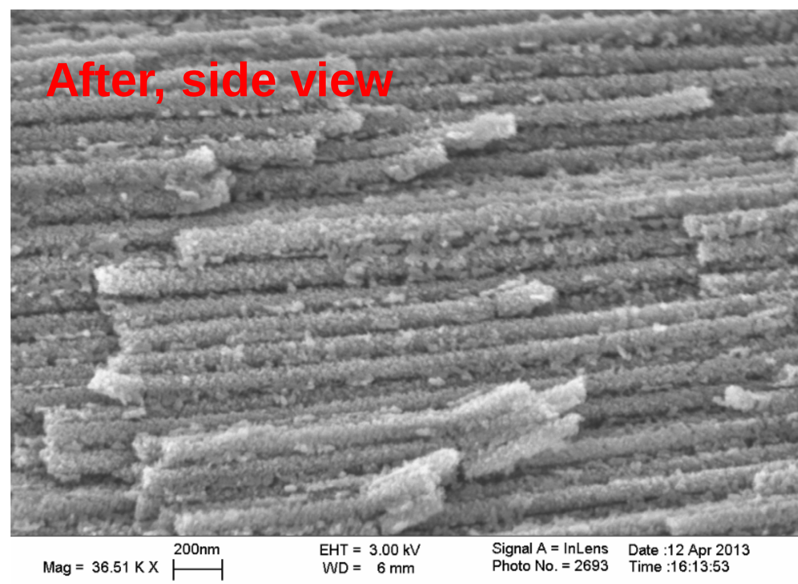




## Next step:

Find the best composition for Pd QDs sensitization to obtain Pd-$TiO_2$ NTs

Different annealing temperature for as-prepared Pd-$TiO_2$ NTs to obtain different Pd-ATNTAs(Annealing $TiO_2$ Nanotube Arrays)



# Quantum dots sensitized $TiO_2$ NTs(part two)

## Palladium Quantum Dots following study



Correlation with phase and electronic structure study of Pd QDs sensitized $TiO_2$ NTs

SEM and Raman spectroscopy will be used to concentrate on the effect of Pd QDs for the phase transformation of $TiO_2$ NTs

HRTEM will be used to focus on the loading amount of Pd QDs on the surface of $TiO_2$ NTs and obtain the particle size distribution

Phase transformation and the light-emitting properties induced by calcination temperatures will be tracked using XANES and XEOL

XANES study:

Ti L3,2-edge and O K-edge comparision between annealing-$TiO_2$ NTs arrays(ATNTA) and Pd-ATNTA will be used to concentrate on the effect of Pd QDs for the structure and bonding of $TiO_2$ NTs

Ti L3,2-edge and O K-edge of Pd-ATNTA obtained from different annealing temperature will be used to distinguish different crystal phases among amorphous, anatase and rutile, and concentrate on the effect of Pd QDs for the phase transformation of $TiO_2$ NTs

Pd L-edge comparision between Pd-ATNTA and pure Pd will be used for the study of Pd electronic structure within Pd-ATNTA?

## Palladium Quantum Dots following study



# XEOL study:

XEOL comparision between ATNTA and Pd-ATNTA will be used for the optical luminescence study and for the effect of Pd QDs sensitization

XEOL comparision among Pd-ATNTA samples obtained from different annealing temperature will be used for optical luminescence study

XEOL will be used to track XANES using photoluminescence yield(PLY/XANES) to reveal the element of the site among Pd-ATNTA samples obtained from different annealing temperature that is responsible for the luminescence

# Nanotube-based newly $TiO_2$ NP(part three)



improving crystallinity

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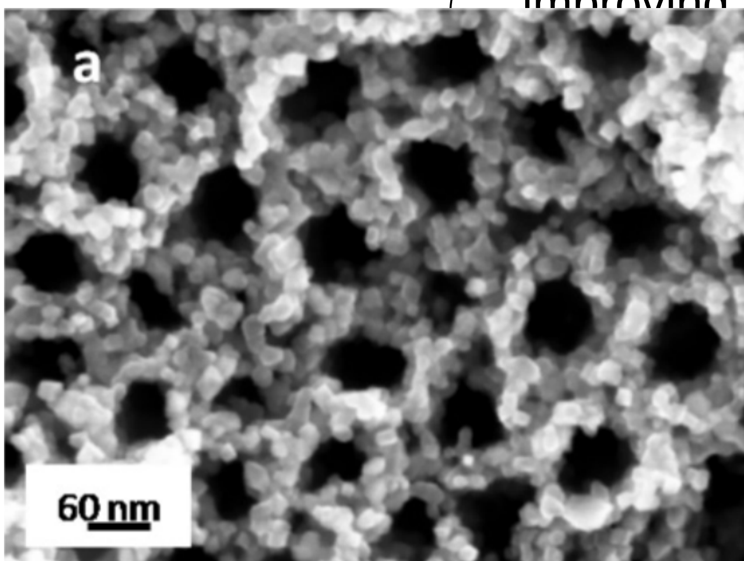
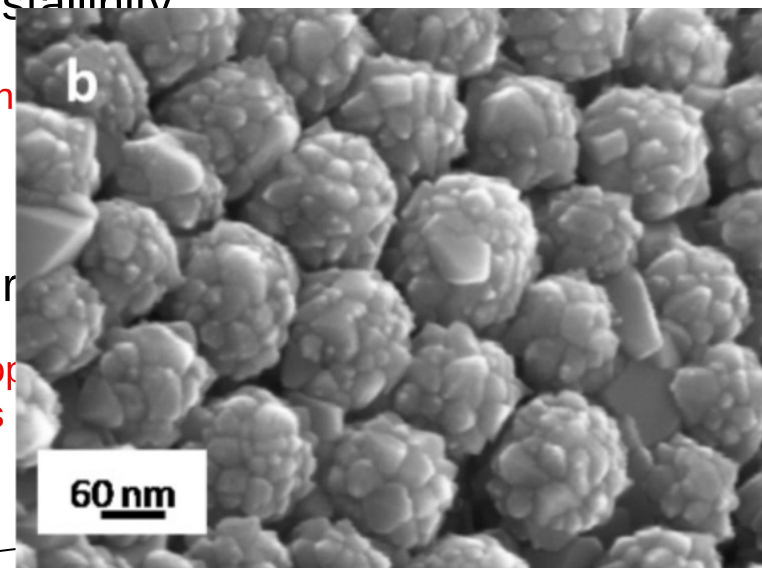



Tranformation from $TiO_2$ nanotube to nanoparticles

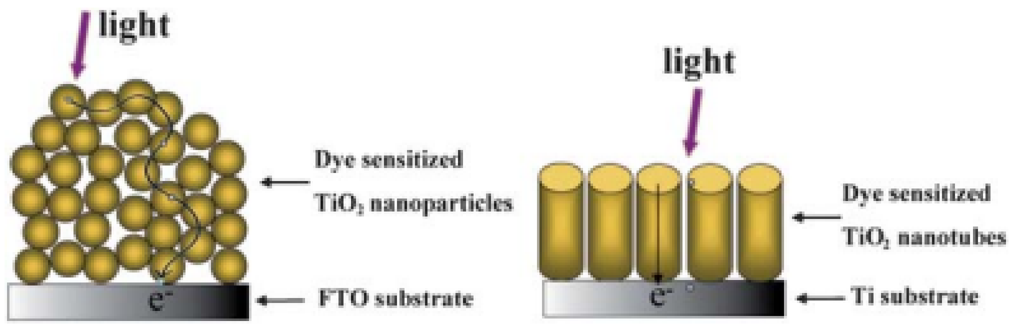
**NPs-NTs transformation to obtain NTs-based newly $TiO_2$ NP**



Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanotube-based newly $TiO_2$ NP(part three)






A comparison of the electron pathways through nanoparticle and nanotubular structured $TiO_2$.

The anodized tube structures are expected to greatly improve the charge collection efficiency due to directional electron conduction with minor charge recombination in comparison to $TiO_2$ nanoparticle films

Then what kind of new properties can we get from this NTs-based newly $TiO_2$ NP with a much higher surface area



J. F. Yan and F. Zhou, Journal of Materials Chemistry, 2011, 21, 19417-19418

# Nanotube-based newly $TiO_2$ NP(part three)

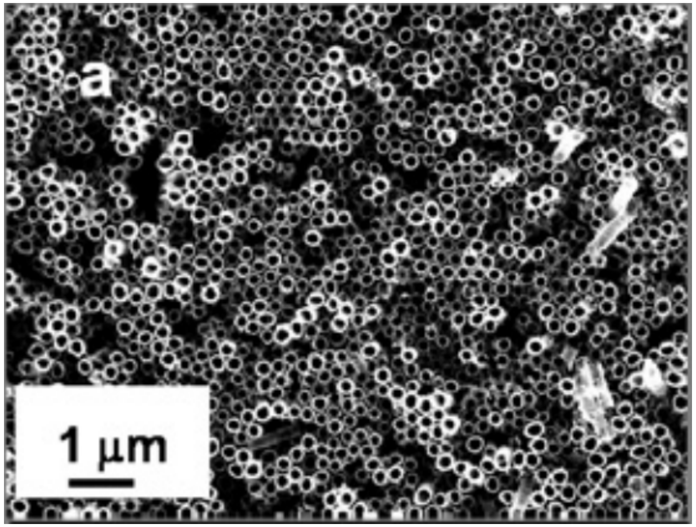


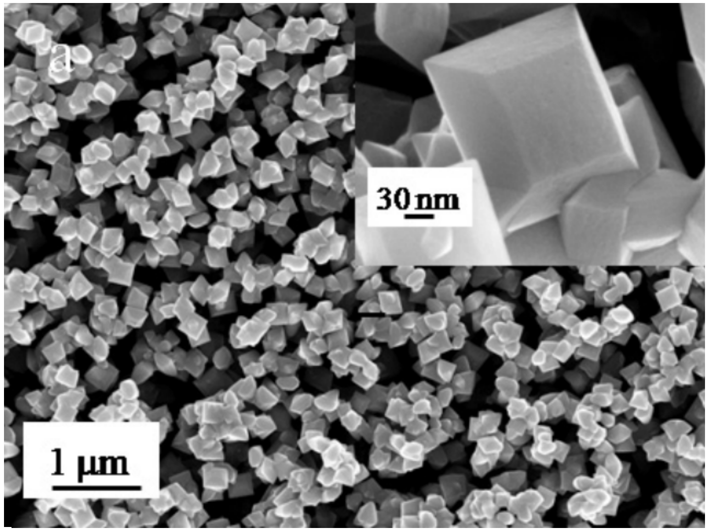
Basic Outline:

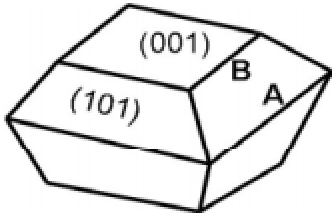
$NH_4F$ is used in the electrolyte for orderly $TiO_2$ NTs growth

Fluoride residue in the obtained NTs can change the morphology of $TiO_2$ NTs during a sealed annealing system

eg. Thermally annealing on a glass slide at 500℃ for 30min with a ramping rate 16℃/min, the transfromation happens:




Truncated tetragonal bipyramidal shape NP



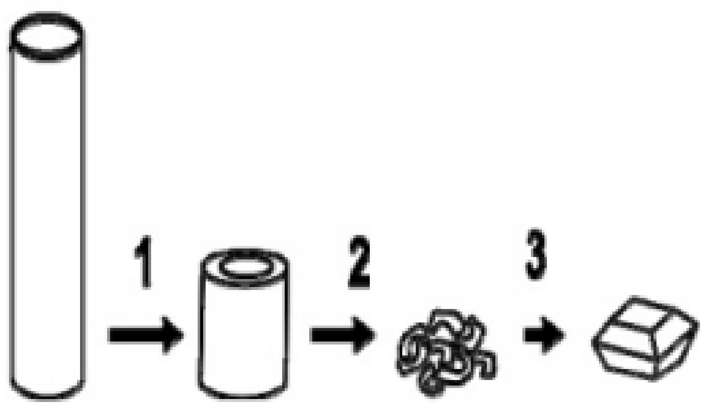
Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanotube-based newly $TiO_2$ NP(part three)



**Transformation mechanism**

Lower $F^-$ residue concentration




Higher $F^-$ residue concentration

(1) NT contraction
(2) breaking of the contracted NT into small parts
(3) merging of the broken parts and crystallizing into truncated pyramid shape nanoparticles

After contraction, the top of the thick NT walls crystallized directly to NPs before breaking down, without breaking the tubular geometry

Thus NTs-based newly $TiO_2$ NPs can be obtained from sealed annealing with a higher $F^-$ residue concentration

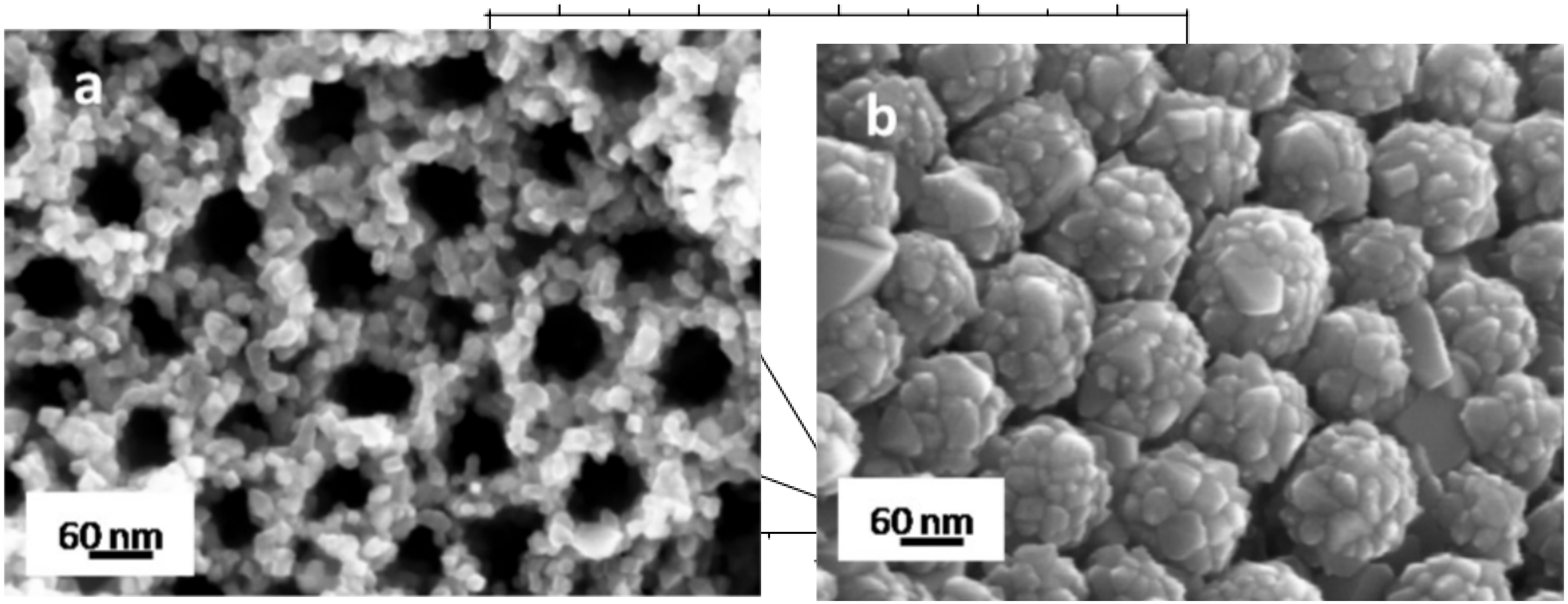


Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanotube-based newly $TiO_2$ NP(part three)



Control growth: the most important part is the initial concentration of $NH_4F$ in electrolyte




Top view (a) and bottom view (b) of selected areas of $TiO_2$ NT samples showing initial stages of the NT–NP transformation after 1 min annealing. The $NH_4F$ concentration was 2% in these experiments.

on a glass slide. Inset: a sketch of the truncated bipyramidal shape $TiO_2$ NPs show … and (1 … ts. … parameters as illustrated in the figure.

**Extended surface area**

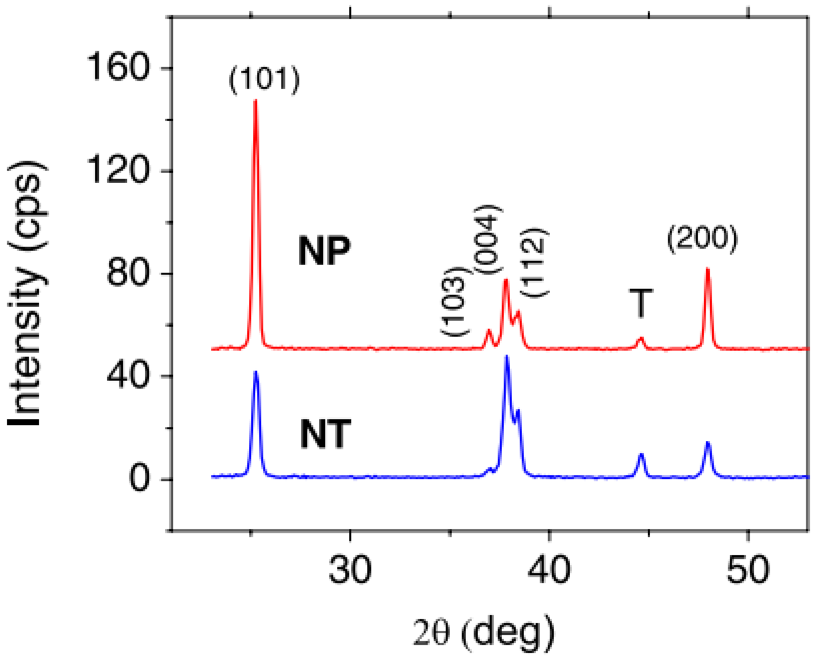
**Next, new research using this newly NT-based NP**



Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanotube-based newly $TiO_2$ NP(part three)






GAXRD spectra of the NP side (labeled 'NP') and the NT side (labeled 'NT') of the $TiO_2$ nanostructure sample. T refers to the diffraction peak of Ti foil.

(101)(103)(002) anatase peaks intensity for the NP side is 2.5 times greater than the NT side

the full width at half-maximum of these three peaks of the NP side is smaller than the NT side

**Crystal quality: NP>NT**

(004)(112) peaks intensity for the NP side is 1.7 times lower than the NT side

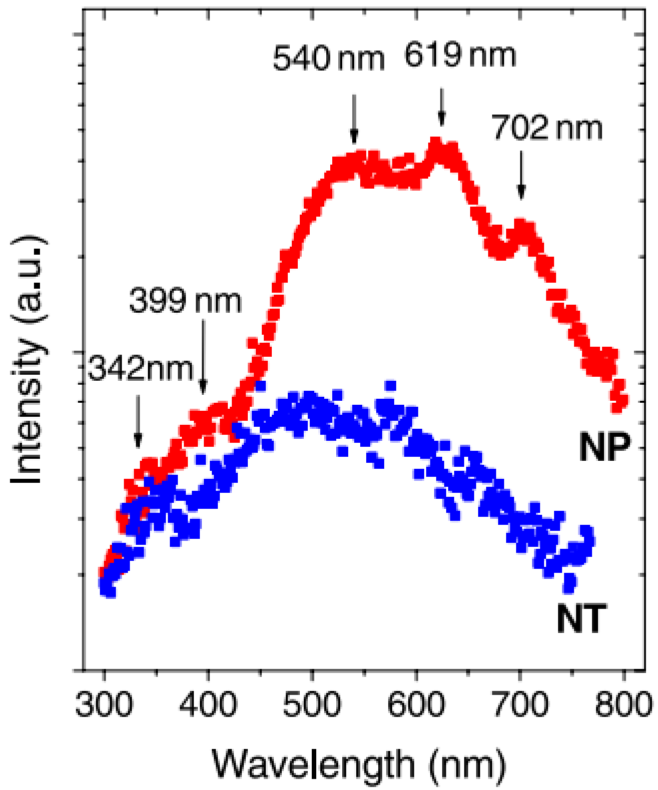
**More preferential orientation of $TiO_2$ NTs compared to NPs**



Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanotube-based newly $TiO_2$ NP(part three)






Room temperature photoluminescence spectra of the NP side (labeled 'NP') and the NT side (labeled 'NT') of the $TiO_2$ sample.

**Conventional anatase peaks:**

**342nm(3.62eV):** band-to-band direct recombination in $TiO_2$

**540nm(2.3eV):** radiative recombination of self-trapped excitons localized on $TiO_6$ octahedra

**Newly additional peaks for NP:**

**399nm(3.1eV):** radiative annihilation of excitons

**619nm(2.0eV)** and **702nm (1.76eV)**: defect-mediated electron-hole recombination

The detailed mechanism of the luminescence process in this newly structure is still remained to be well understood

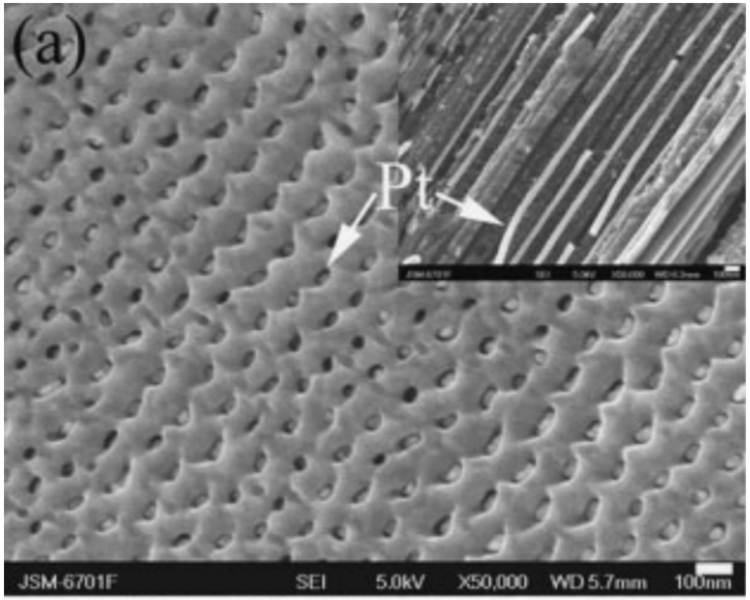
**However, for photoluminescence technique, only the electronic transitions from valence electrons to the conduction band are excited**

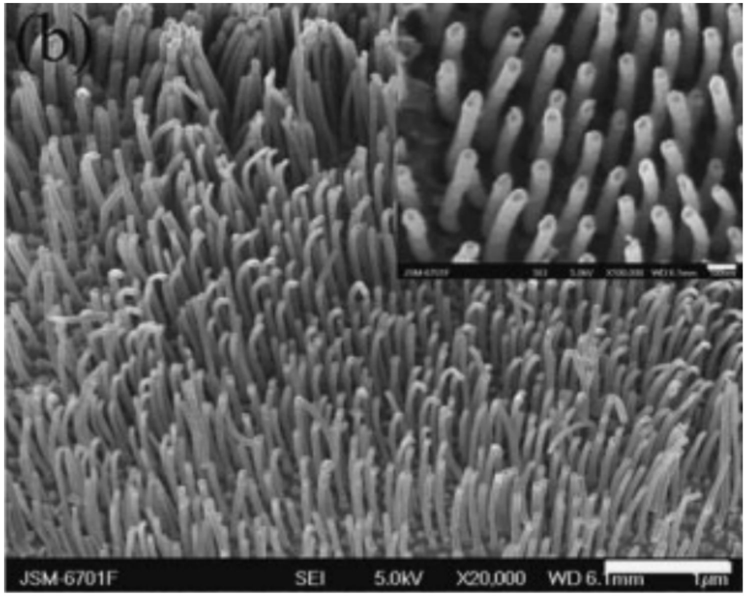


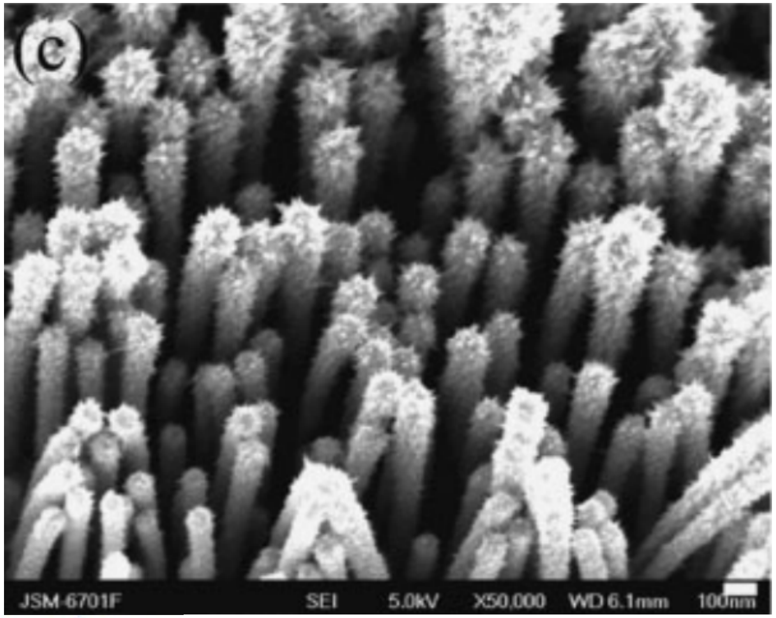
Y. Alivov and Z. Y. Fan, Nanotechnology, 2009, 20

# Nanowire growth based on $TiO_2$ NTs(part four)






The composite materials of $TiO_2$ NTs and the 1D deposited Nanowire can be used as newly photocatalyst

D Wang, B Yu et al. Advanced Materials, 2009, 1964-1967

a) Electrodeposited Pt that just fills the NTs, and the cross-section view. b,c) High-aspect-ratio Pt nanoarrays grown out of NTs.

Research Continues......

Thank you