JINST 19 P07014 (2024)

Water-based Quantum Dots Liquid Scintillator

Outline

1. Introduction
2. Quantum Dots
3. Optical measurements
4. Cosmic ray test
5. Next step

Water-based quantum dots liquid scintillator for particle physics

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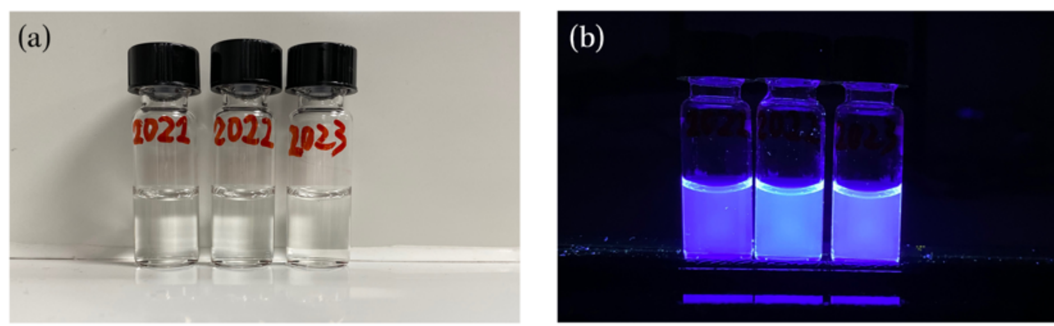


Teppei Katori @teppeikatori
King's College London
Sussex HEP seminar, Univ. of Sussex, April 3, 2025

1. Introduction

2. Quantum Dots

3. Optical measurements

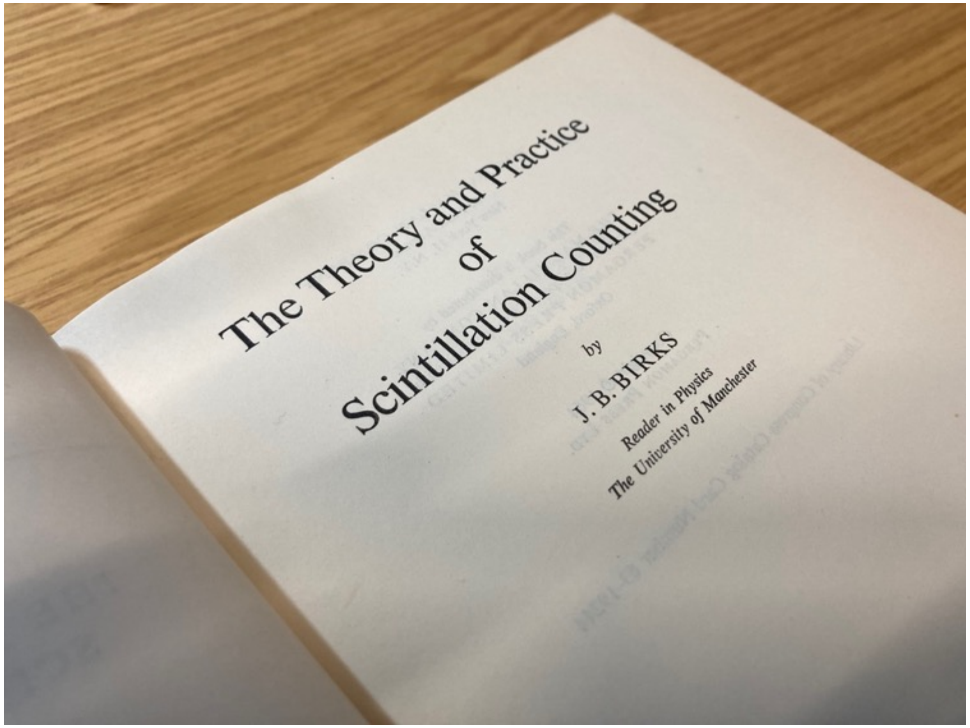
4. Cosmic ray test

5. Next step

1. Theory and Practice of Scintillation Counting by Birks (1964)

History

“...at one famous laboratory during this period all intending research students were tested in the dark room for their ability to count scintillations accurately. Only those whose eyesight measured up to the standards required were accepted for nuclear research; the others were advised to take up alternative, less physically exacting, fields of study”



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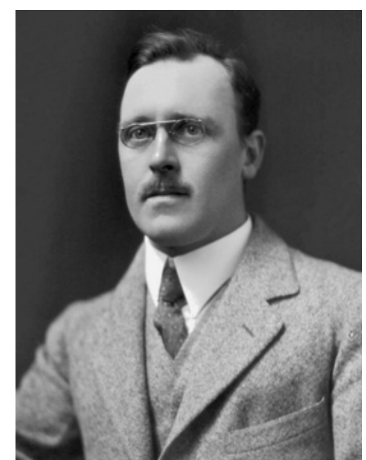
"Marsden has recalled how on train journeys his colleague Geiger would urge him not to put his head out of the window, lest a chance smoke particle should impair his efficiency as a human scintillation counter."

Discovery of atomic structure (Rutherford, 1911) was based on visual scintillation counting by Geiger and Marsden! (Geiger-Marsden experiment, 1909)

Geiger and Rutherford

Marsden



1. Theory and Practice of Scintillation Counting by Birks (1964)

Future

Reines and Cowan (1959) have used giant liquid scintillators to measure the cross-section for the absorption of anti-neutrinos by protons

$$\bar{\nu} + p \rightarrow e^{+} + n$$

Reines (1961) has discussed the possible use of giant liquid scintillators to increase the present known limit on the proton lifetime beyond 10^{26} yr...

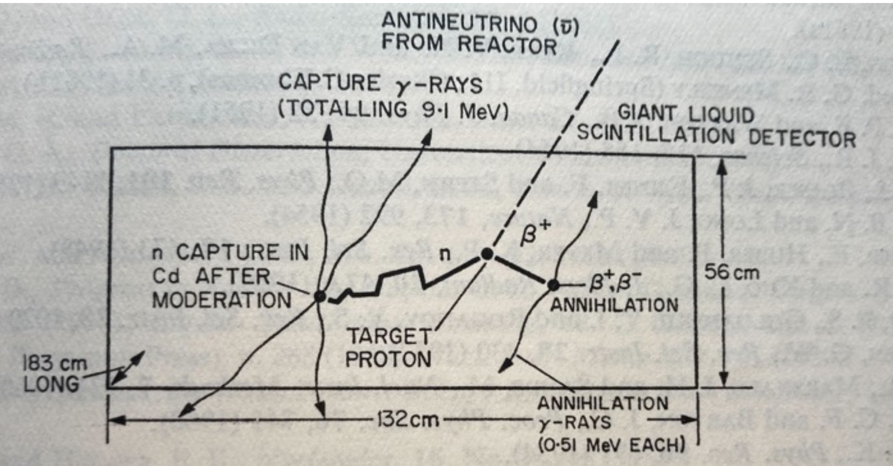
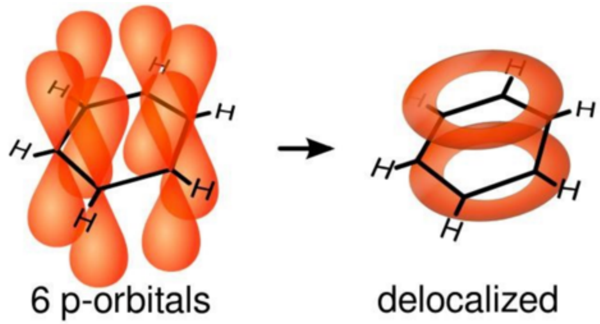


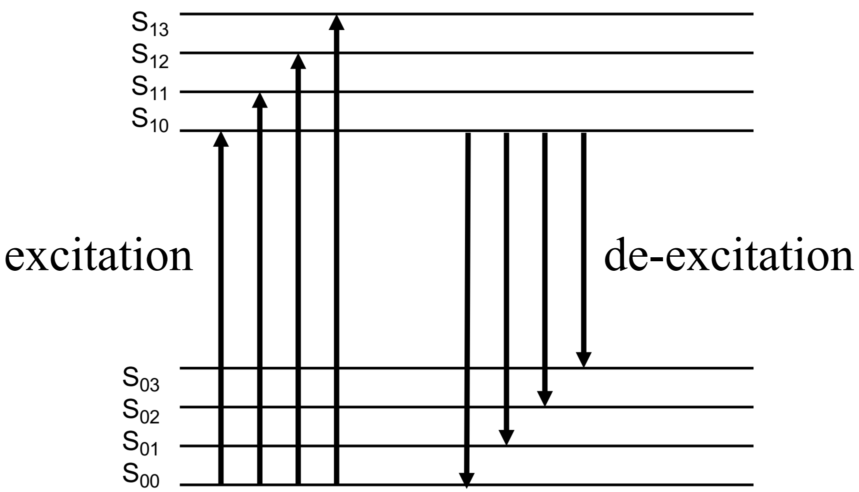
FIG. 10.20. Schematic of antineutrino detector (Reines and Cowan, 1959). The 1400 l. detector consists of triethylbenzene containing 3 g l^{-1} TP, 0·2 g l^{-1} POPOP, and 1·8 g l^{-1} cadmium, as cadmium octoate. An anti-neutrino is shown transmuting a proton to produce a neutron and positron. The positron slows down and annihilates, producing annihilation radiation. The neutron is moderated by the hydrogen of the scintillator and is captured by the cadmium, producing capture γ-rays.

1. Theory and Practice of Scintillation Counting by Birks (1964)

Types of scintillation
1. Organic scintillation
2. Inorganic scintillation
3. Gas scintillation



π-electron excitation
- Molecules with benzene ring (phenyl)
- Stokes shift to avoid self-absorption
- Higher excitation
- Internal conversion to triplet states



1. Theory and Practice of Scintillation Counting by Birks (1964)

Types of scintillation
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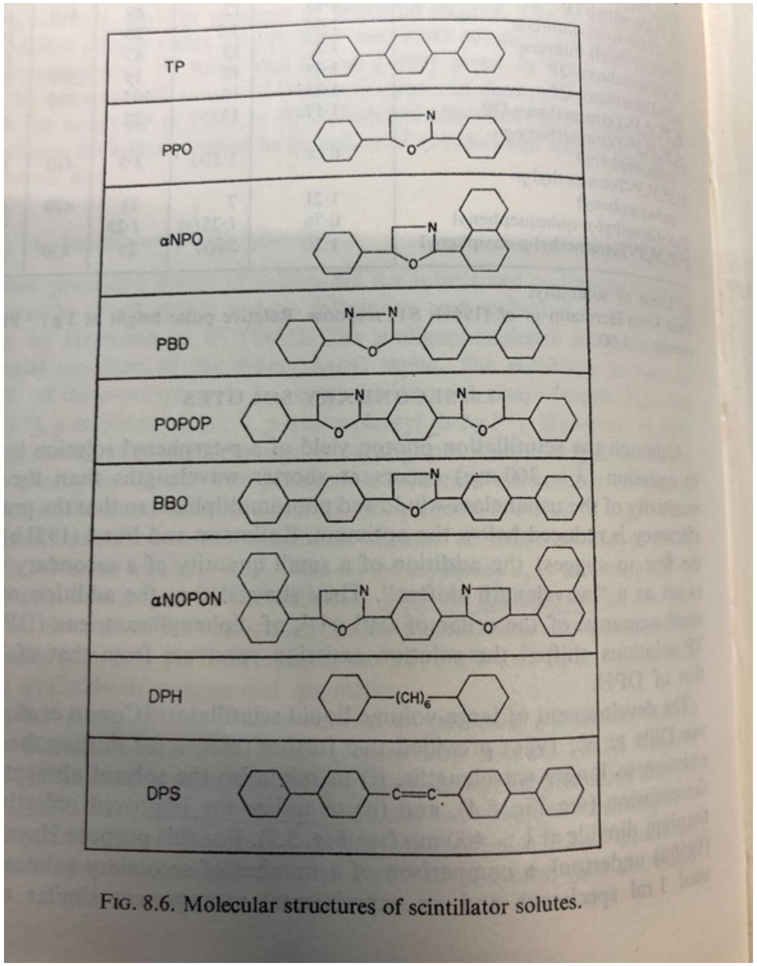
Discovery of oxazole (dioxazole) compound
- Solubility booster
- PPO, PBD, POPOP, etc

Discovery of POPOP
- minimum solvent absorption (~444 nm)
- match TiO_2 reflector
- Wavelength shifter for large scintillator



1. Theory and Practice of Scintillation Counting by Birks (1964)

Types of scintillation
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2. Inorganic scintillation
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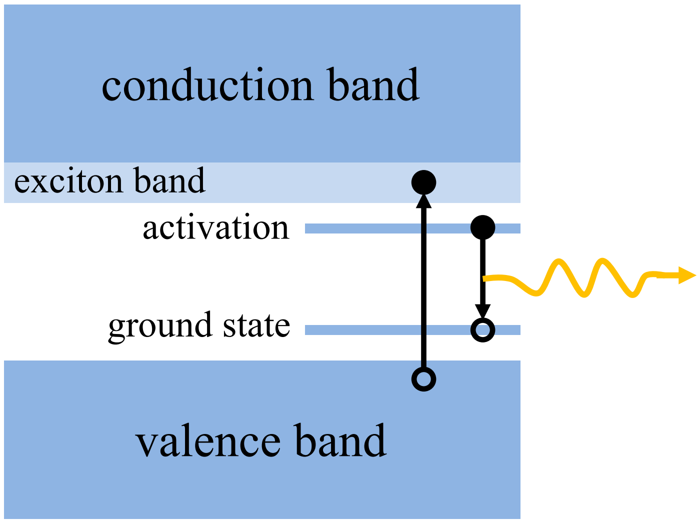
Crystal with energy band
- Production of exciton (electron-hole pair)
- De-excitation through activation state (impurity)
- No impurity in quantum dots



1. Theory and Practice of Scintillation Counting by Birks (1964)

Types of scintillation
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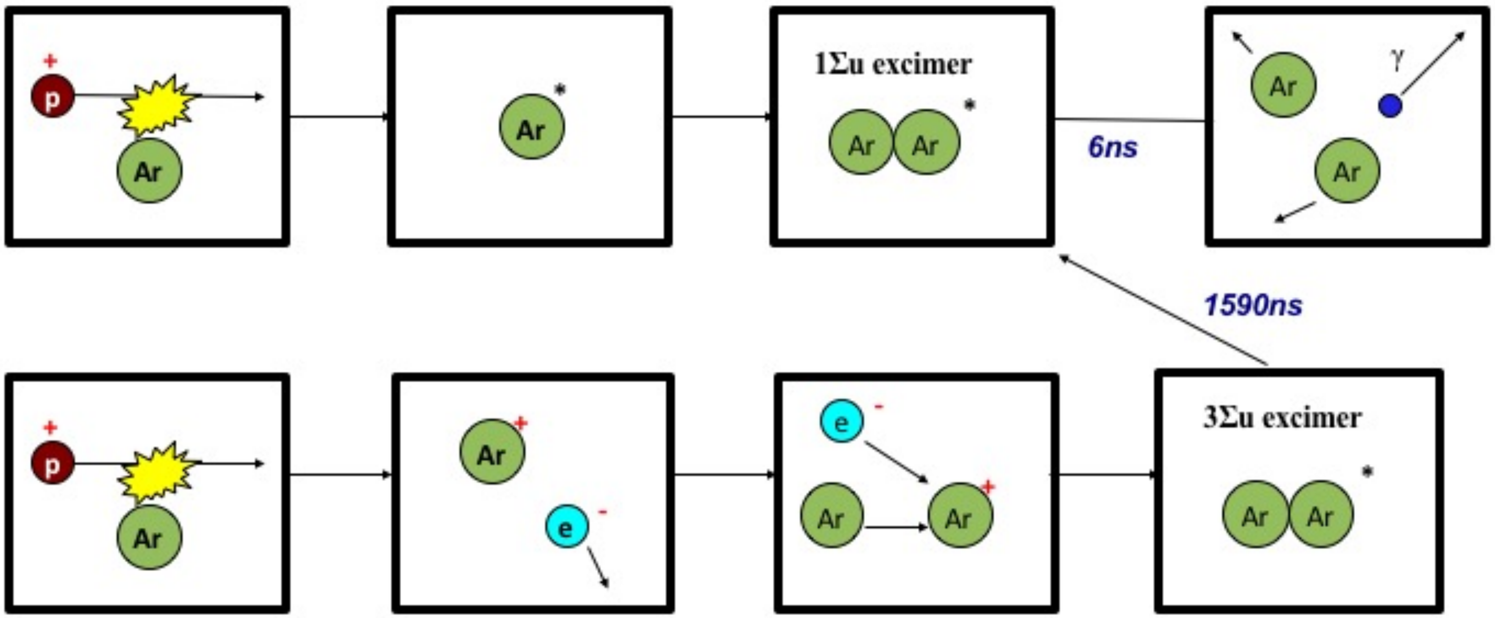
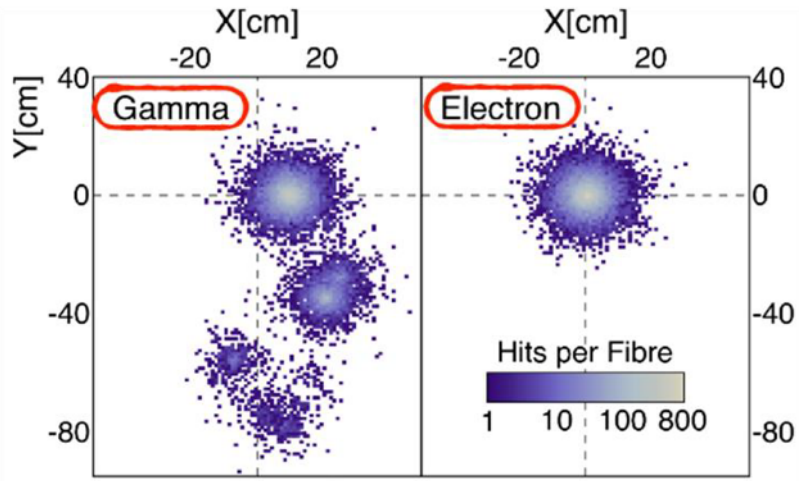
Excimer production
- Vacuum UV emission (<200 nm)

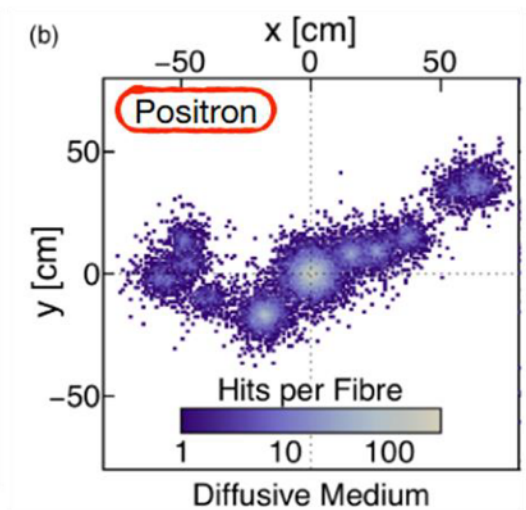


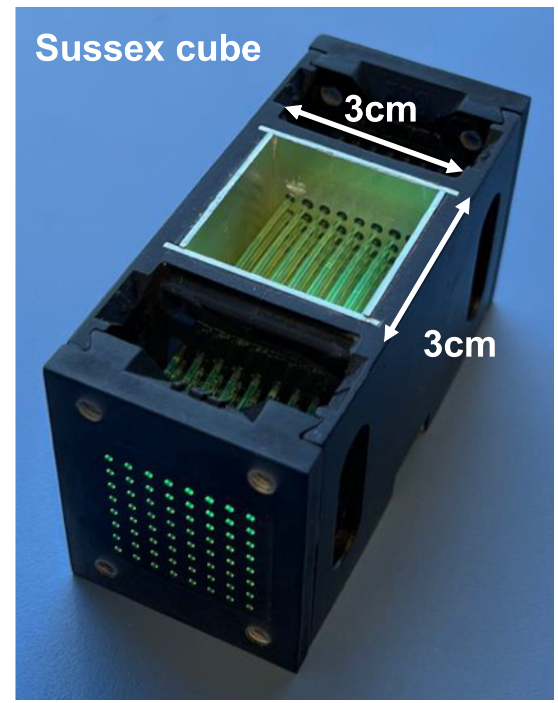
1. Modern liquid scintillators

DRD2 collaboration meeting
https://indico.cern.ch/event/1485254/
1. Opaque scintillator
2. Slow scintillator
3. Gd-doped scintillator
4. Water-based liquid scintillator

Confine light locally by scatter
- maintain long absorption length







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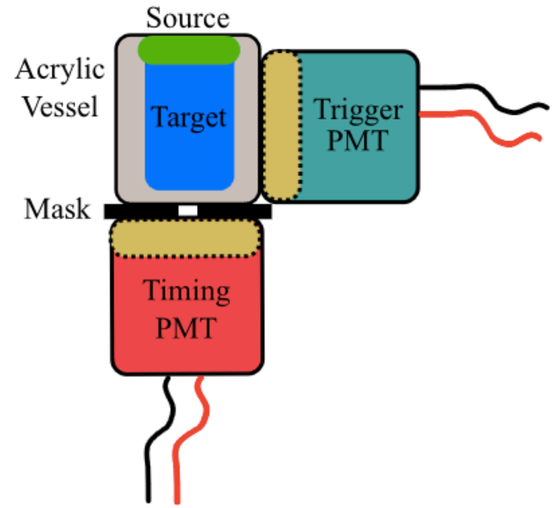
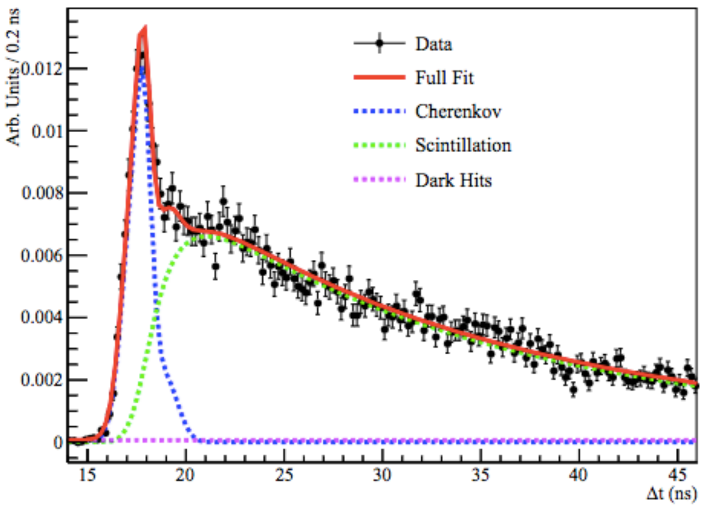
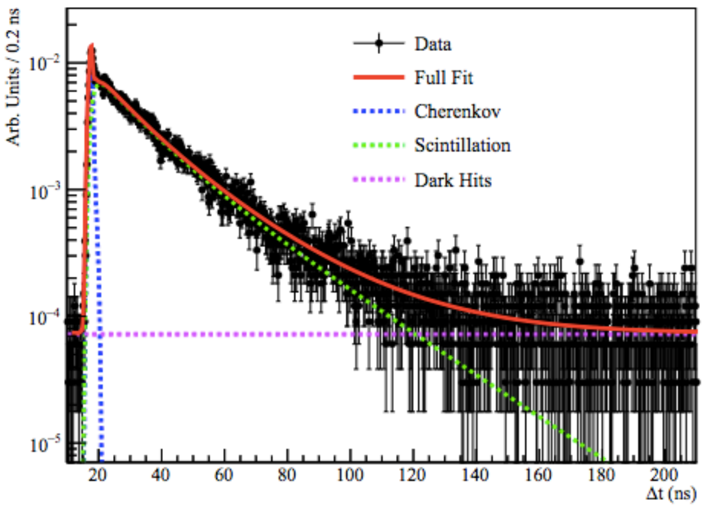
Cherenkov – Scintillation separation
- Low fluor concentration
- Slow fluors
- Multi-solvent



90% LAB + 10% DIN + 1.0g/L PPO





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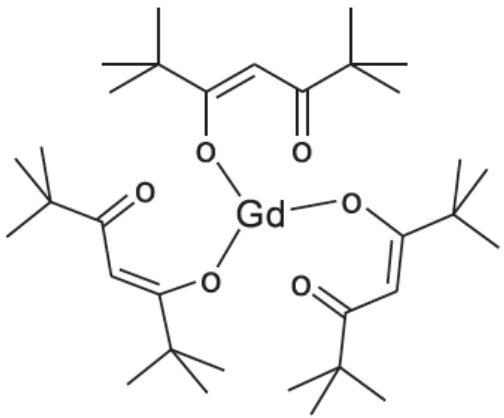
Gd neutron capture ($Gd + n \rightarrow Gd^* + 8\ MeV$)
- Ligand (surfactant) is required for organic solvent
- Gd ion in water



Scheme 1. The chemical structure of Gd(TMHD)$_3$.

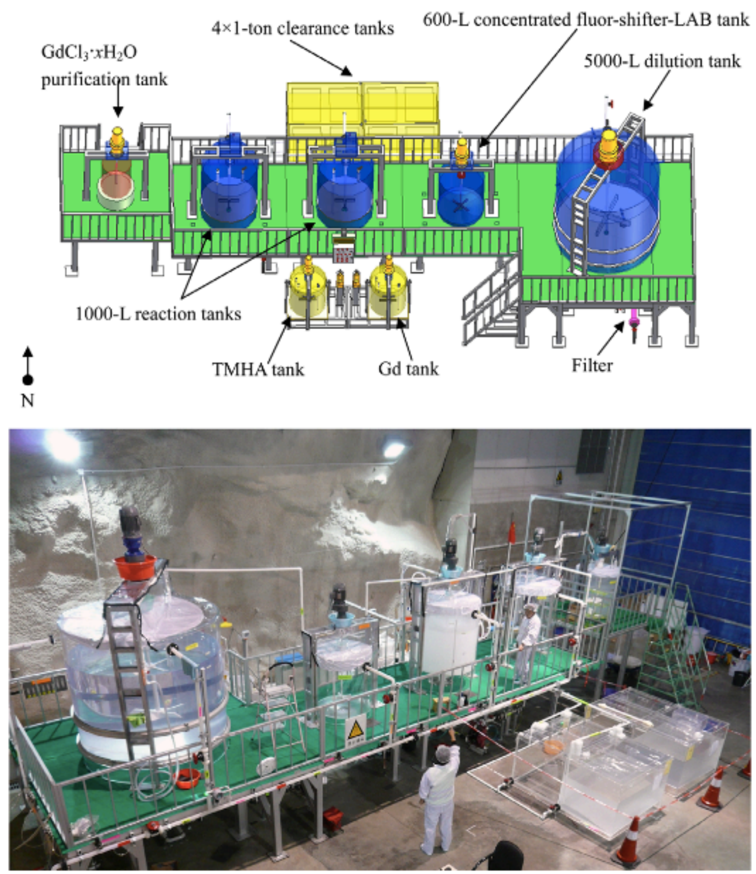


Fig. 1. (a) Three-dimensional diagram (south to north) and (b) photograph of the operation of the production system for liquid scintillators (north to south).

1. Modern liquid scintillators

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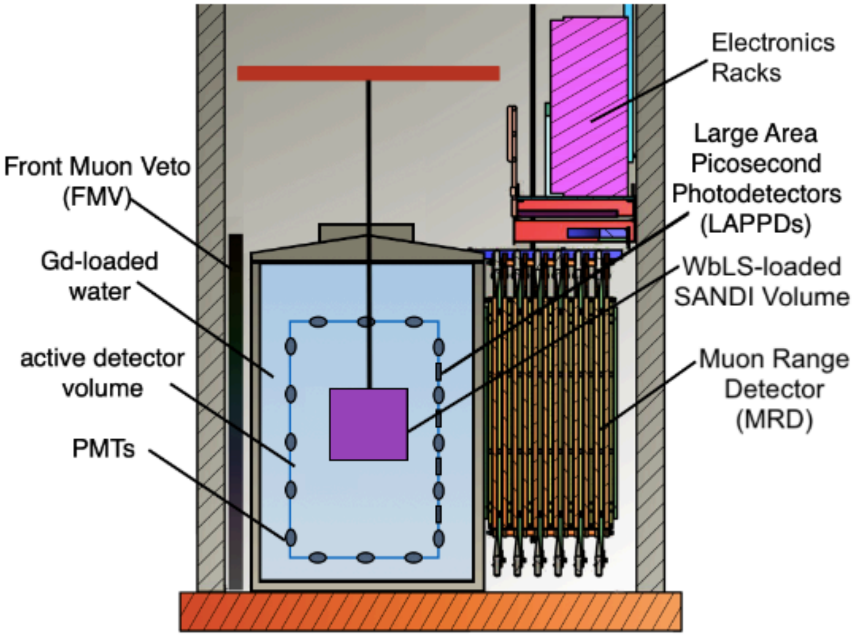
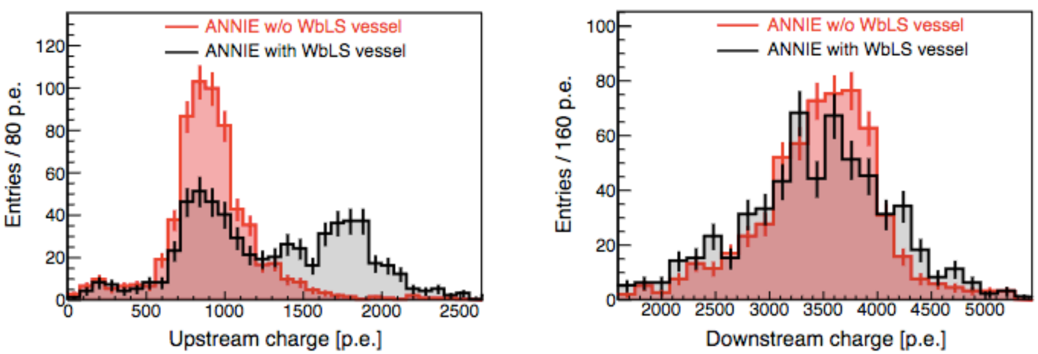
Water solvent
- Safe, cheap
- Water Cherenkov detector application
- Organic fluors need ligand





(a) (b)

Yeh et al., NIMA660 (2011) 51, *ANNIE, JINST19 (2024) P05070*

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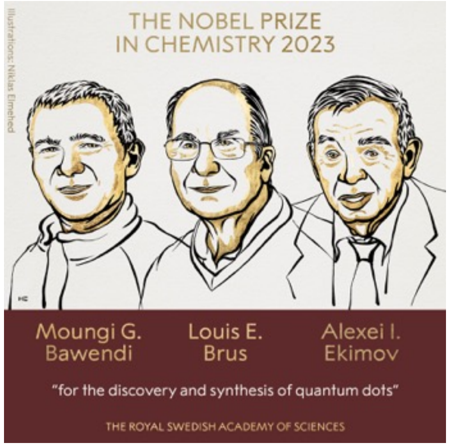
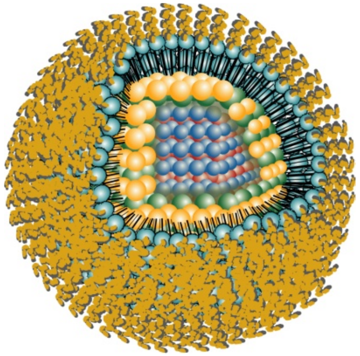


Noble prize in Chemistry (2023)

Nano-crystals are emerging technology, and they are potential new scintillator with many advantages
- Possible to do all of above
- Tunable absorption and emission spectrum
- Change chemical properties easily by adding more layers



1. Introduction

2. Quantum Dots

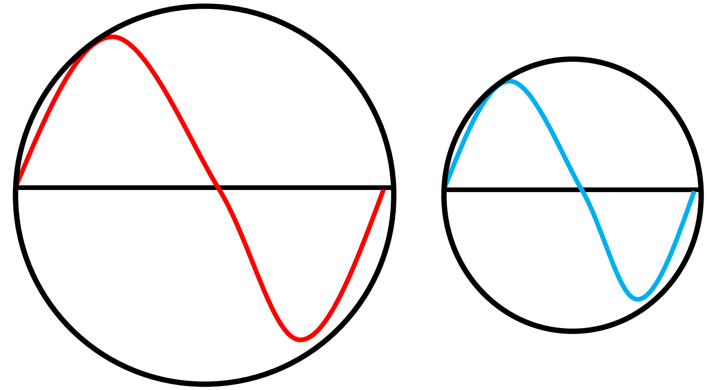
3. Optical measurements

4. Cosmic ray test

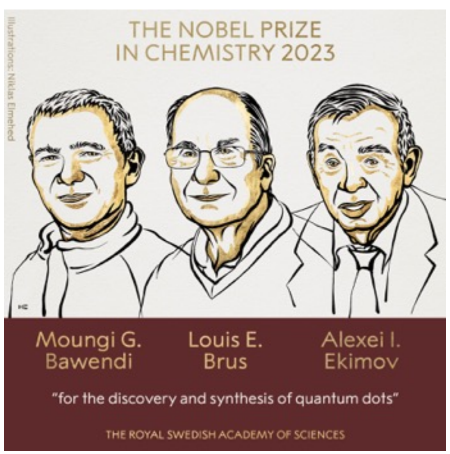
5. Next step

2. Quantum Dots

Semiconductor nano-particle
- Smaller than exciton radius (quantum confinement)



Quantum confinement
- Exciton (~10nm) > quantum dot size
- Discrete, wider gap (Brus equation)



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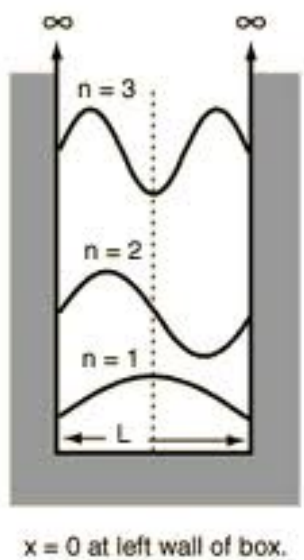
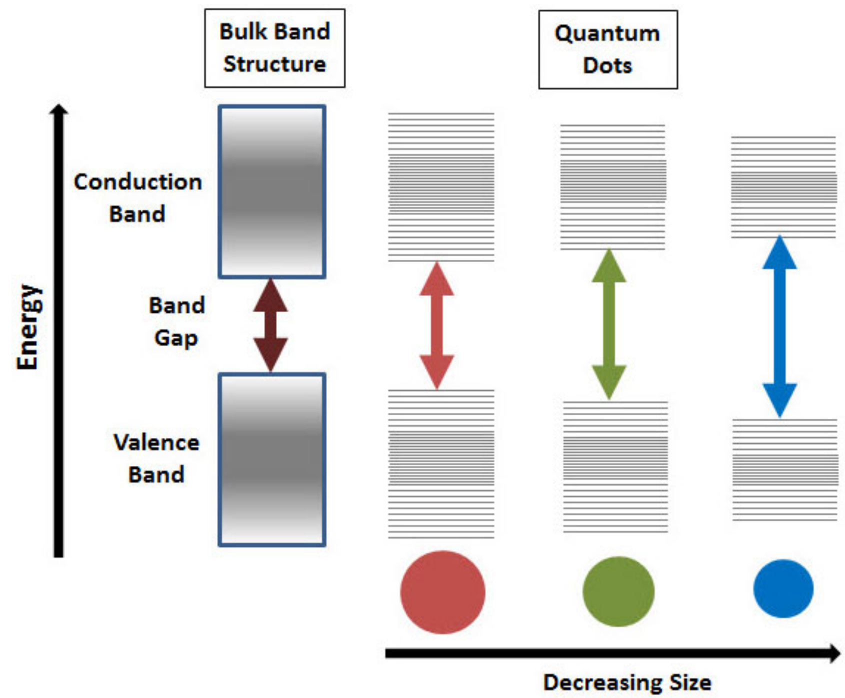
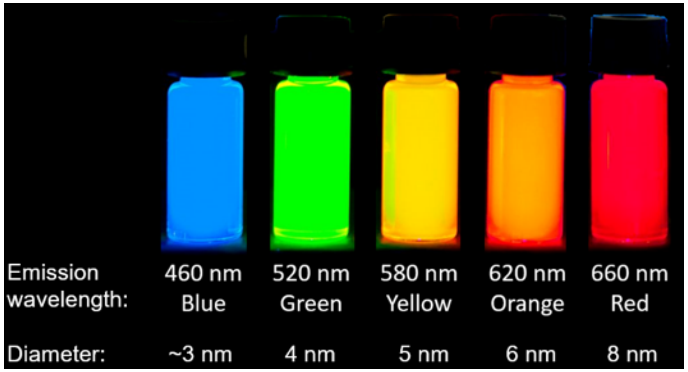




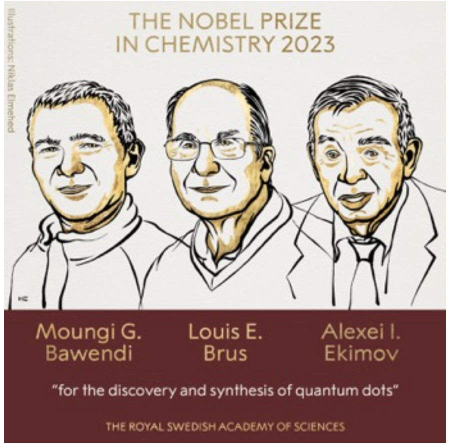
2. Quantum Dots

Semiconductor nano-particle

- Smaller than exciton radius (quantum confinement)
- ~2 – 10 nm, UV to infrared emission
- Tunable sharp emission spectrum
- Large category of choices (core type, size)
- High quantum yield (~50%)



CdSe core QDs with CdS/ZnS shell
https://www.lateralflows.com/quantum-dots/



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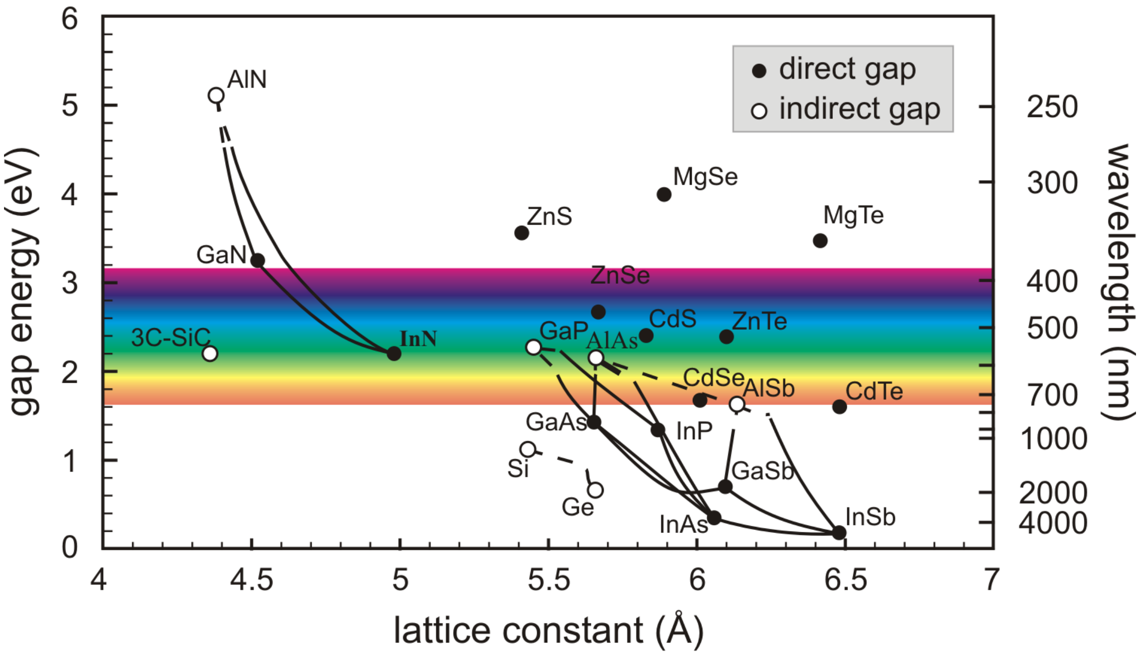
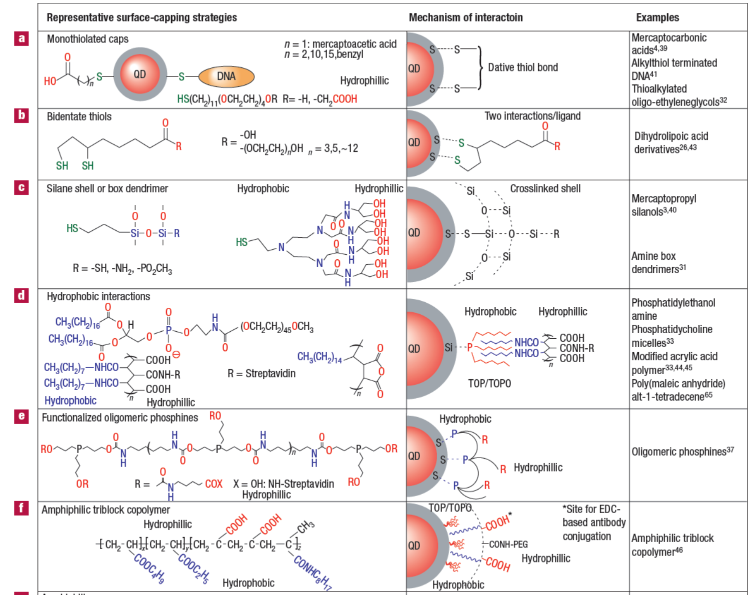


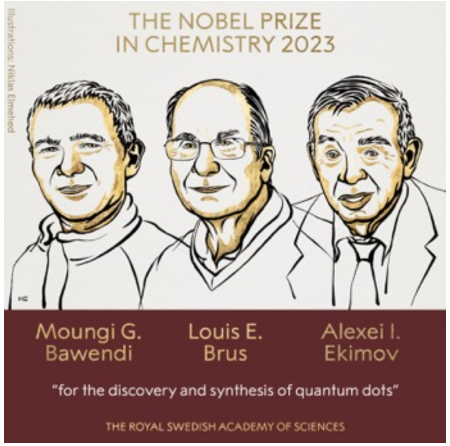
2. Quantum Dots



Semiconductor nano-particle

- Smaller than exciton radius (quantum confinement)
- ~2 – 10 nm, UV to infrared emission
- Tunable sharp emission spectrum
- Large category of choices (core type, size)
- High quantum yield (~50%)

- Surface layer engineering to change properties
  - Stability
  - Water solution



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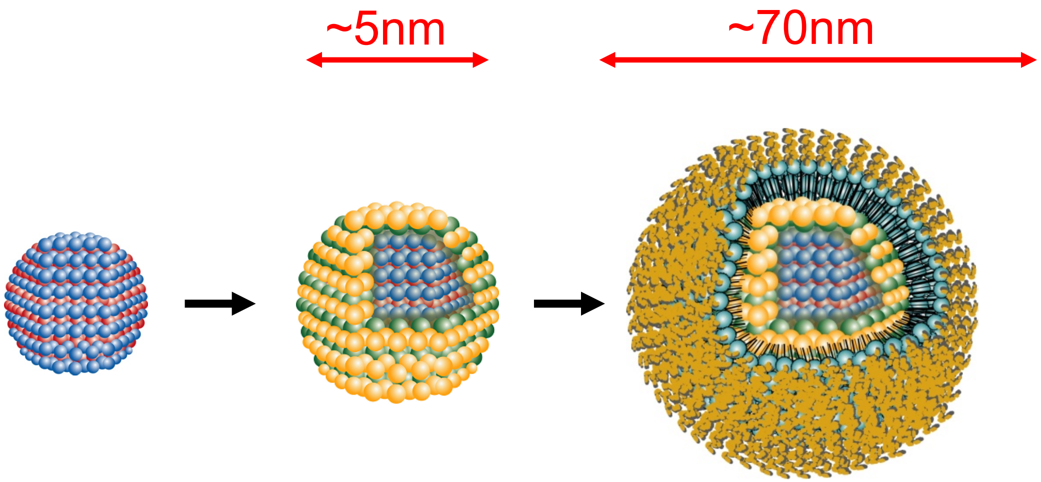
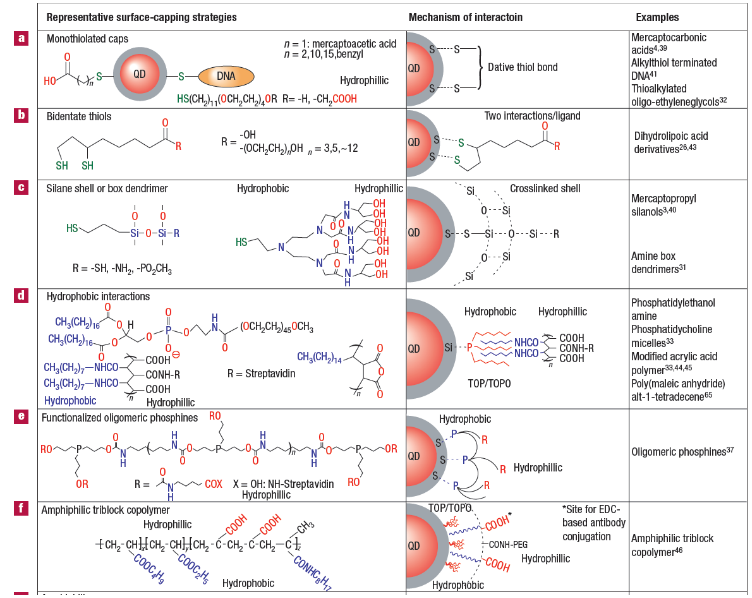


Quantum dot core (fragile) | QD with shell (stable) | QD with shell and ligand (collide)

2. Quantum Dots



Semiconductor nano-particle

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- ~2 – 10 nm, UV to infrared emission
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- Large category of choices (core type, size)
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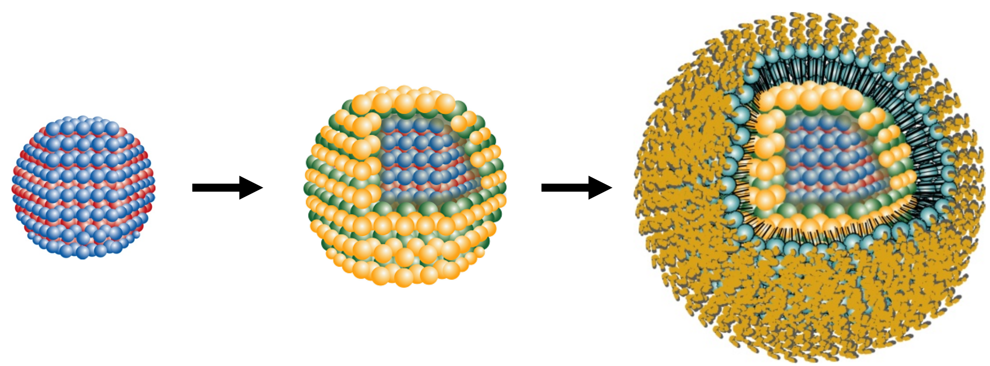
- Surface layer engineering to change properties
  - Stability
  - Water solution

~5nm ~70nm



Cons:

- often toxic
- expensive

Quantum dot core (fragile) QD with shell (stable) QD with shell and ligand (collide)

2. Quantum Dots

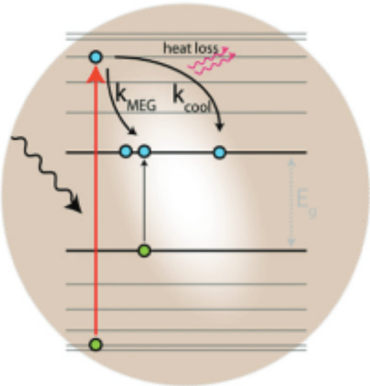
Display
- Tunable, sharp emission

Solar cell
- Multiple exciton generation

Biometric marker
- Water soluble
- Infrared
- Single molecular tracking

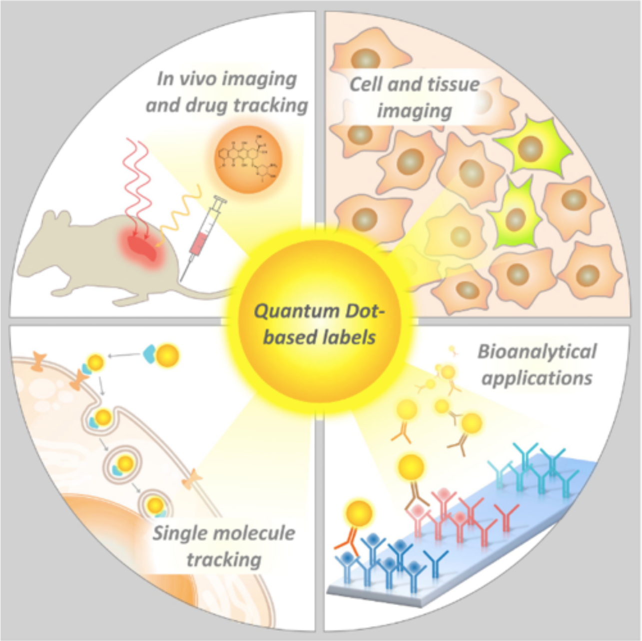
Quantum computer
- Spin qubit quantum computer

etc



Energ. Environ. Sci. 13 (2020) 1347

Samsung QLED smart TV

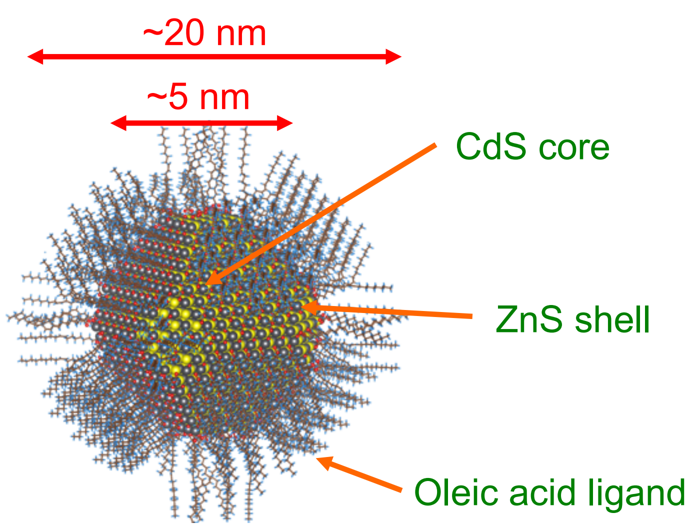


ChemBioChem 17 (2016) 2103

2. Quantum Dots

Requirement
1. High emission (quantum yield ~ 50%) ✅
2. Stability (company value, 3 yr) ✅
3. Emission (> 450nm) ⚠️
4. Affordable ❌

Cadmium sulfide (CdS) core zinc sulfide (ZnS) shell type coating quantum dots
- High emission at short wavelength (460 nm)
- Neutron capture target
- Double beta decay target

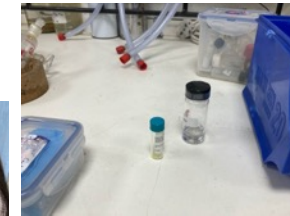


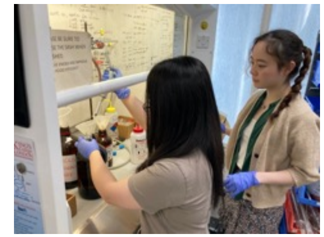
Concentration is chosen so that Cd ~ 0.01% by mass
- Potential neutron capture application

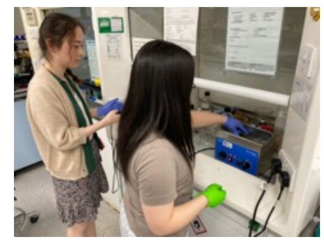
10mg CdS-ZnS ~ £300
- ~100 mL WbLS (1 ton detector ~ £3M)
- Concentration vs emission needs R&D

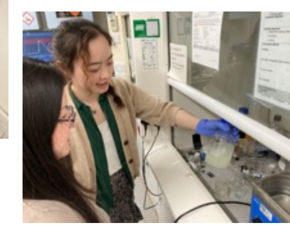
https://dx.doi.org/10.1021/acsomega.7b00316

2. Phase transfer



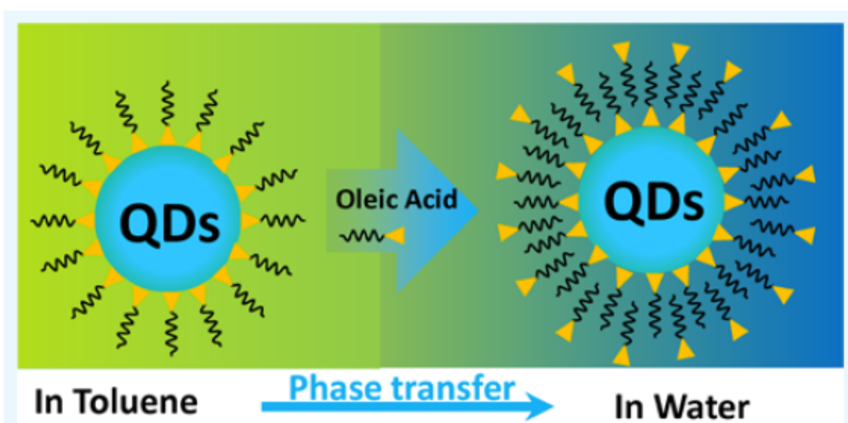


Chemistry is complicated

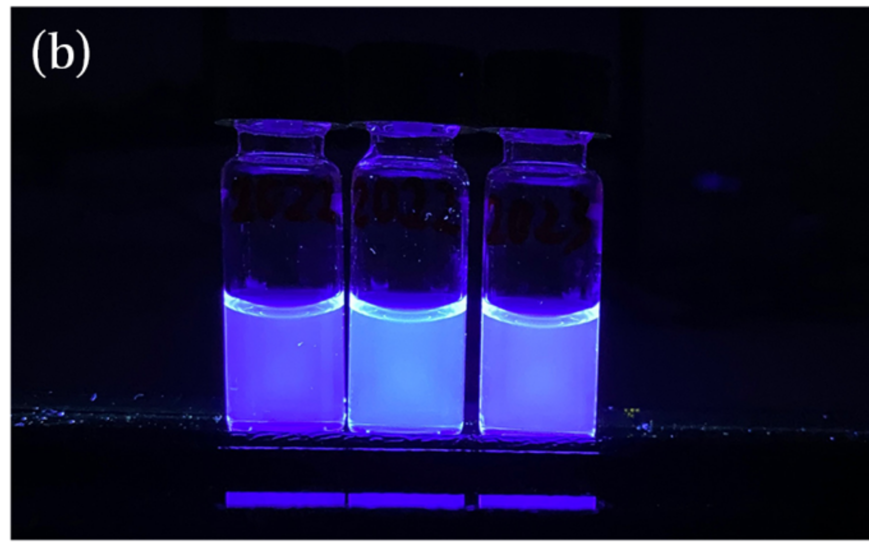
How to make water-based quantum dot solution

1. Dissolve CdS-ZnS QDs (10mg) in toluene
2. Evaporate toluene
3. Add hexane, sonic bath 1min
4. Add oleic acid
5. Add water
6. Sonic bath
7. Shake
8. Sonic bath, shake ... (1hr)
9. Leave in dark 24 hours



2. Water-based quantum dots liquid scintillator

We made 3 water-based QDs sample
- 2021, 2022, 2023
- Optical measurements are based on 2023 sample in 2023
- Cosmic ray test is based on 2022 sample in 2022
- 2022 and 2021 samples are also used to study ageing



1. Introduction

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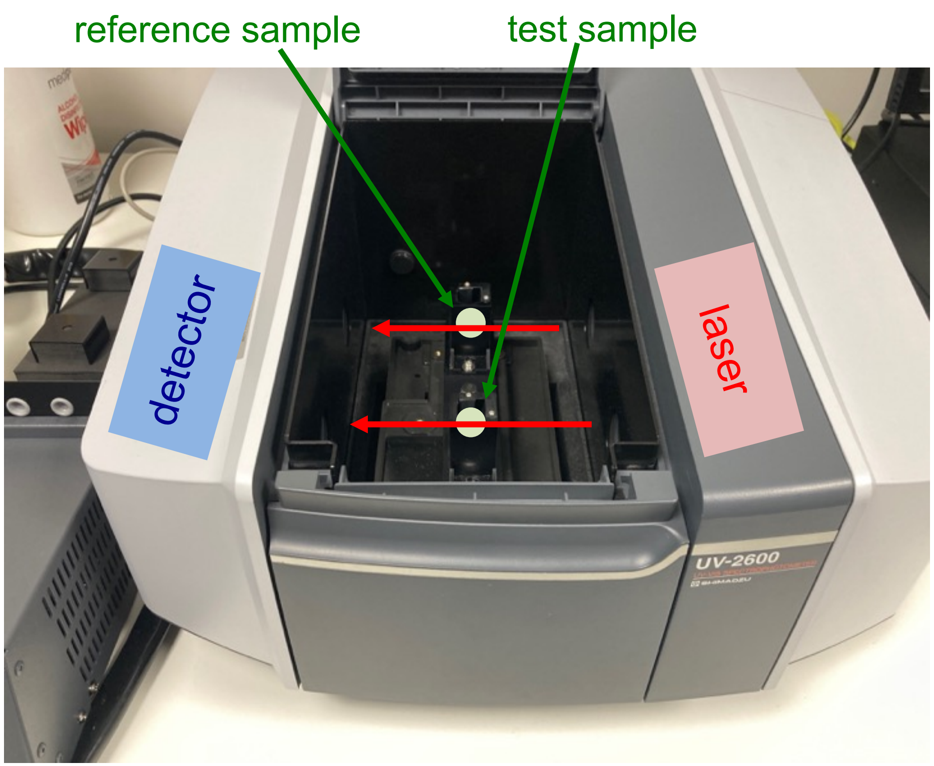
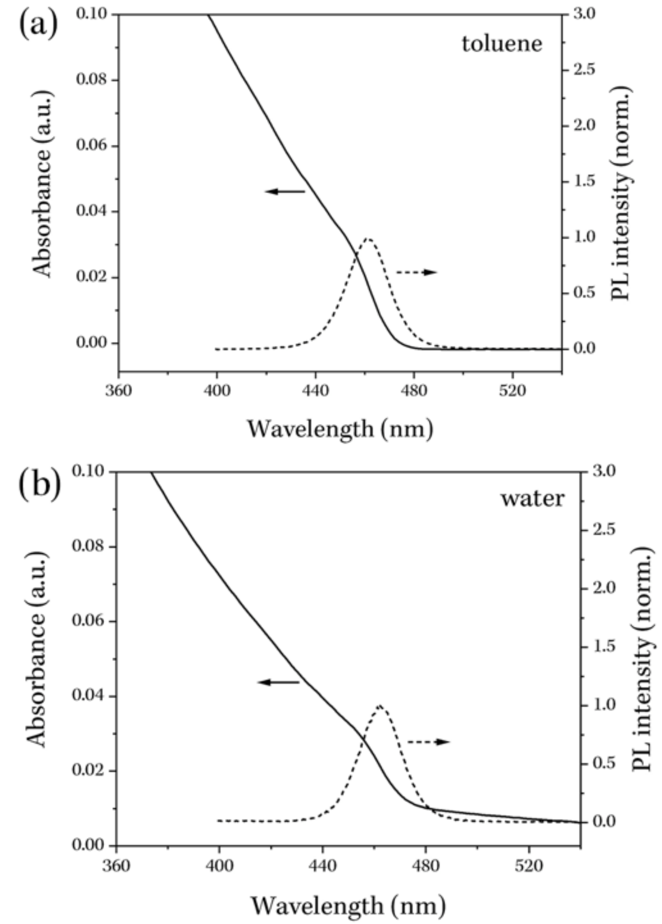
5. Next step

3. Absorbance measurement

Shimadzu UV-2600i spectrometer

- toluene QDs and water QDs show the same absorption peak (~460nm)
- No significance change of QD core by phase transfer





3. Fluorescence measurement

Agilent Technologies Cary Eclipse Fluorescence Spectrometer
- toluene QDs and water QDs show the same emission peak
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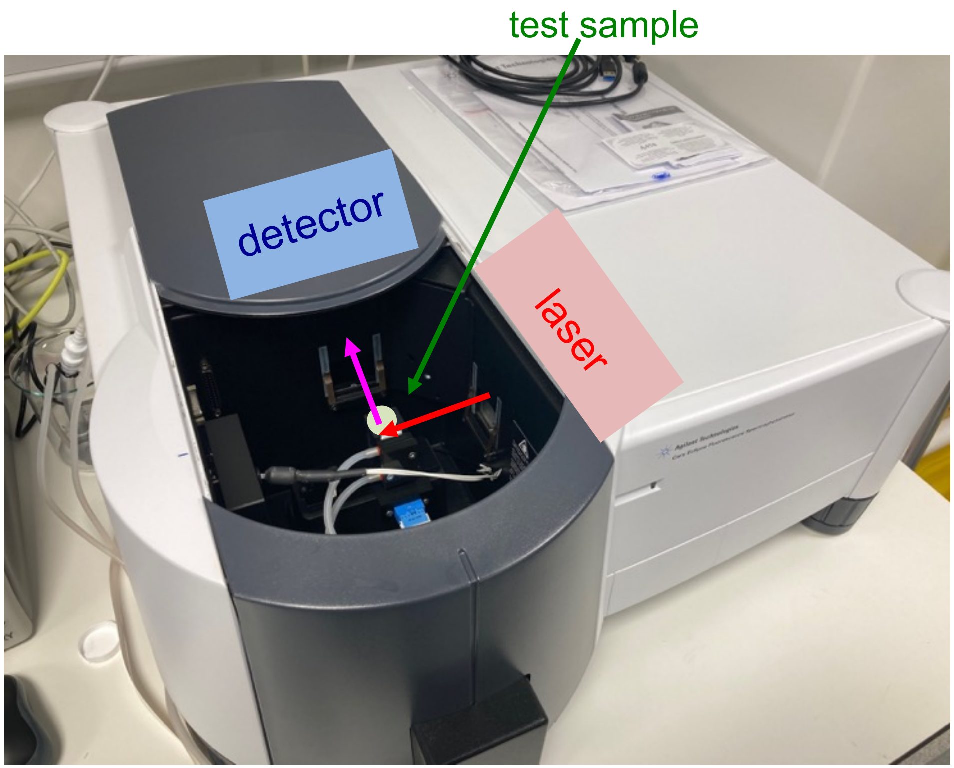

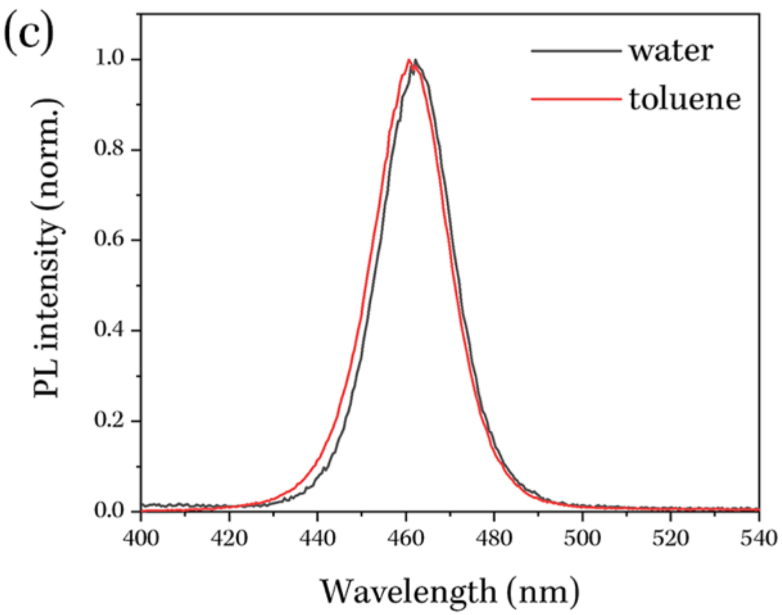

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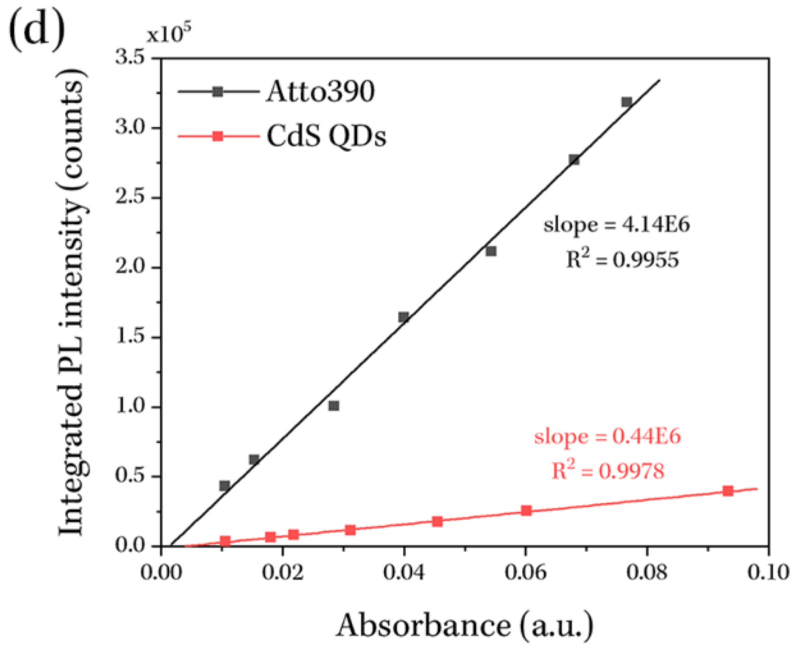
Photoluminescence quantum yield (PLQY)

$$I(A) = I_o + K \cdot A$$

- Integrated PL intensity is a linear function of absorbance. Both integrated PL intensity and absorbance are measured with different concentration of the sample
- Obtained slope "K" is compared with the reference dye Atto390
- Measured PLQY is lower than the company value (~50%) suggesting the phase transfer lose some PLQY



PLQY = 9.5±0.5%

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PLQY = 9.5±0.5%

Extinction peak

$$A(\lambda) = A_0 + A_{max} \cdot exp\left[-0.5\left(\frac{\lambda - \lambda_c}{w}\right)^2\right]$$

Empirical law with extinction peak
- mean QD diameter D

$D_{Empirical} = 5.22\pm0.01$ nm

- concentration C

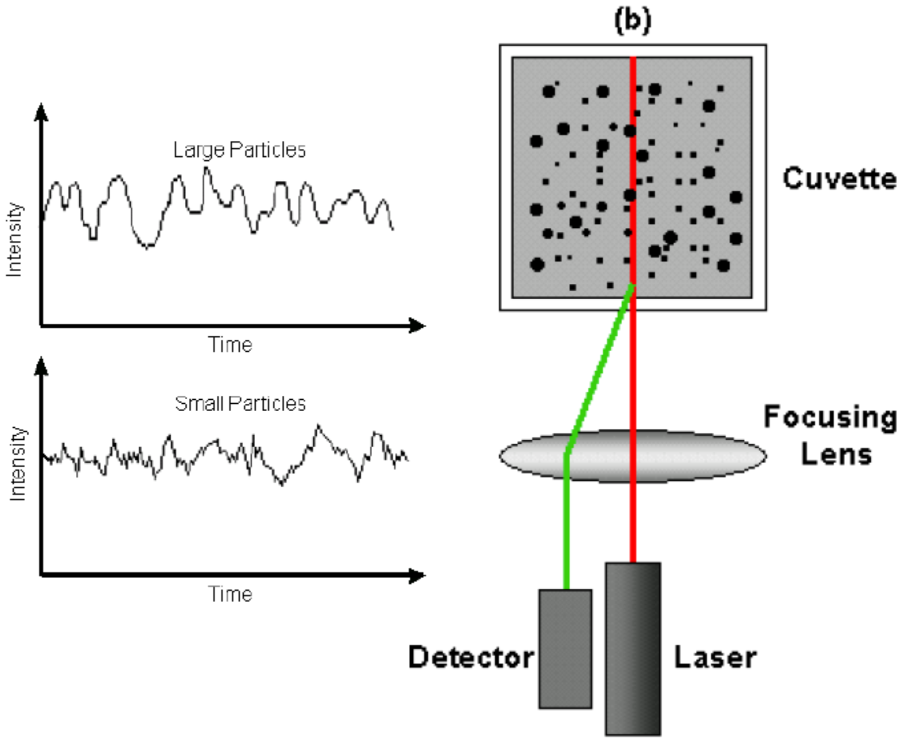
C = 42±1 nM

Typical organic scintillator (20% PPO)
- concentration ~ 4-30 mM
- cross-section area ~ 0.5-1nm^2

3. Dynamic light scattering (DLS) measurement

Malvern instruments Zetasizer Nano

- Measure the size of QDs from the back-scatted light
- Brownian motion gives time-dependent data



https://www.malvernpanalytical.com/en/products/technology/light-scattering/dynamic-light-scattering

3. Dynamic light scattering (DLS) measurement

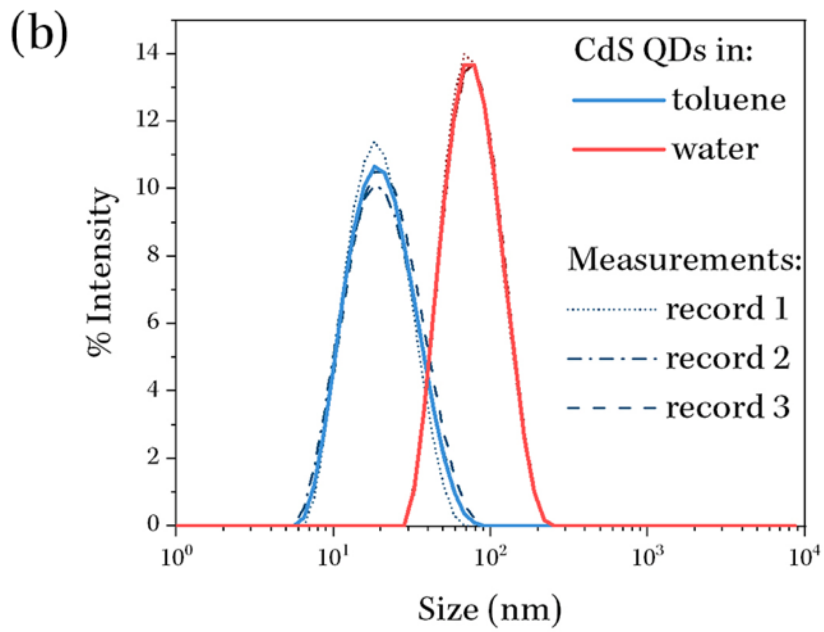
Malvern instruments Zetasizer Nano
- Measure the size of QDs from the back-scatted light
- Brownian motion gives time-dependent data

Hydrodynamic diameter d_H

$$D_H = \frac{k_B T}{3\pi\eta D}$$

- Correlation function to extract average hydrodynamic diameter of QDs
- Phase transfer adds oleic acid hydrophilic layer to the QDs
- Interesting to check the result by other method to measure the QD size

$D_H^{Toluene} = 25 \pm 9$ nm
$D_H^{Water} = 71.6 \pm 0.3$ nm



3. SEM, AFM, TEM

Scanning electron microscope (SEM)

- Sample is dried
- Gold is vacuum evaporated to make it conductive
- Not sensitive to QD size (~20nm)

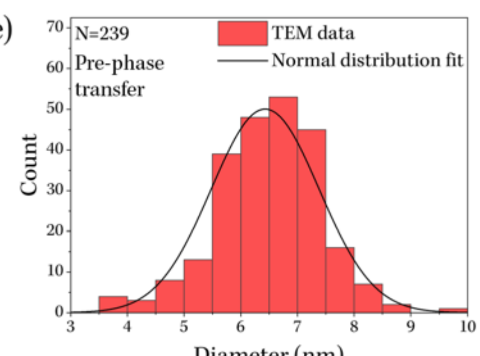
Atomic force microscope (AFM)

- Sample is dried
- Not sensitive to X-Y because of large tip
- Z measurement may be good?

Transmission electron microscope (TEM)

$$D_{TEM}^{Toluene} = 6.4 \pm 1.0 \text{ nm}$$
$$D_{TEM}^{Water} = 6{,}4 \pm 1.2 \text{ nm}$$

(e)



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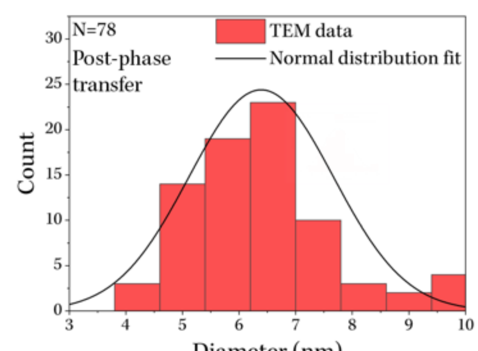
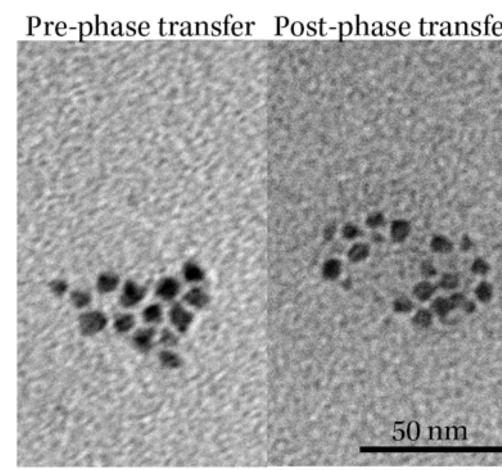


Scanning electron microscope (SEM)

Atomic force microscope (AFM)

(d)



TEM image

3. Ageing

Sample		PLQY (%)	D_h (nm)	ζ (mV)
2021 WbQD	as prepared	15.6 ± 1.2	52.2 ± 0.3	not available
	in 2023	8.8 ± 0.8	48.7 ± 0.1	−13.8 ± 0.8
2022 WbQD	as prepared	8.8 ± 1.5	60 ± 1	−24 ± 2
	in 2023	14.5 ± 0.7	55.7 ± 0.3	−47 ± 2
2023 WbQD	as prepared	9.5 ± 0.5	71.6 ± 0.3	−24.6 ± 0.7

Absorbance and fluorescence

- No change over the period of 3 years

Size

- Slight decrease of the size (a few nm)
- Likely not losing layers, but re-organization of surface structure
- Zeta potential (surface charge) is changing over time, supporting this interpretation
- No sign of agglomeration

Photoluminescence quantum yield (PLQY)

- Large sample variation makes difficult to conclude

It seems water QDs are stable, but without ageing information of PLQY it's hard to say if they are suitable for particle detectors (~several years operation)

1. Introduction

2. Quantum Dots

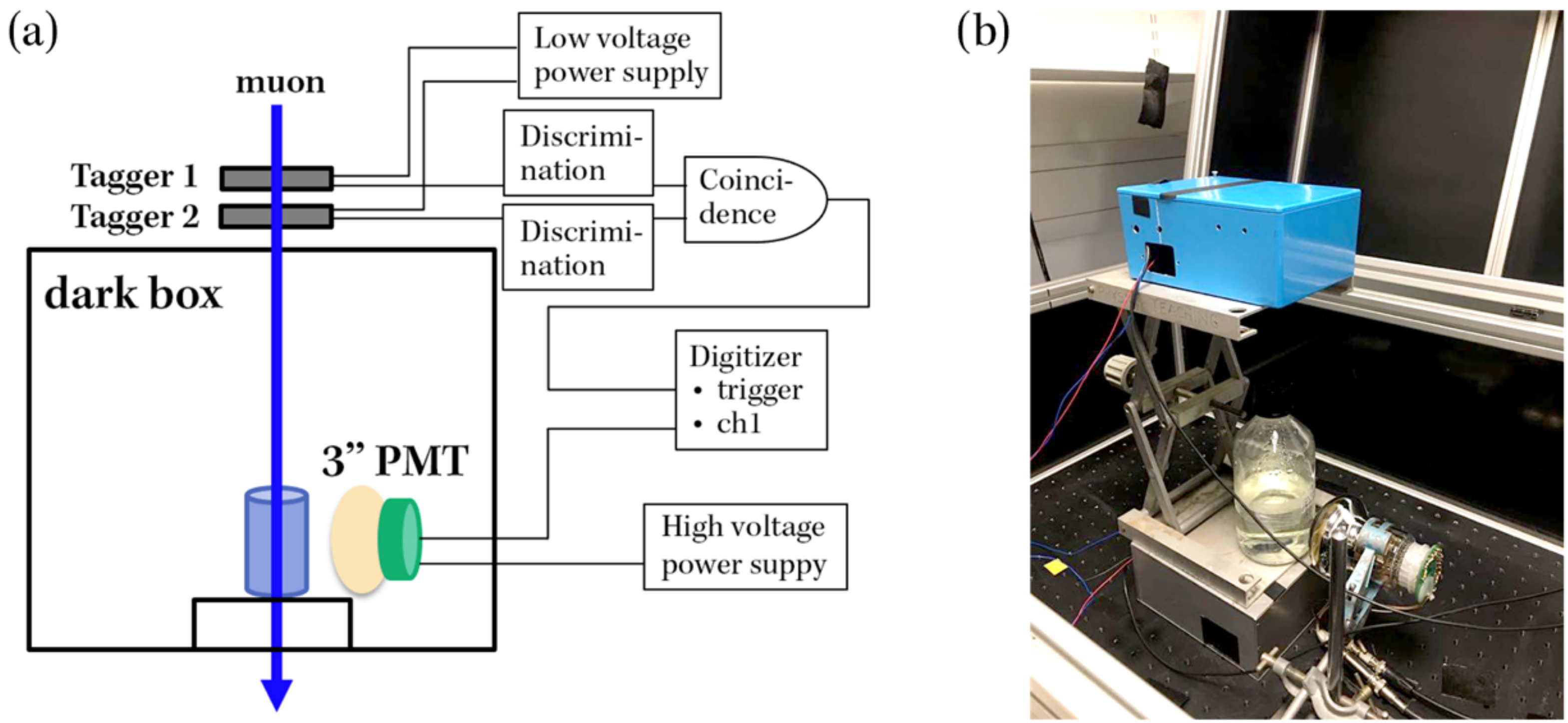
3. Optical measurements

4. Cosmic ray test

5. Next step

4. Cosmic ray test

Set up
- Cosmic ray triggers (plastic scintillator + SiPM)
- 3-inch NNVT PMT
- CAEN 250MS/s digitizer



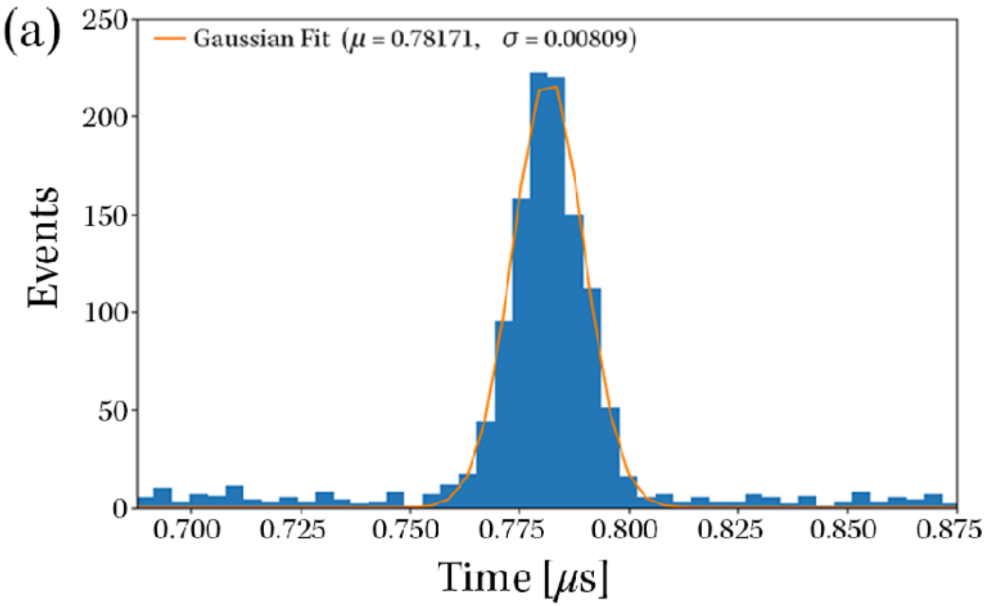
3. Cosmic ray test

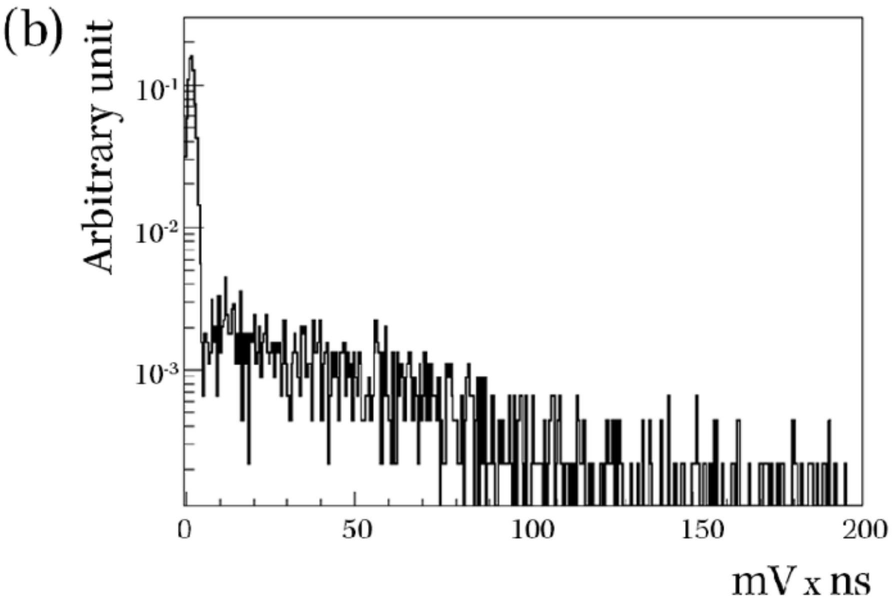
Timing data

- Quantum dots decay time is around 5ns
- Too fast to measure by 250MS/s (4ns bin) digitizer (τ < 8ns)

Charge data

- Need simulation to extract information

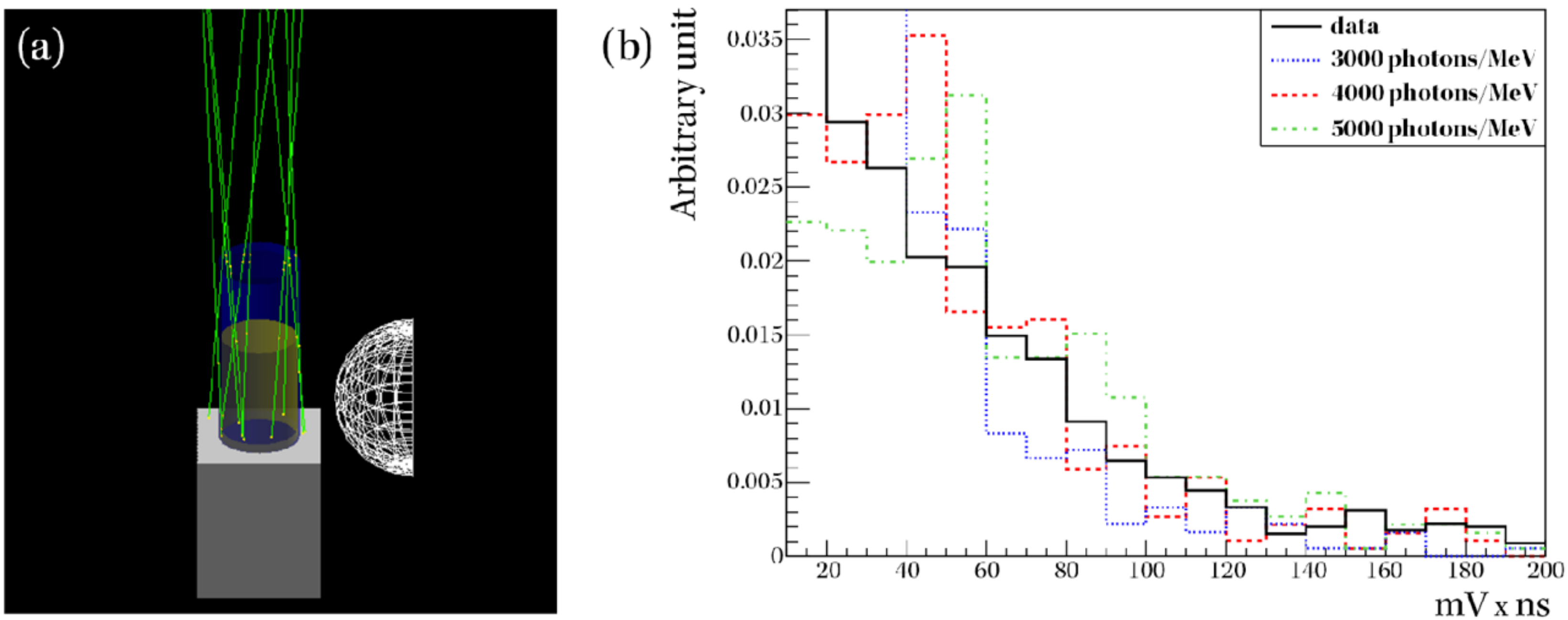




3. Cosmic ray test

Data-Simulation comparison

- Geant4-based simulation
- Simulation is adjusted to match the tail of the charge distribution
- Data seems to have several 1000s photons / MeV
- Comparable emission strength with modern organic scintillator



1. Introduction

2. Quantum Dots

3. Optical measurements

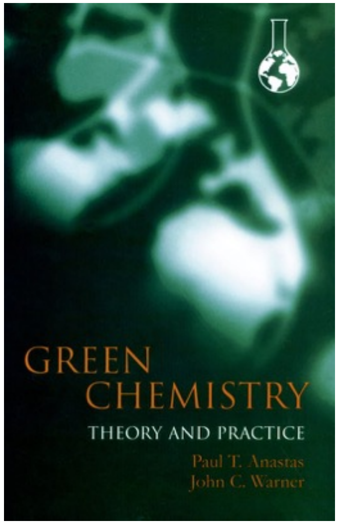
4. Cosmic ray test

5. Next step

5. Next step

Nanocrystal water liquid scintillator works, but...
- 1L WbQDLS~£3k → ~£3M for 1 ton detector, £3B for 1 kton detector
- water is safe, but many nanocrystals are not safe

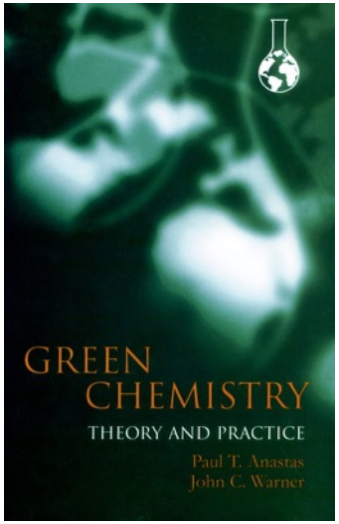
Future: Sustainable nanocrystal water liquid scintillator
- no heavy metal: cheap, safe, Cd, Te, ... → B, C, ...
- environment-friendly: green synthesis, recyclable



5. Sustainable quantum dots liquid scintillator

Nanocrystal water liquid scintillator works, but...

- 1L WbQDLS~£3k → ~£3M for 1 ton detector, £3B for 1 kton detector
- water is safe, but many nanocrystals are not safe



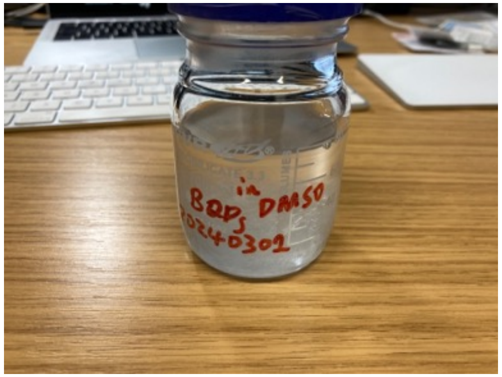
Future: Sustainable nanocrystal water liquid scintillator

- no heavy metal: cheap, safe, Cd, Te, ... → B, C, ...
- environment-friendly: green synthesis, recyclable

Boron QD

- Affordable, safe element ✅
- Neutron tagging ✅
- Commercially not available ❌

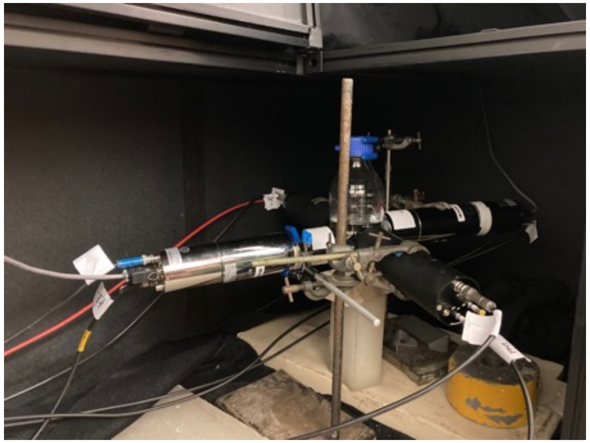
Boron QD sample

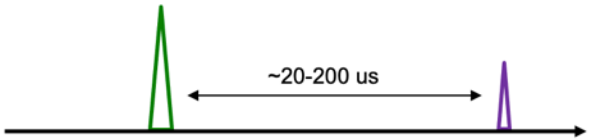


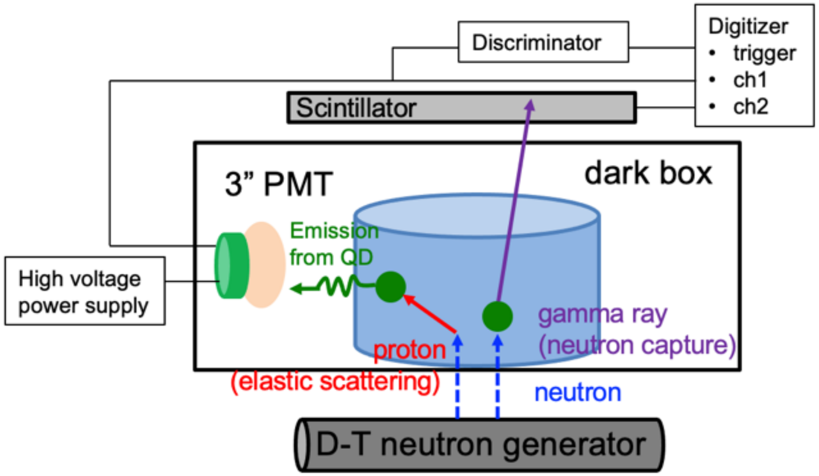
5. Neutron tagging quantum dots liquid scintillator

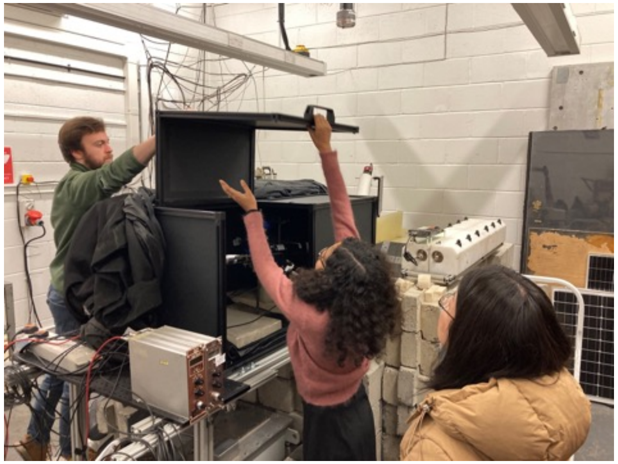
Sheffield fast pulse D-T generator
- ~16 us fast pulse
- Expected neutron lifetime ~ 100-200 us

Backgrounds are the issue
- Suppress ambient neutrons
- Tag neutron signal in a better way









5. Opaque quantum dots liquid scintillator?

TiO_2 engineering

- Scintillator reflector
- Important for biology application
- TiO_2 can be attached to quantum dots
- TiO_2 colloid can be added in water
- TiO2 layer on quantum dots?

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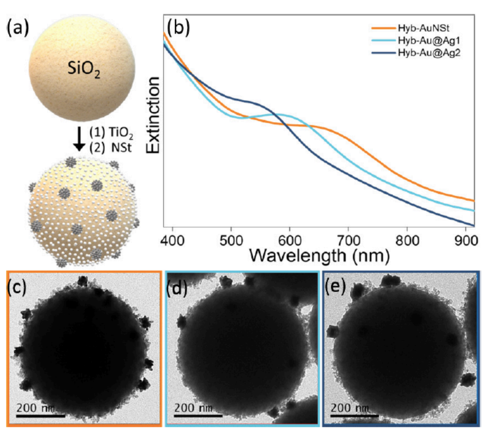
Unveiling multimodal hot carrier excitation in plasmonic bimetallic Au@Ag nanostars for photochemistry and SERS sensing

Yoel Negrín-Montecelo[1,§], Amir Elsaidy[2,§], Jesús Giráldez-Martínez[3], Enrique Carbó-Argibay[4], Zhiming Wang[5], Alexander O. Govorov[6], Ramon A. Alvarez-Puebla[1,7], Miguel A. Correa-Duarte[3,8], and Lucas V. Besteiro[3]



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Anisotropic Plasmonic CuS Nanocrystals as a Natural Electronic Material with Hyperbolic Optical Dispersion

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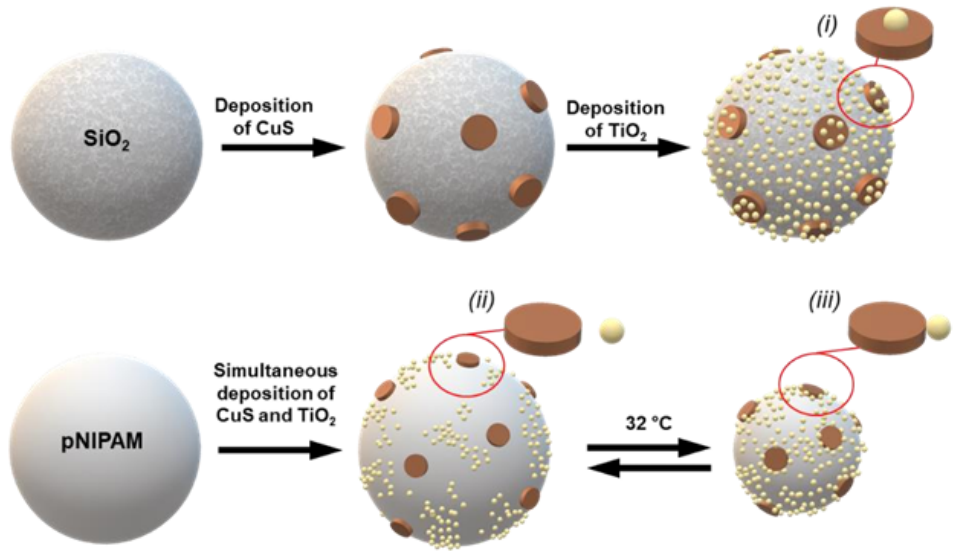
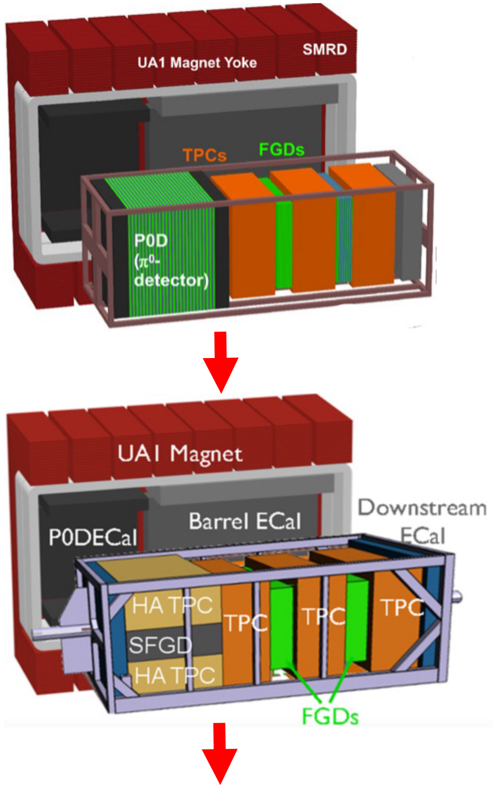


5. ND280++

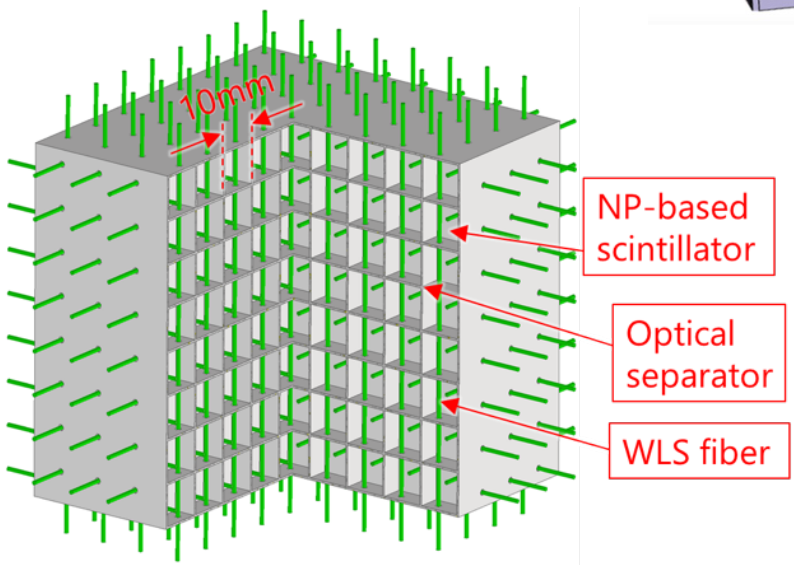


???

Hyper-Kamiokande near detector
- T2K installed the new near detector, ND280+ (2024)
- At 2027, some of them are ~17 years old

Water-based liquid scintillator
- Active R&D topic
- 3-d fiber reading
- water-based quantum dots liquid scintillator?

Water-based liquid scintillator detector ND280++ (Kikawa)



5. Conclusions

Water-based liquid scintillator is successful made using CdS-ZnS quantum dots.

Water QDs photoluminescence quantum yield is 9.5±0.5%, lower than the company value (~50%).

Hydrodynamic diameter is measured by DLS, and water QDs (~70nm) is larger than toluene QDs (~20nm) as expected.

QD sizes change slightly aver the time, and no sign of agglomeration. Absorbance and emission spectrum don’t change over 3 years. PLQY ageing result is not conclusive.

Scintillation response is measured from cosmic muons. Time constant seems very fast as expected (<8ns), and charge response suggests photon yield is comparable as typical organic liquid scintillators.

Sustainable liquid scintillator is the next step.

Thank you for your attention!

Backup

2. Brus equation

Masses
- electron mass, m_e
- effective electron mass, $\sim 0.1 m_e$ (CdSe)
- effective hole mass, $\sim 0.45 m_e$
- effective exciton mass, $\mu \sim 0.08 m_e$

Size
- Exciton radius r ~6 nm

Exciton diameter 2r ~12 nm
- Quantum dots diameter: 2-10 nm

Band gap (Brus equation)

$$E_{QD} = E_{gap} + \frac{\hbar^2 \pi^2}{2 r^2 \mu}$$

- Band gap is wider in quantum dots
- Quantum confinement