Photosensitization of nanostructured TiO_2 electrodes with CdSe quntum dots: effects of microstructure in substrates

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BACKGROUNDS

- ***Nanocrystalline TiO_2*** has received much attention in numerous fields of applications (e.g., photocatalysis, photoelectrochemical solar cell and gas sensor).

- ***Dye-Sensitized Solar Cell (DSSC)*** with high energy conversion efficiency exceeding 10□ has been developed by
  (a) preparation of highly porous, nanostructured TiO_2 electrodes to increase the surface area;
  (b) dye or semiconductor quantum dot sensitization to extend the photoresponse of TiO_2 to the visible region.

- ***For higher efficiency***, further research on the nanostructured TiO_2 electrodes (morphology, optical absorption, charge injection, transport and recombination) is essential.

RESEARCH OBJECTIVES

TiO_2 electrodes

- Anatase-type TiO_2 nanoparticles made from $TiCl_4$ hydrolysis and oxidation processes.
- Composition of different size anatase-type TiO_2 nanoparticles.
- Composition with rutile-type content on anatase-type TiO_2 nanoparticles.
- TiO_2 nanotubes and nanowires.
- TiO_2 photonic crystals.

Sensitizer

CdSe quantum dots.

Advantages of semiconductor quantum dots

- Quantum confinement allows for *energy gap tunable* across the solar spectrum.
- *Large extinction coefficient* resulting from quantum confinement.
- *Large intrinsic dipole moment* which may lead to rapid charge separation.
- Robust *inorganic* nature.
- Impact ionization occurs with the possibility of high efficiency.

MOTIVATIONS

- **In order to investigate morphological dependence, two types of nanostructured TiO_2 electrodes were prepared and CdSe quantum dots with various sizes were adsorbed on TiO_2 as sensitizer.**

- **TiO_2 electrodes were characterized using SEM, XRD, photoacoustic (PA) and photoelectrochemical current (PEC) methods.**

PA method *is powerful for the investigation of optical absorption of optically opaque or scattering solid materials.*

TiO_2 electrode preparation

Nanocrystalline TiO_2 powder (30 wt)

A (15 nm)

B (27 nm)

Pure water

Acetylacetone 10 wt%)

Polyethylene glycol PEG) (MW:500000)

(40 w vs TiO_2)

Stirring for one hour

TiO_2 paste

Depositing TiO_2 paste on FTO using squeegee method.

Heating in air at 450 for 30 min.

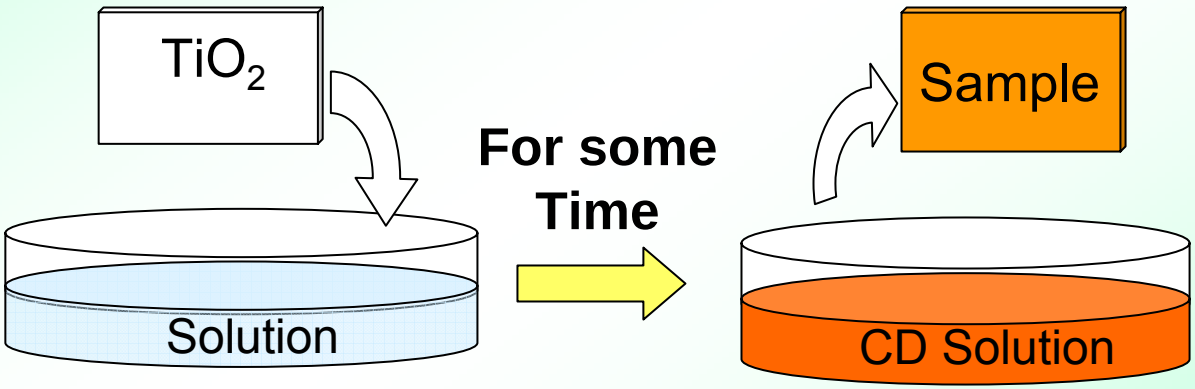
Two types of TiO_2 electrodes

Chemical solution deposition (CD) method of CdSe quantum dots on the TiO_2 electrode

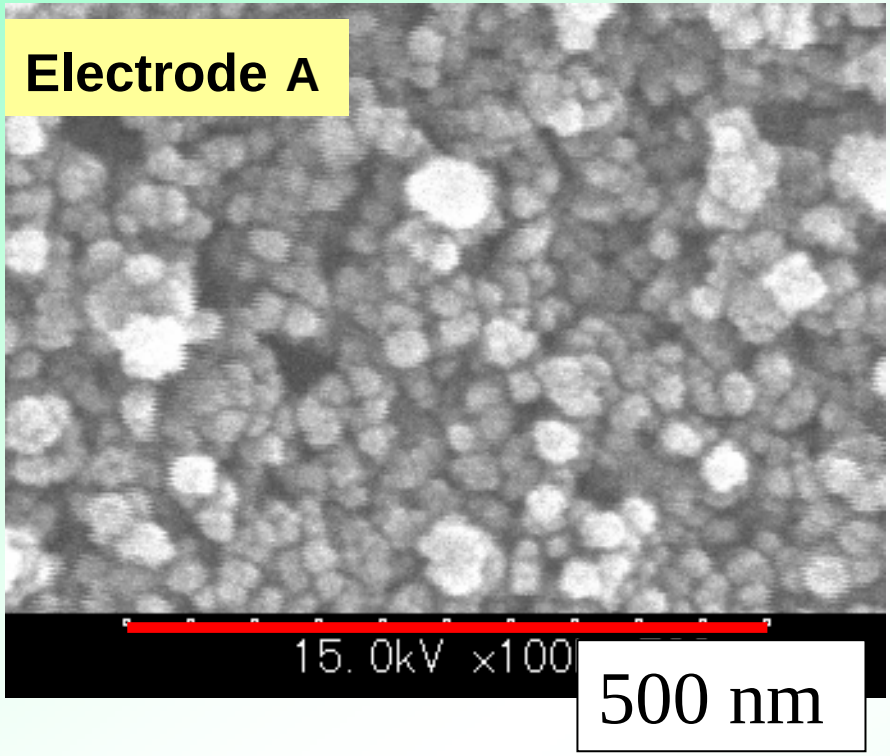
S. Gorer, G. Hodes, J. Phys. Chem. 98 (1994) 5338.

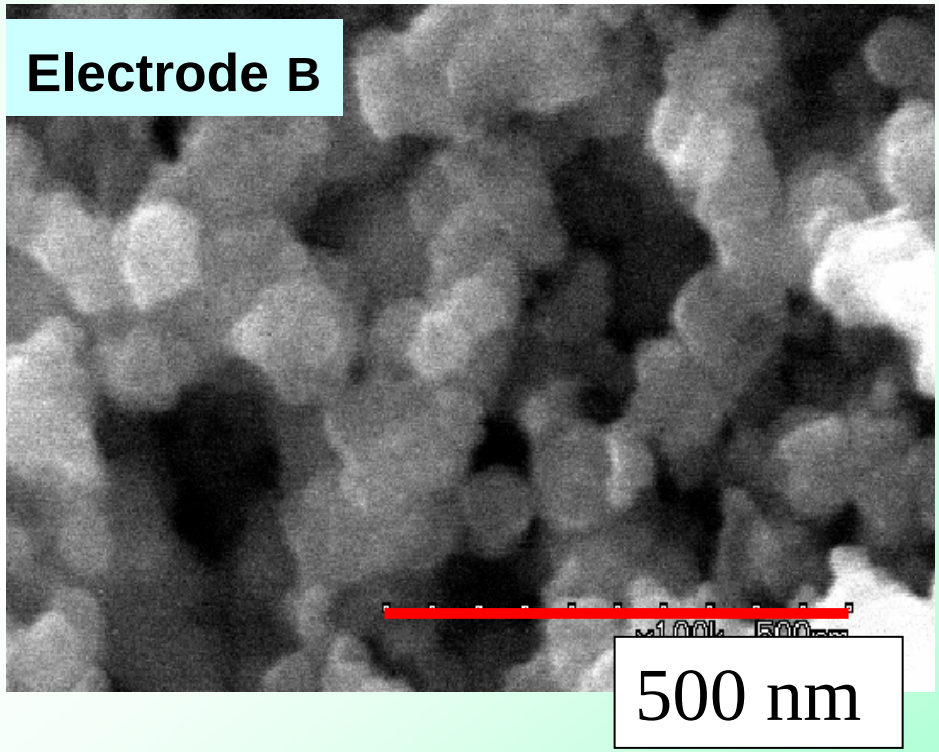
- 80mM $CdSO_4$
- 120mM $N(CH_2COONa)_3$ (NTA)
- 80 mM Na_2SeSO_3

mixed (1:1:1) → **Chemical Deposition (CD) Solution**



SEM micrographs of TiO_2 electrodes

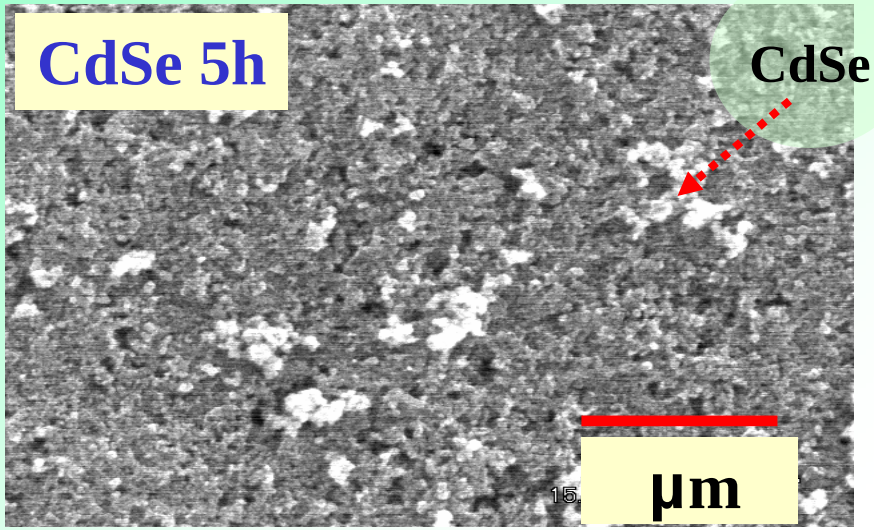


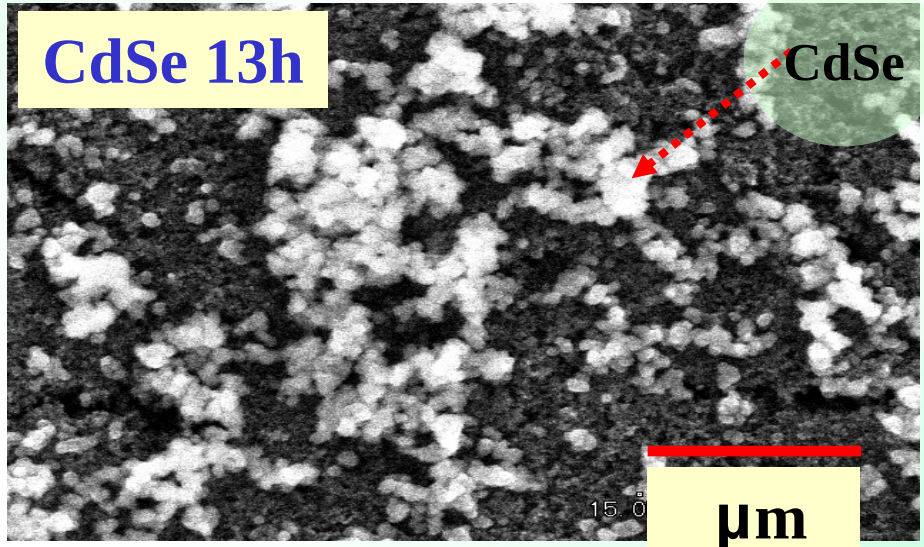


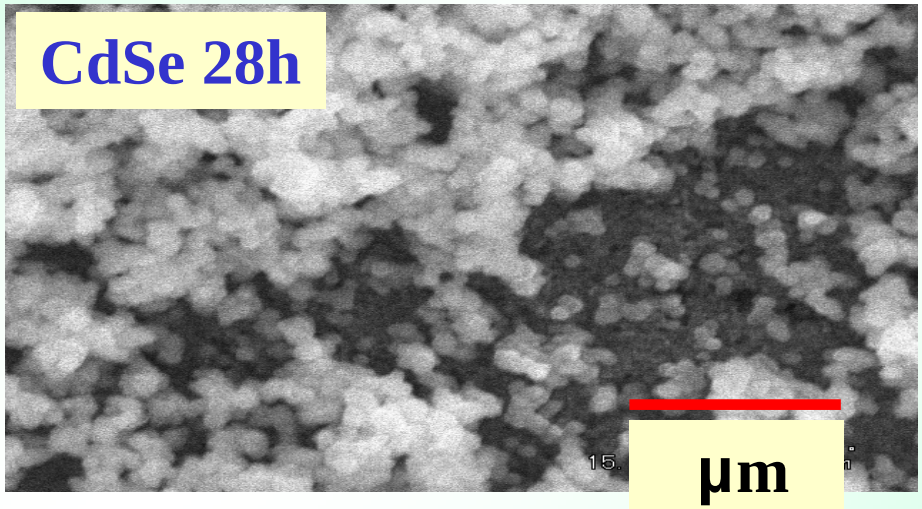
Size of TiO_2 in the paste: 15 nm

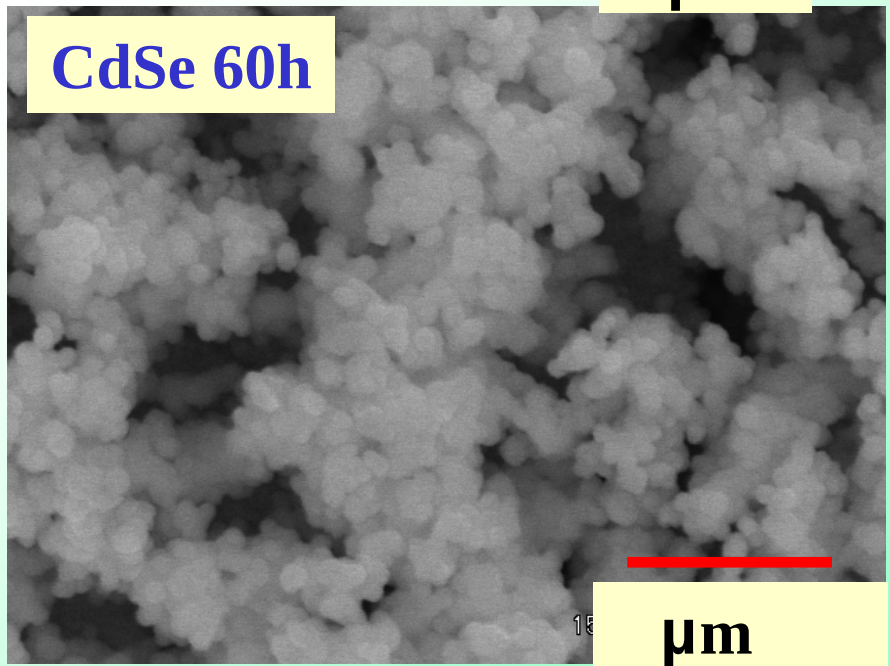
Size of TiO_2 in the paste: 27 nm

SEM micrographs of CdSe-quantum dots adsorbed on TiO_2 electrodes

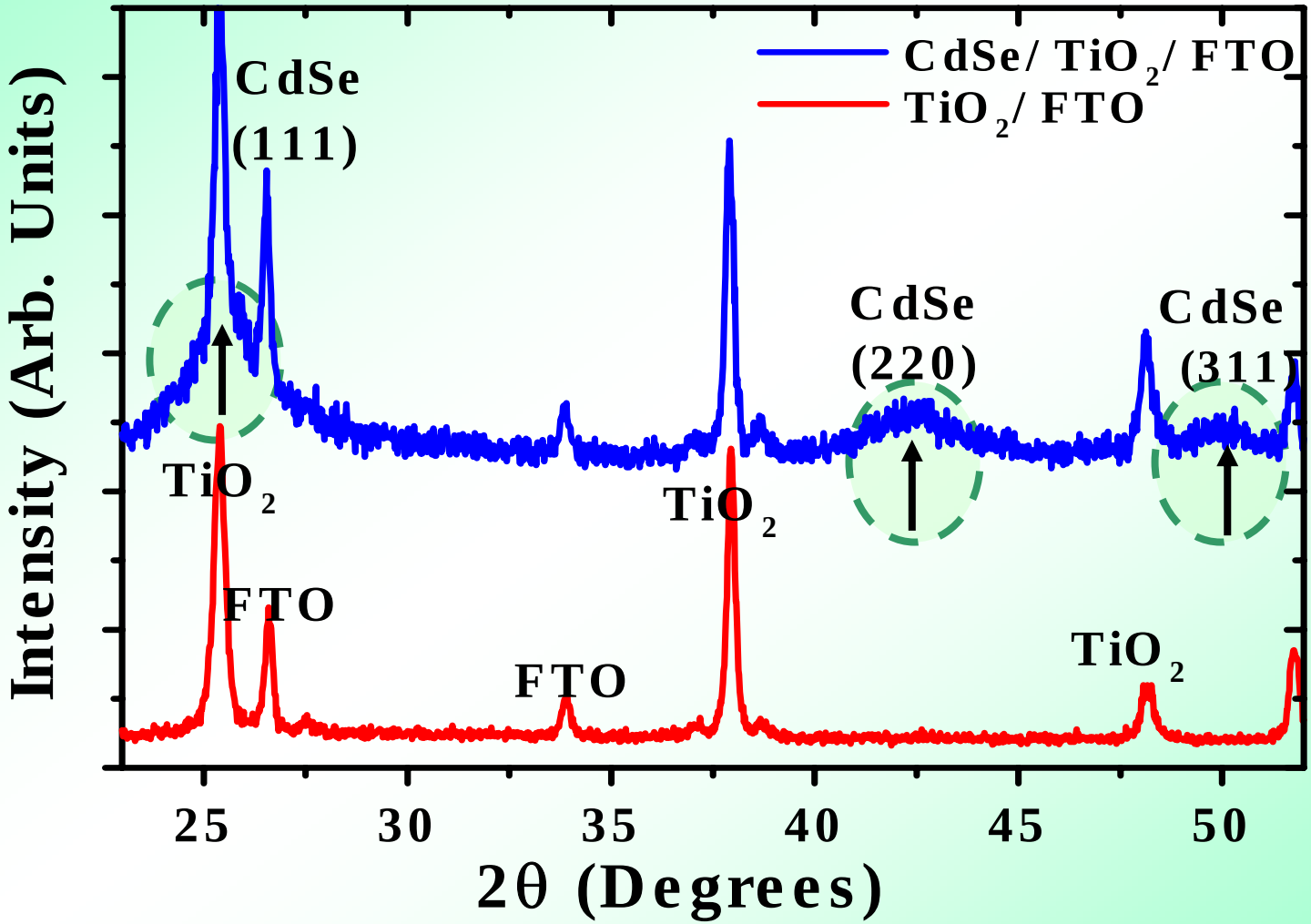


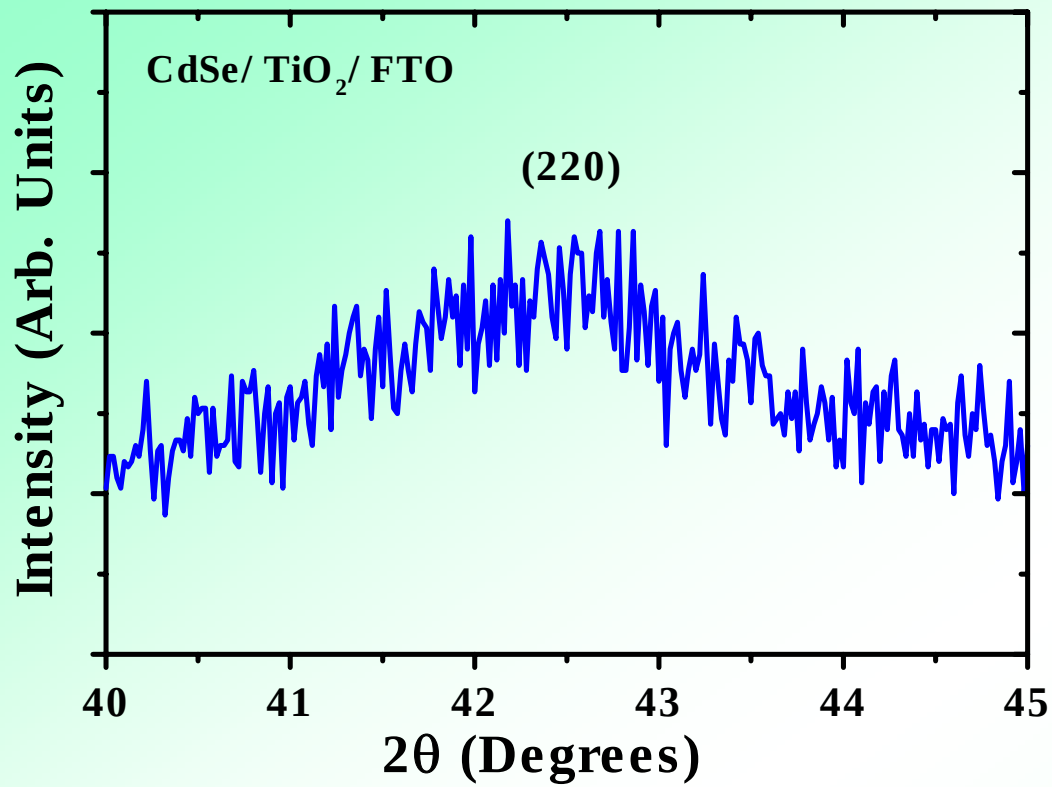






X-Ray diffraction patterns





Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos\phi}$$

D: CdSe quantum dot size

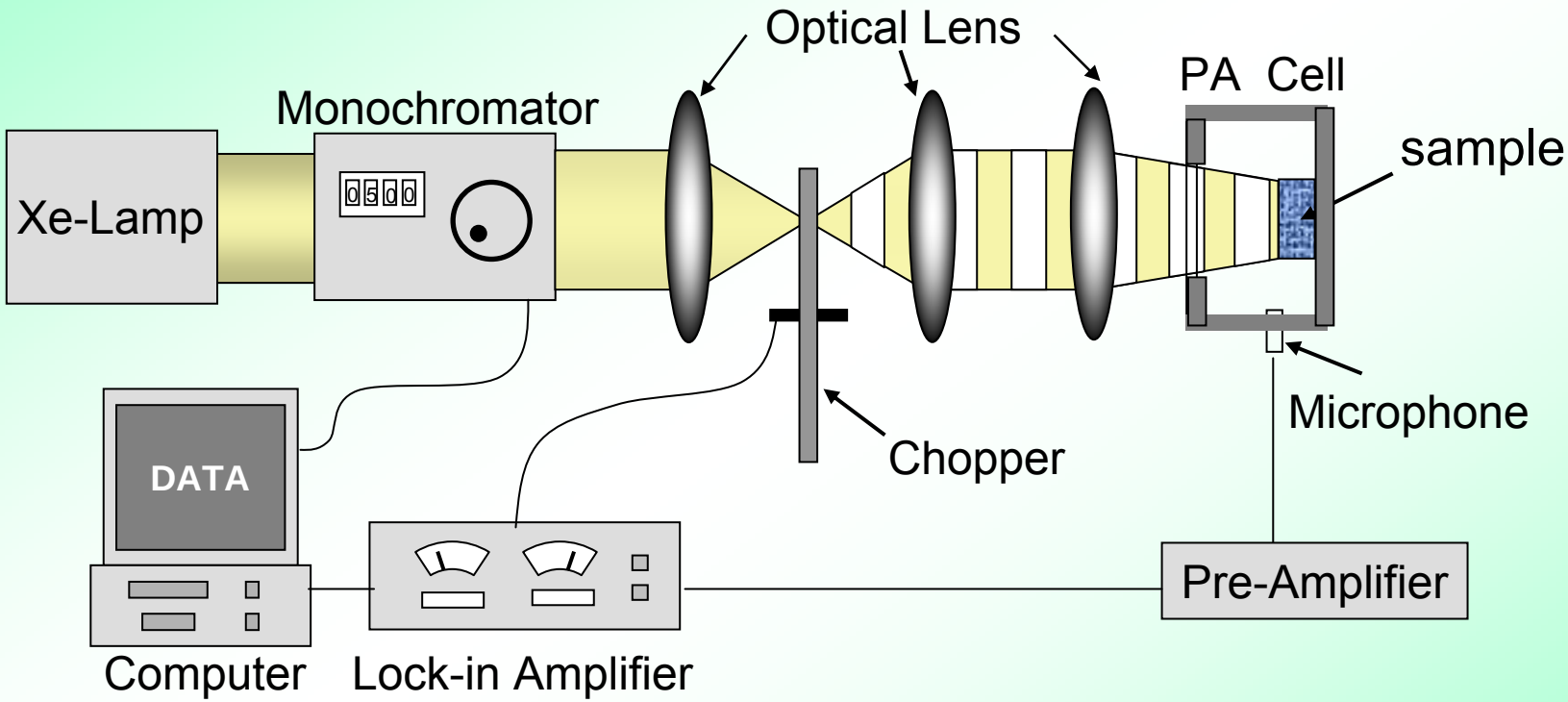
β: half-width of the diffraction peak

Φ: diffraction angle

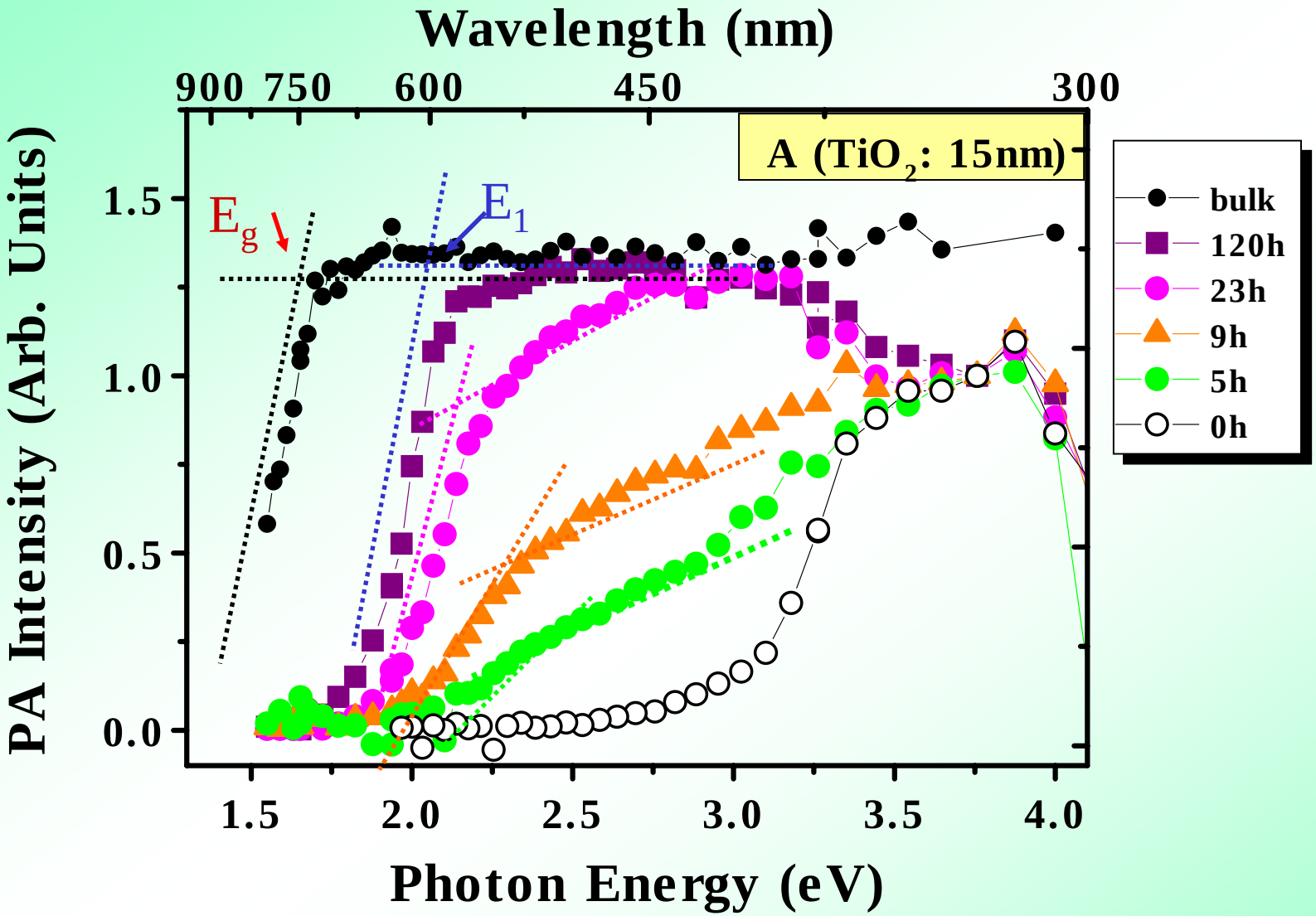
λ: 0.154 nm

D 5-6 nm (CdSe120h)

Photoacoustic Spectroscopy (PAS)



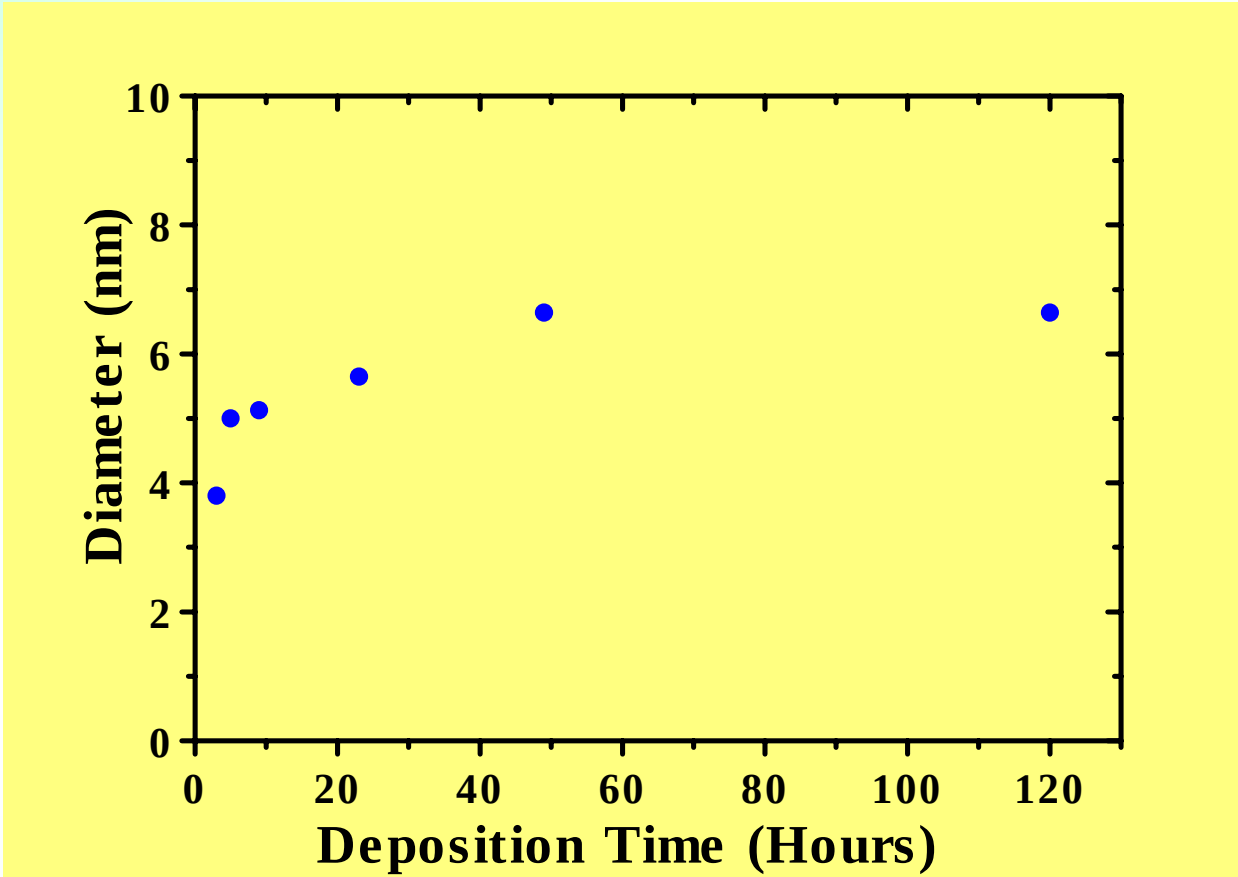
Light source : 300W xenon arc lamp
Normalization : carbon black sheet
Wavelength range 250nm 800nm
Modulation frequency : 33Hz



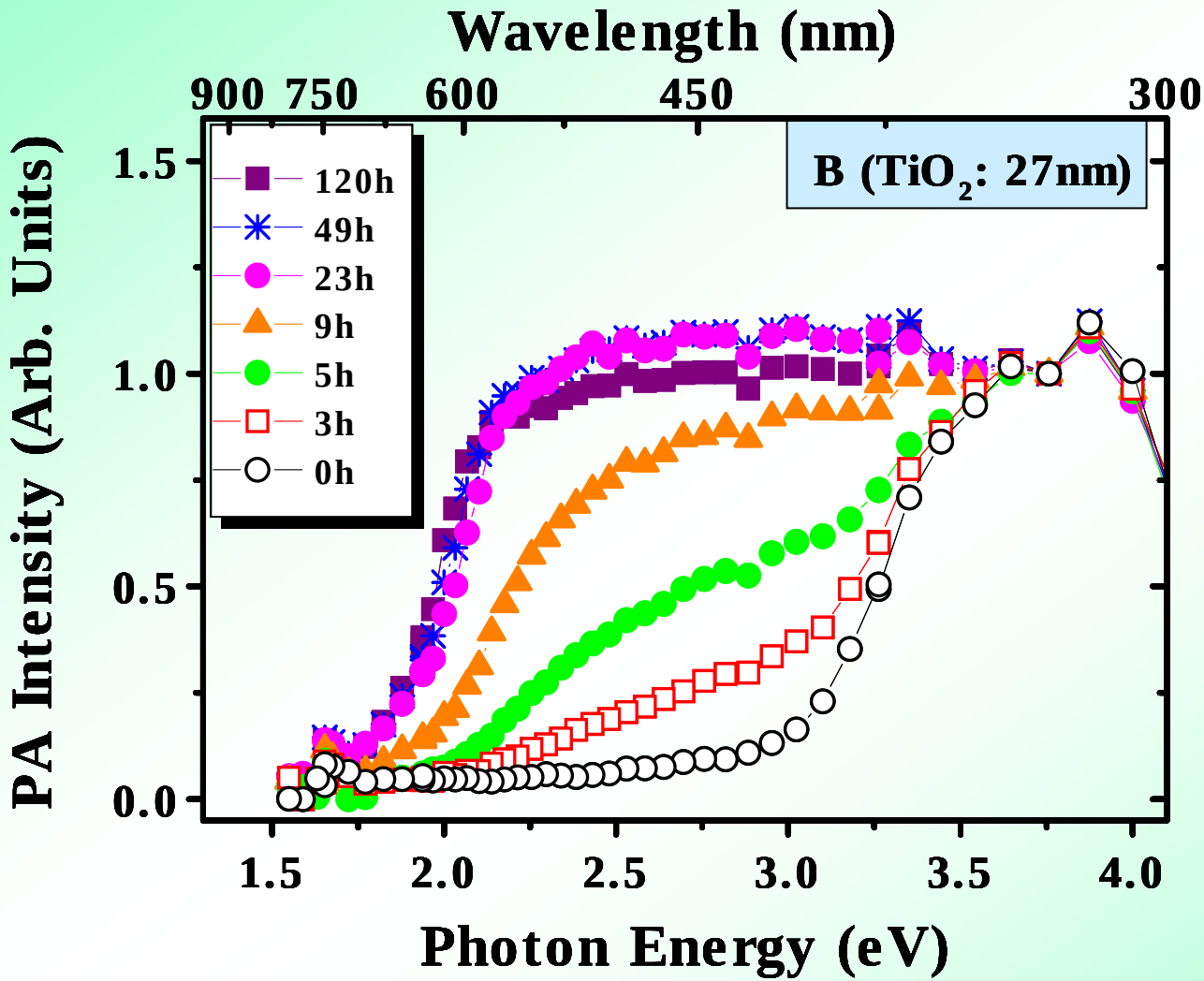
PA spectra of TiO_2 electrodes A (TiO_2:15nm) deposited with CdSe quantum dots for various times.

Effective mass approximation :

$$\Delta E = E_1 - E_g = \frac{h^2}{8\mu a^2} \qquad (D = 2a)$$

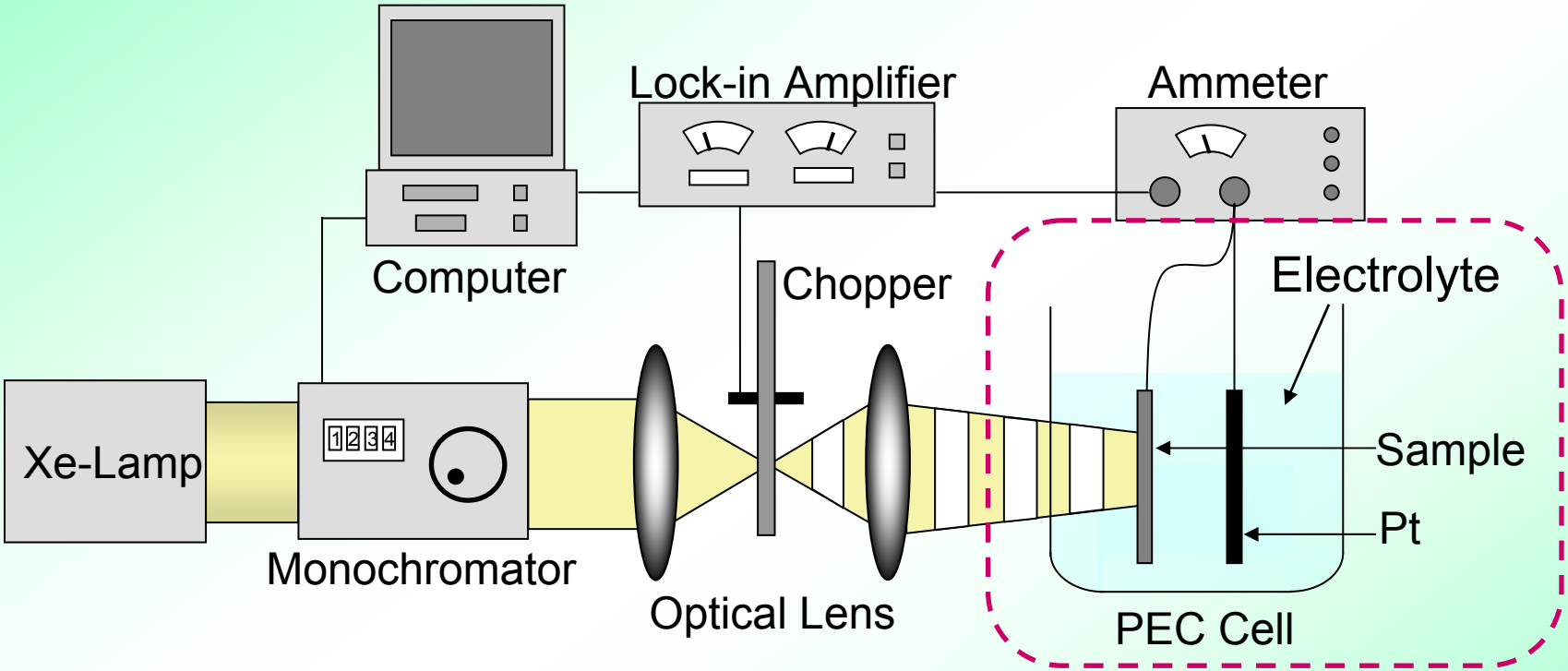


Dependence of CdSe quantum dot size on deposition time.

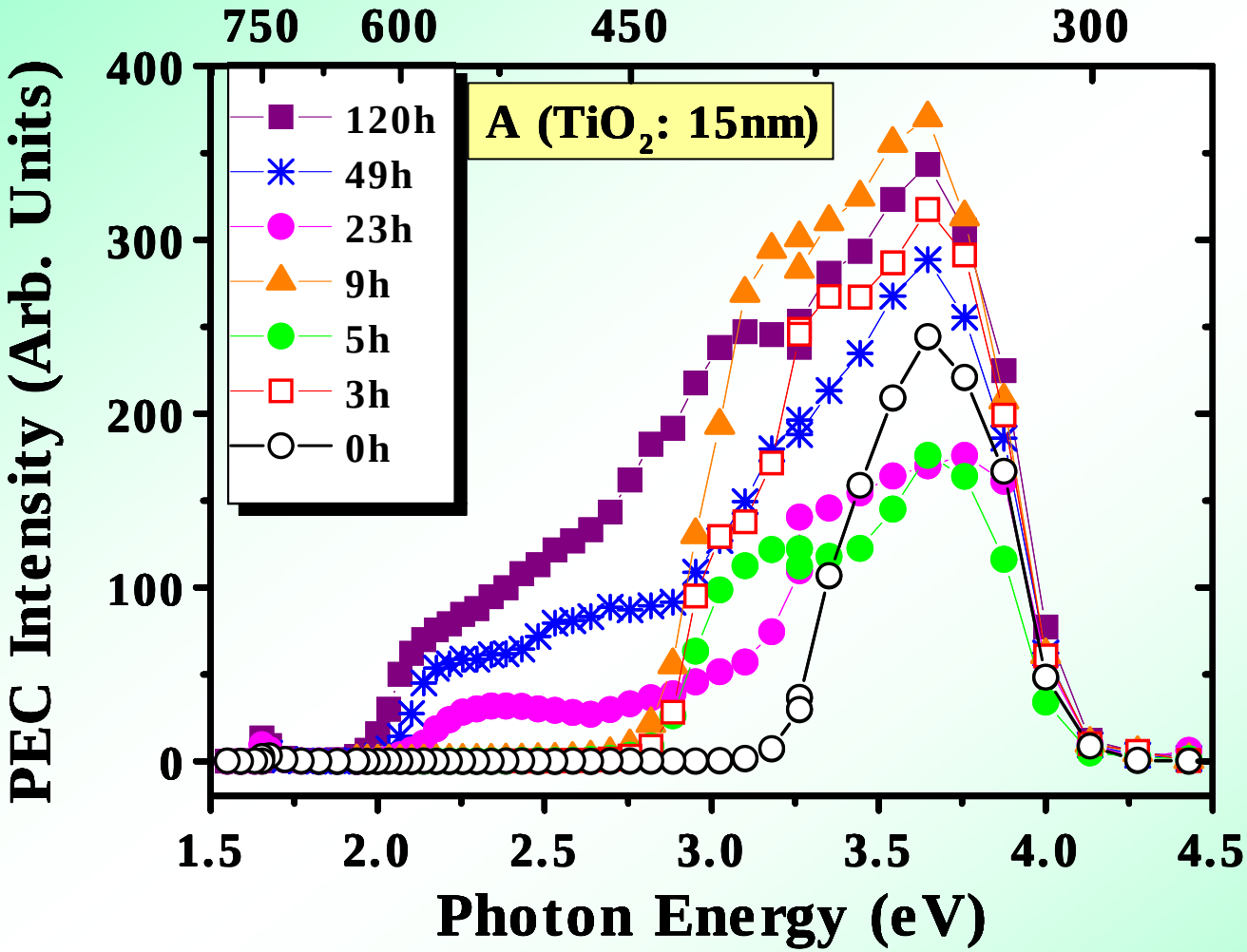


PA spectra of TiO_2 electrodes B (TiO_2:27nm) deposited with CdSe quantum dots for various times.

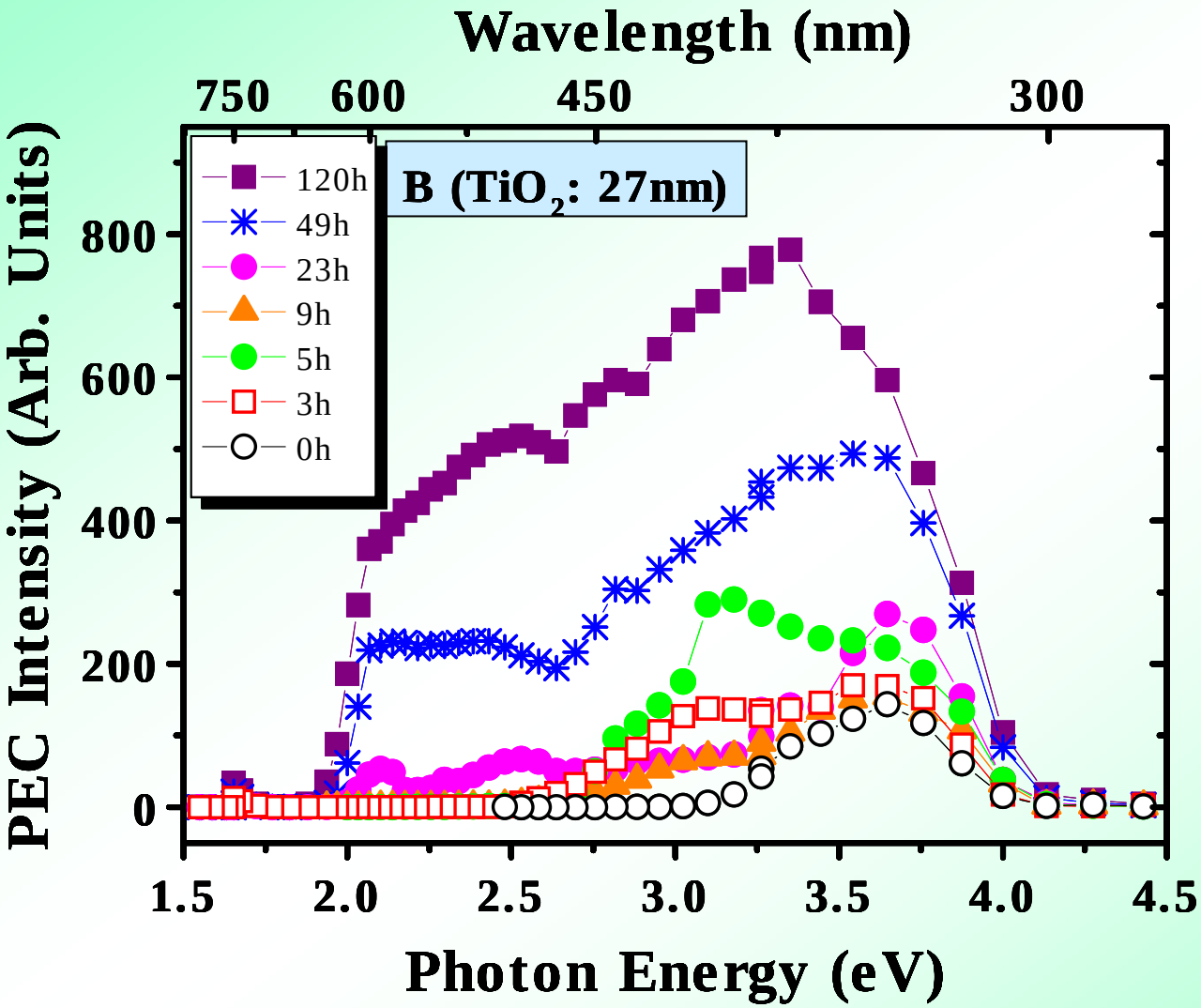
Photoelectrochemical Current（PEC）Spectroscopy



Light source : 300W xenon arc lamp
Normalization : carbon black sheet
Material of the PEC cell quartz
Wavelength range 250nm 800nm
Electrolyte : 1M KCl + 0.1M Na_2S



PEC spectra of TiO_2 electrodes A (TiO_2:15nm) deposited with CdSe quantum dots for various times.

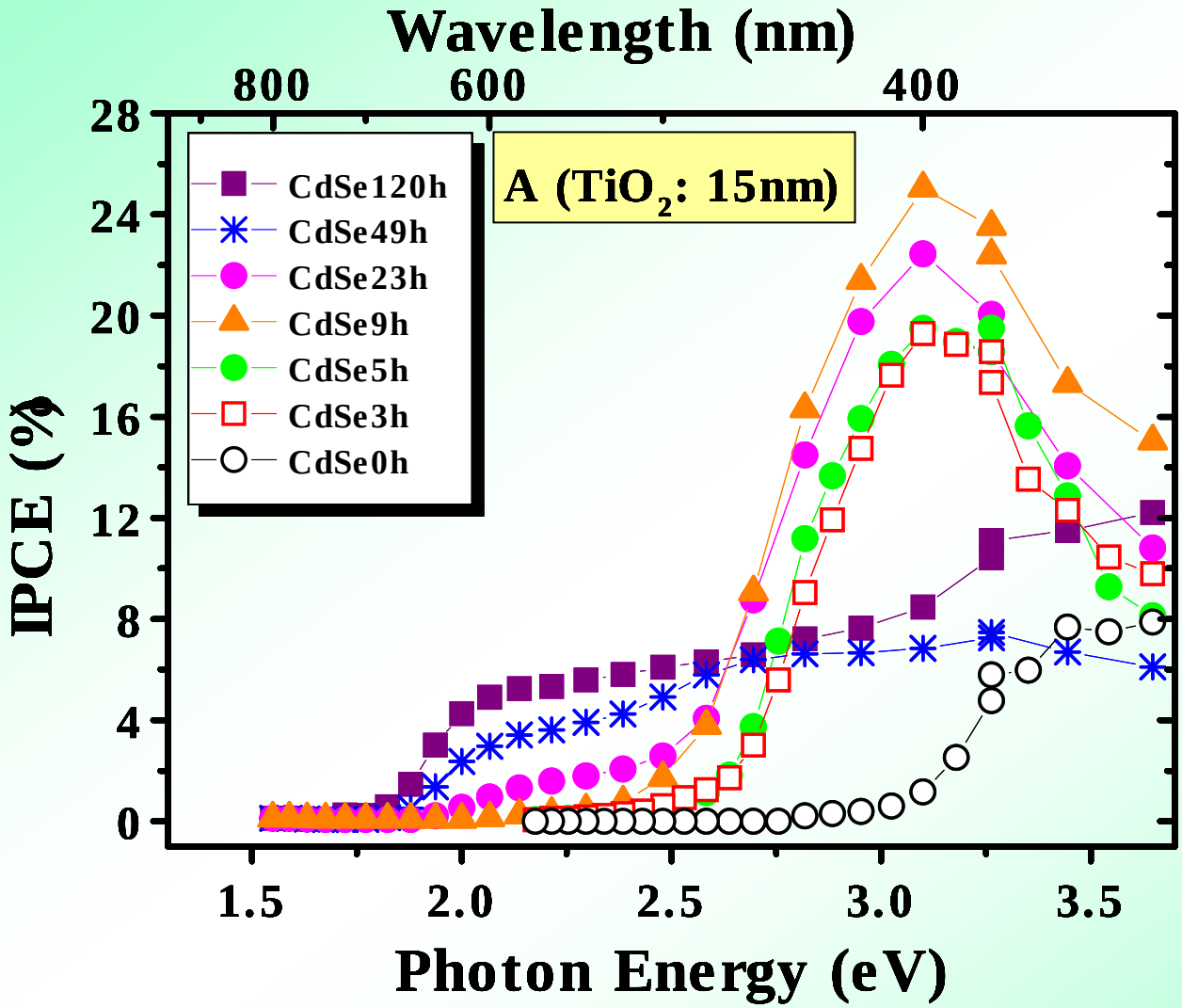


PEC spectra of TiO_2 electrodes B (TiO_2:27nm) deposited with CdSe quantum dots for various times.

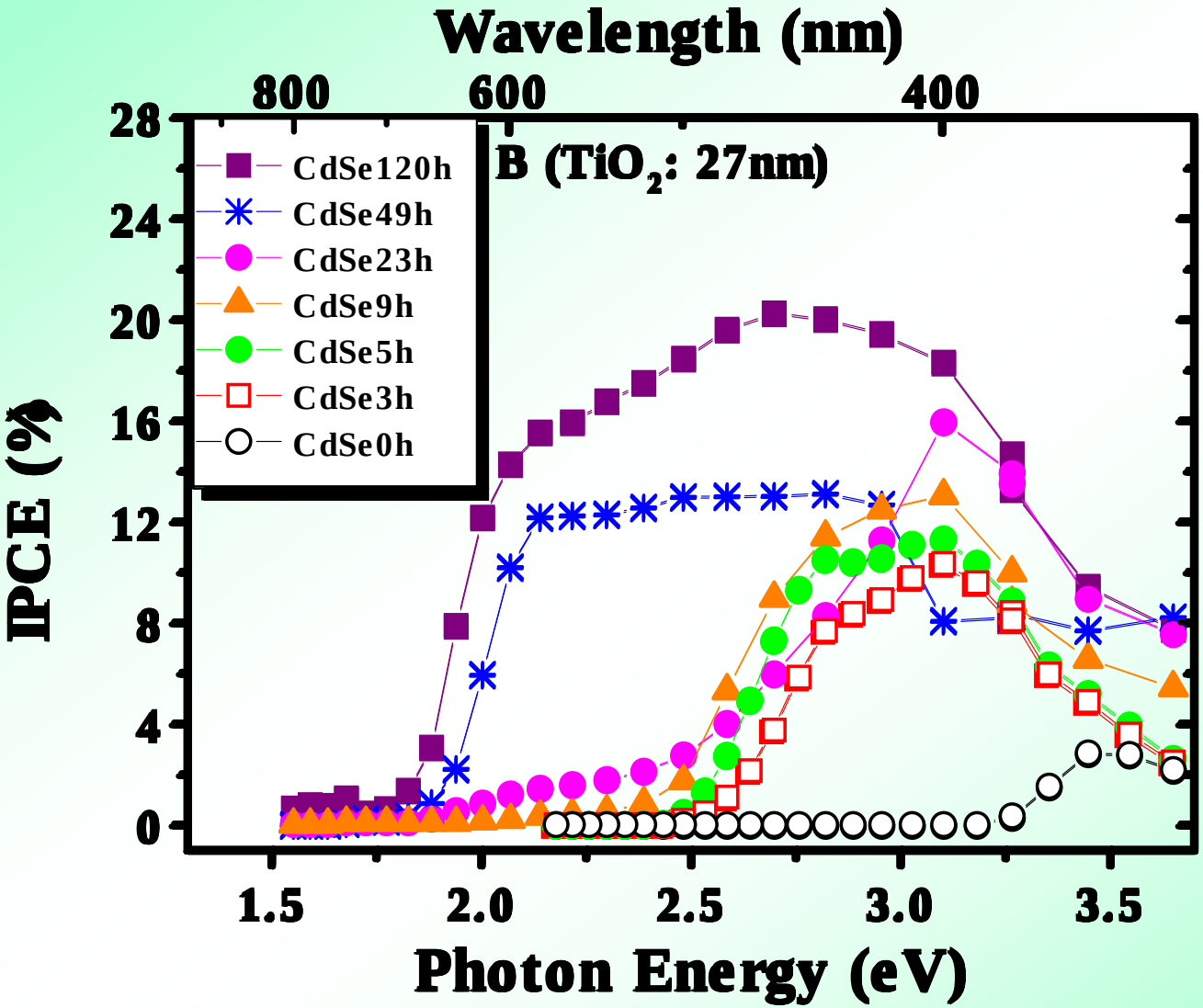
IPCE: incident photon-to-current conversion efficiency for monochromatic radiation

$$\mathrm{IPCE}(\%) = \frac{\text{injected electron numbers}}{\text{incident photon numbers}}$$

$$= \frac{1240\ (\mathrm{eV}\cdot\mathrm{nm}) \times \text{photocurrent density}\ (\mu\mathrm{A}\cdot\mathrm{cm}^{-2})}{\text{wavelength}\ (\mathrm{nm}) \times \text{photoflux}\ (\mu\mathrm{W}\cdot\mathrm{cm}^{-2})}$$



IPCE spectra of TiO_2 electrodes A (TiO_2:15nm) deposited with CdSe quantum dots for various times.



IPCE spectra of TiO_2 electrodes B (TiO_2:27nm) deposited with CdSe quantum dots for various times.

Summary

Two types of nanostructured TiO_2 electrodes A (15nm) and B (27nm) deposited with CdSe quantum dots by chemical deposition, have been characterized using PA, PEC spectra and IPCE measurements.

- **Photosensitization by CdSe quantum dots was demonstrated and red shift of the spectra with increasing CdSe sizes can be clearly observed.**

- **PEC and IPCE spectra in the visible region are quite different for the two types of TiO_2 electrodes, even for the same deposition time of CdSe quantum dots.**

The electron diffusion coefficient of the TiO_2 electrode A was found to be two times larger than that of electrode B using transient photocurrent responses.

PEC and IPCE in the visible region in the CdSe-sensitized TiO_2 nanostructured electrodes largely depend on both the microstructure and electron transport property in the TiO_2 electrodes as well as the size and quantity of CdSe nanoparticles .

Future studies:

TiO_2/CdSe interfacial property;

Energy conversion efficiency;

Ultrafast relaxation dynamics etc.

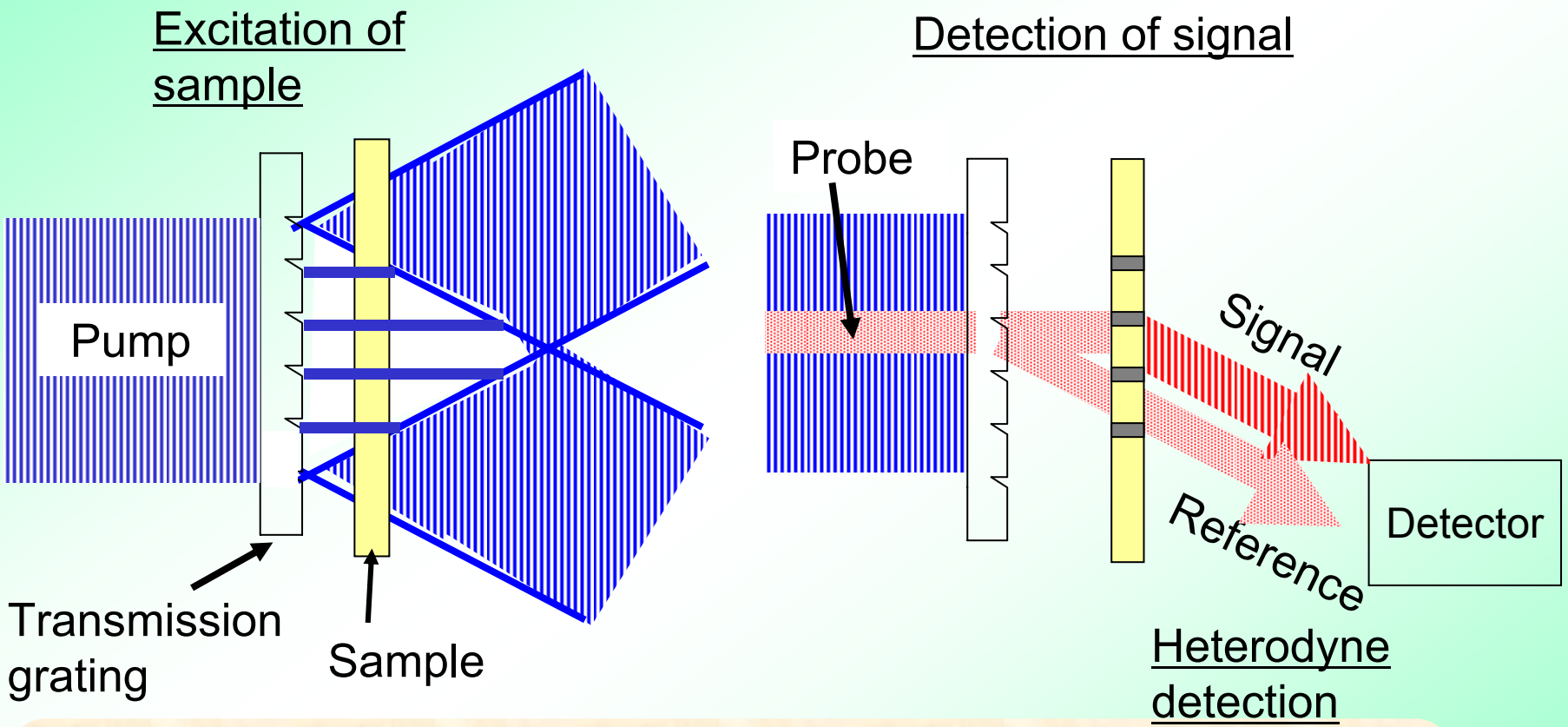
Ultrafast Carrier Dynamics of CdSe Quantum Dots Adsorbed on Nanostructured TiO_2 Films

- **The *ultrafast carrier dynamics* were investigated by using lens-free heterodyne detection transient grating (LF-HD-TG) technique.**

One kind of optical pump and probe technique:

Measurements of the decay of excited carrier densities after pulsed injection.

LF-HD-TG method

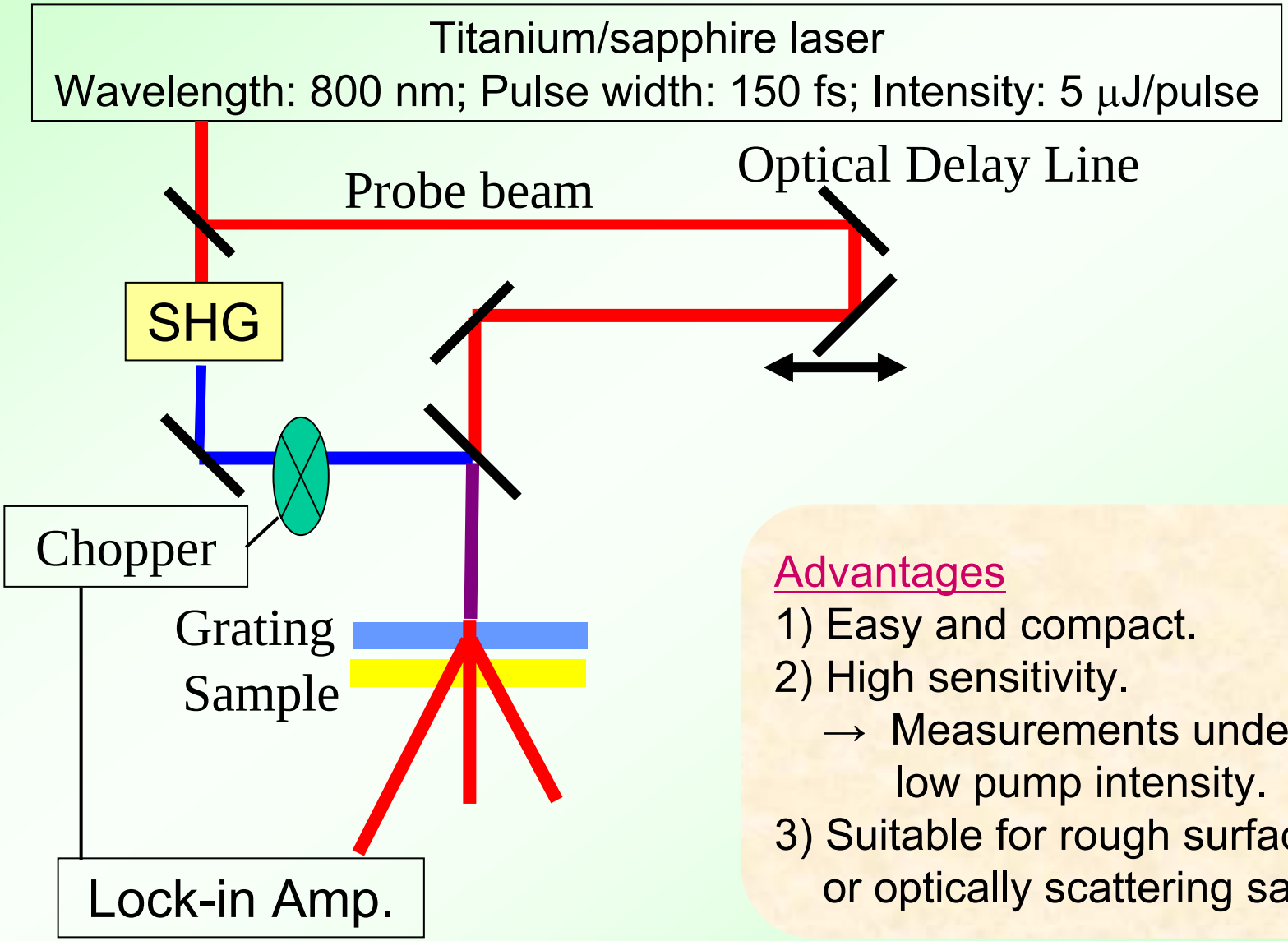


By approaching a sample to the grating, 1: Grating excitation
2: Heterodyne detection

→ Easy TG method without lenses (No daily setup)

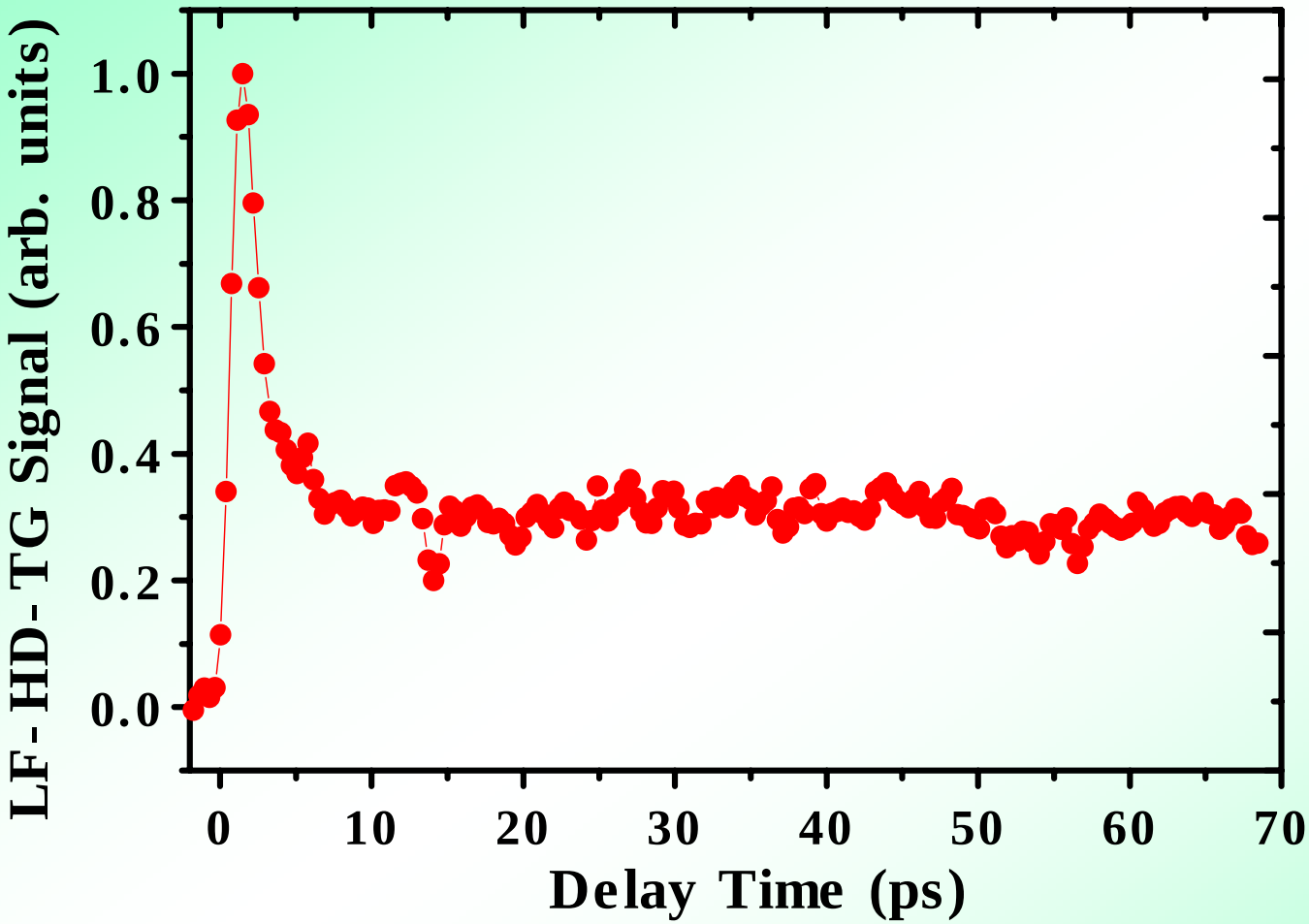
K. Katayama et al., APL **82**, 2775 (2003).

Lens-free heterodyne detection transient grating technique (LF-HD-TG)

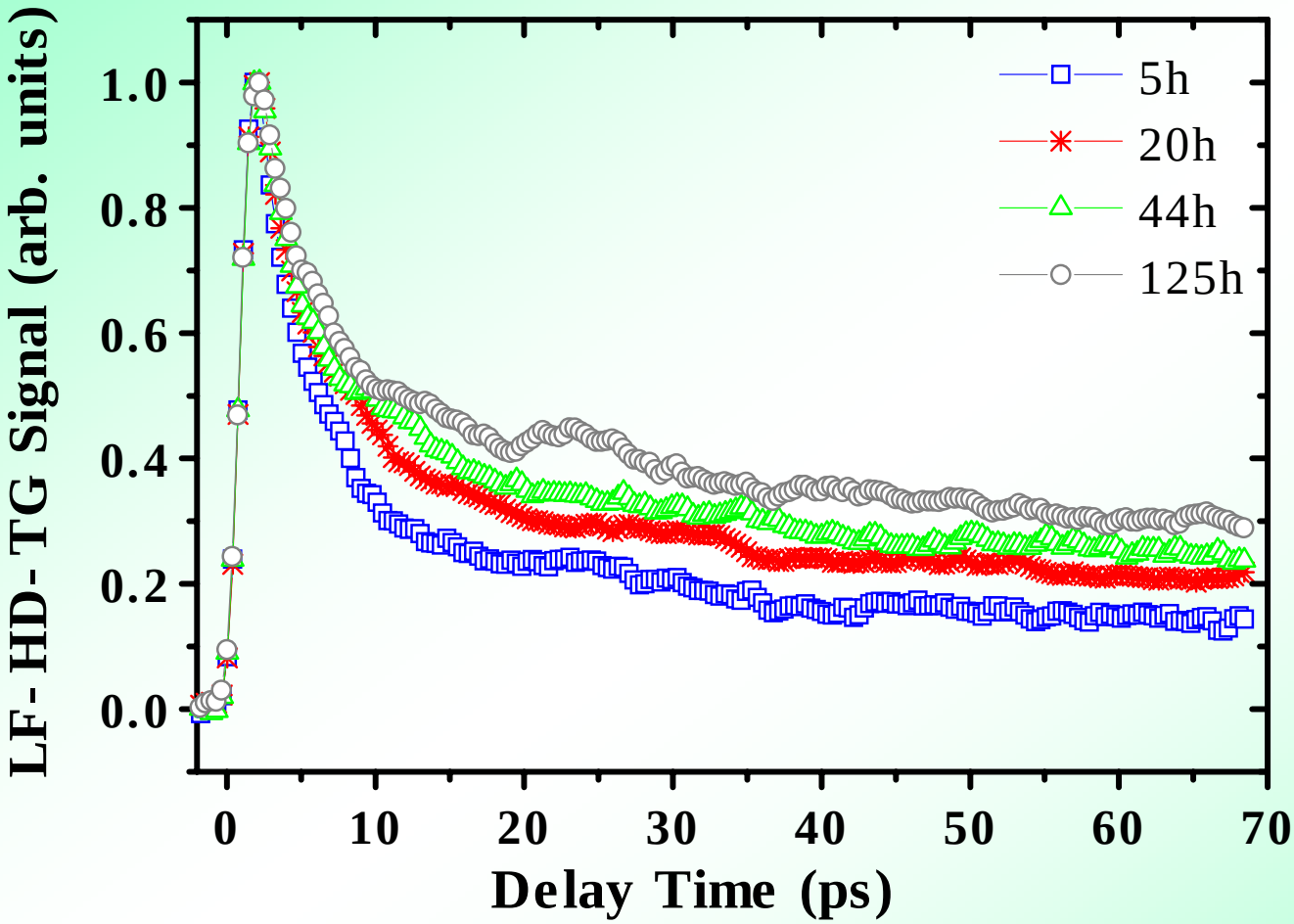


Advantages

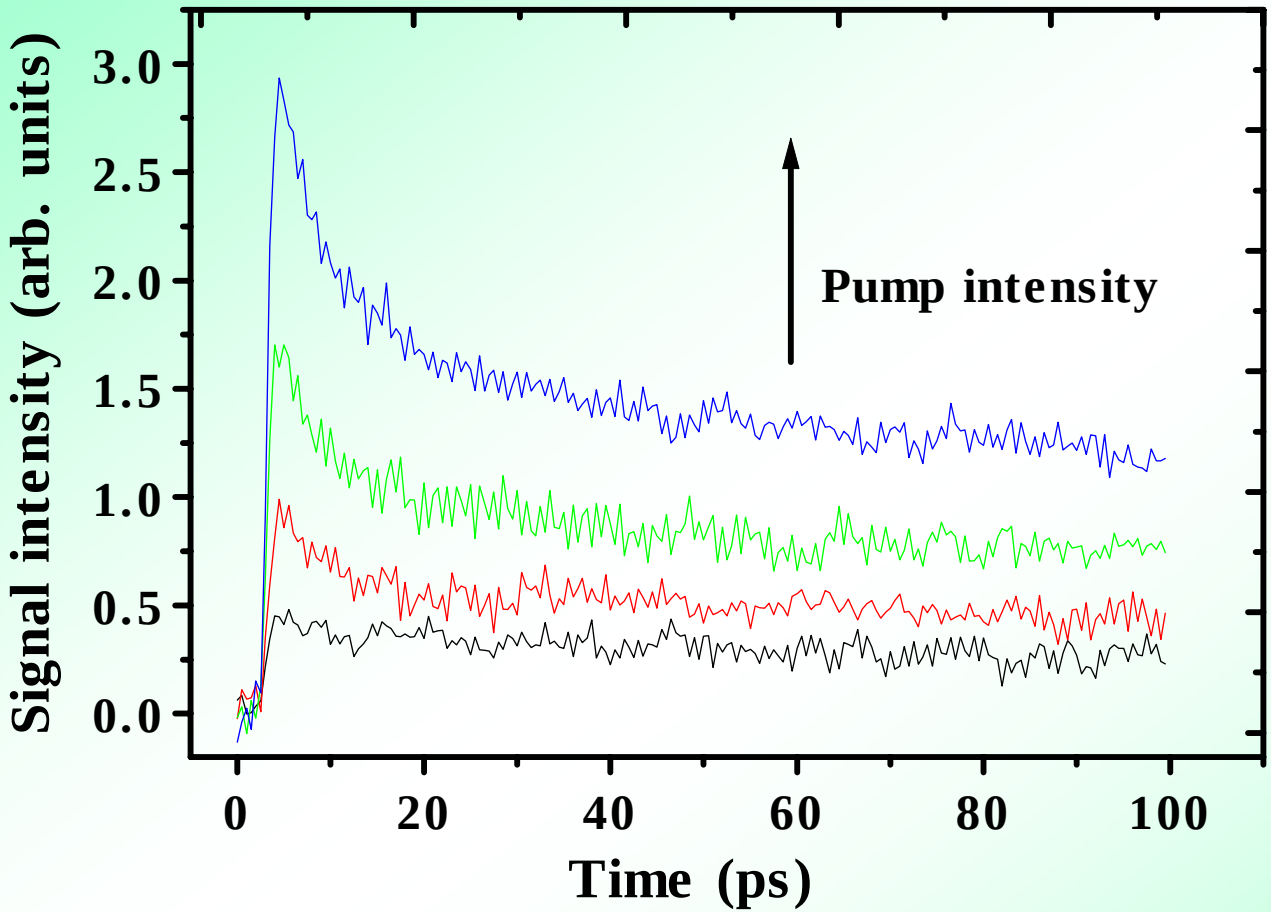
1) Easy and compact.
2) High sensitivity.
   → Measurements under low pump intensity.
3) Suitable for rough surfaces or optically scattering samples.



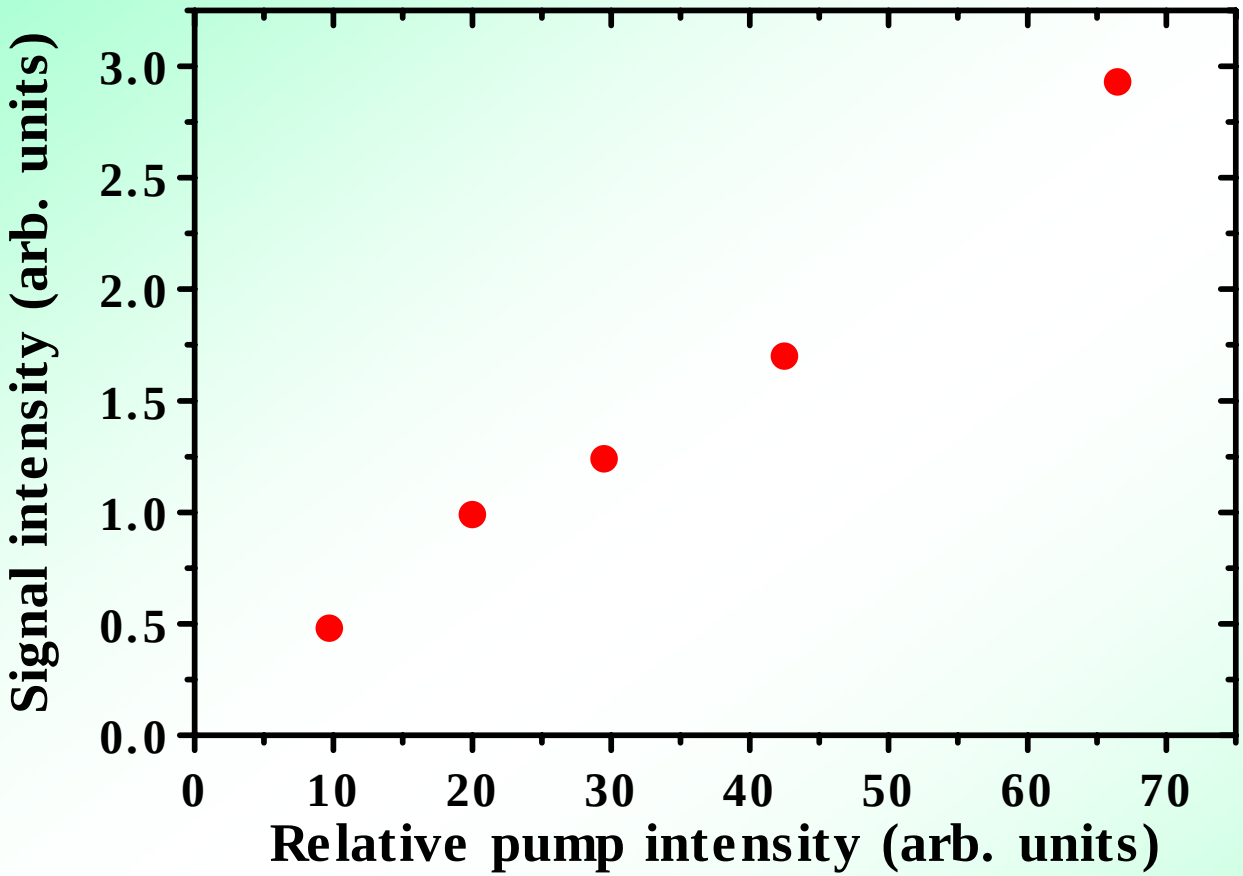
LF-HD-TG response of nanostructured TiO_2 electrode without CdSe quantum dots.



LF-HD-TG responses of nanostructured TiO_2 electrodes B (TiO_2: 27 nm) with CdSe quantum dots for different deposition times.



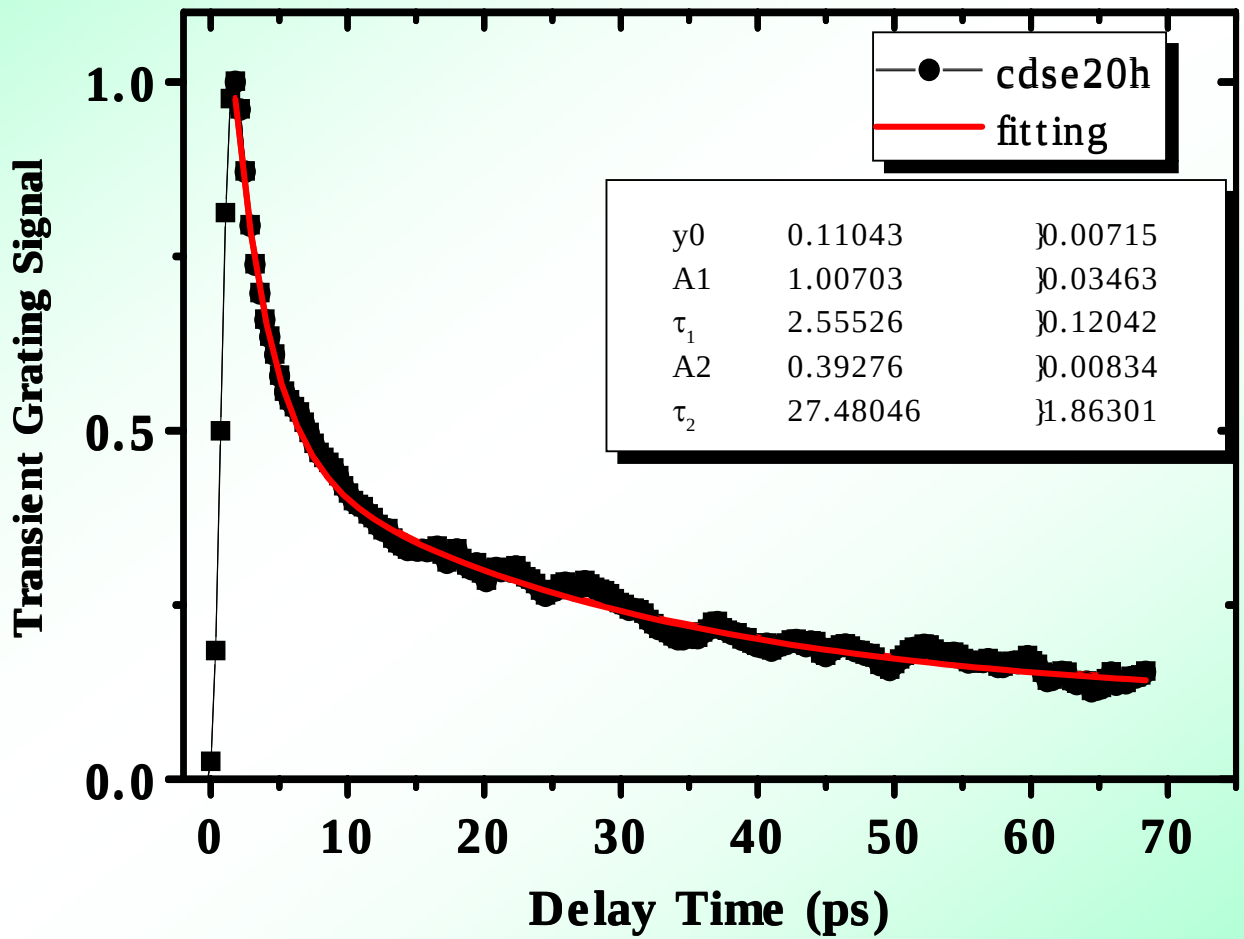
Pump intensity dependence of the LF-HD-TG response of nanostructured TiO_2 electrode B (TiO_2: 27 nm) deposited with CdSe quantum dots for 49h. The pump intensity is ranging from 2.5 to 16.5 µJ/pulse.



The pump intensity dependence of the maximum signal intensity for nanostructured TiO_2 electrode B (TiO_2: 27 nm) deposited with CdSe quantum dots for 49 h.

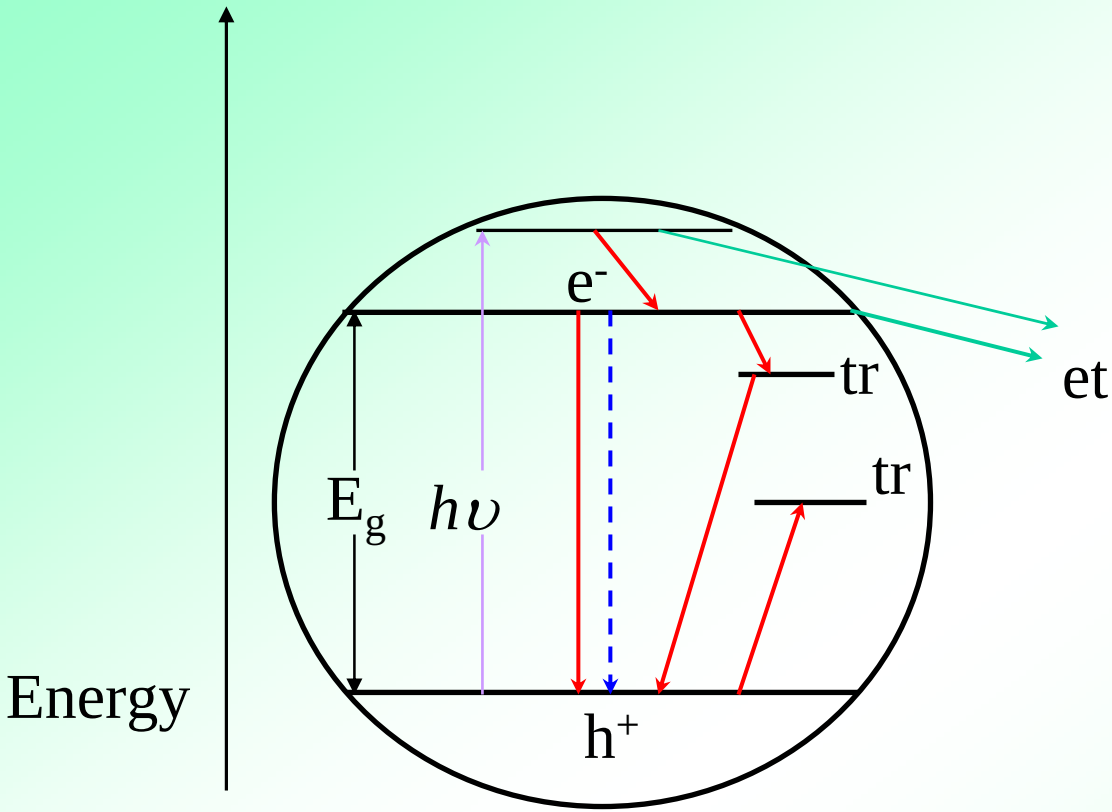
Analyses of LF-HD-TG response

$$y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$



Results of the Fitting Parameters

CdSe deposition time (h)	CdSe size (nm)	τ_1 (ps)	τ_2 (ps)	A_1	A_2	y_0
5	4.8	1.8	16	0.74	0.34	0.15
9	5.1	2.1	19	0.68	0.37	0.16
20	5.8	2.1	20	0.65	0.31	0.20
44	6.5	2.2	29	0.63	0.28	0.18
125	6.7	1.9	30	0.60	0.31	0.27



tr: trapped

et: electron transfer

Eg: energy gap

$h\upsilon$: excitation energy

→ nonradiative

⇢ radiative

→ excitation

(1) Fast decay process (τ_1): decrease of hole carrier numbers by trapping at the CdSe QD surface states;

(2) Slow decay process (τ_2): photoexcited electron relaxation process, i.e. recombination and/or transfer to the TiO_2 electrode;

(3) Base line (y_0): thermal diffusion signal owing to thermal grating.

Summary

Nanostructured TiO_2 electrodes adsorbed with CdSe quantum dots by chemical deposition, have been characterized using LF-HD-TG measurements for the first time.

Three decay processes can be shown with decay time of 2 ps (τ_1), 16-30 ps (τ_2) and larger than a few hundreds ps, respectively.

It is found that τ_1 is independent of quantum dot size, but τ_2 depends on quantum dot size.

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