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Electron irradiation effects on nanocrystal quantum dots used in bio-sensing applications

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Outline

- CdSe Nanocrystals in TOPO or MAA
- Cathodoluminescence spectra of inorganic and bio-compatible nanocrystals
  - Results from photoluminescence are also presented for comparison when appropriate.
- Electron beam induced degradation of optical emission
  - Temperature dependence
  - Dependences on beam energy
  - Variations with nanocrystal
- Discussion
- Summary and conclusions

Motivation

•In contrast to organic fluoroprobes, nanocrystals have a broad absorption spectrum, which allows excitation of various wavelengths (originating from different nanocrystals sizes for example) with a single excitation wavelength.

•These sensors will not be useful in space applications unless they demonstrate certain tolerance to extremes in temperature, radiation, and oxidation conditions. The robustness of these nanocrystals needs to be established before they can fulfill their promise as biological probes for space applications.

•Showing the application of cathodoluminescence CL in electron radiation damage studies, since an energetic electron beam may induce defects in the specimen. CL microanalysis allows the formation of irradiation-induced defects to be monitored and investigated. Since the optical properties of some materials and devices can be characterized with CL spectroscopy, this gives the advantage that a whole irradiation experiment, including monitoring of the degradation in optical properties and identification of localized damage can be done in *in situ*.

Experimental Details

Electron beam induced degradation was investigated in "core shell" CdSe/ZnS nanocrystals coated with trioxylphosphine oxide (TOPO) and in CdSe nanocrystals coated with mercapto-acetic acid (MAA).

Bio-compatible CdSe quantum dots were synthesized and solubilized with cap exchange where MAA was used to replace the TOPO [detailed procedures reported in: J. A. Kloepfer et al., Appl. And Envir. Microbiology, 69, 4205 (2003)].

Cathodoluminescence (CL) imaging and spectroscopy were carried out using a scanning electron microscope equipped with a monochromator attachment for CL spectroscopy and a GaAs photo multiplier detector sensitive in the visible range (300 to 800 nm).

Cathodoluminescence spectroscopy

Obtaining CL results requires testing the QD out of solution – techniques for obtaining PL signals from dried samples were developed.

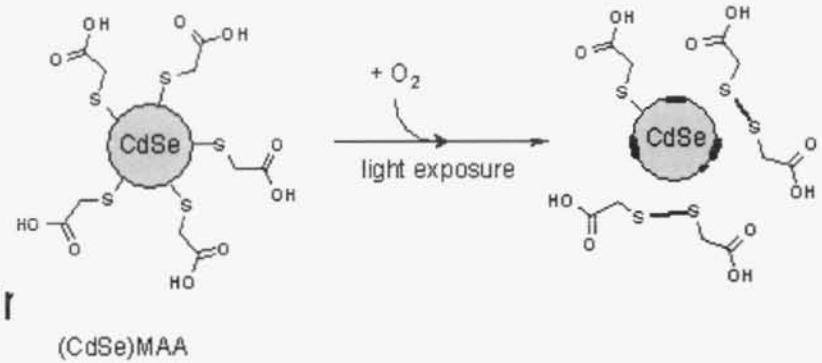
Some of the samples were illuminated prior to drying in order to evaluate how oxide formation around the CdSe quantum dots affects their CL emission.

Images and spectra were collected either at room temperature or at 5 K, and various accelerating voltages, beam apertures, and magnifications were used in order to vary both the irradiation energy and dose rates.

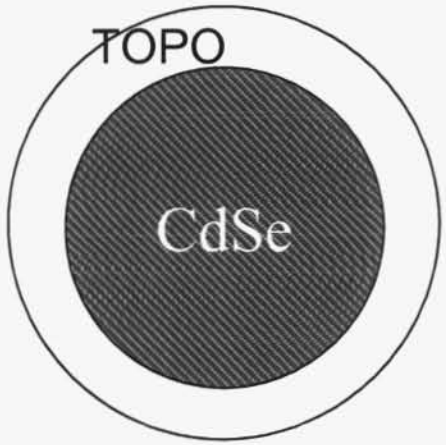
CL emission degradation with electron dose was quantified by measuring the electron beam current, recording the irradiated area and timing the exposure to the electron beam. The beam was turned off for several hours and the CL spectra was recorded again In order to eliminate potential charging effects.

TOPO vs. MAA

Results are compared for CdSe QDs coated with trioctylphosphine oxide (TOPO), and QDs coated with mercaptoacetic acid (MAA). Optical properties from CdSe or CdSe/ZnS QDs ir TOPO are better known than the ones of any QD coated in MAA.

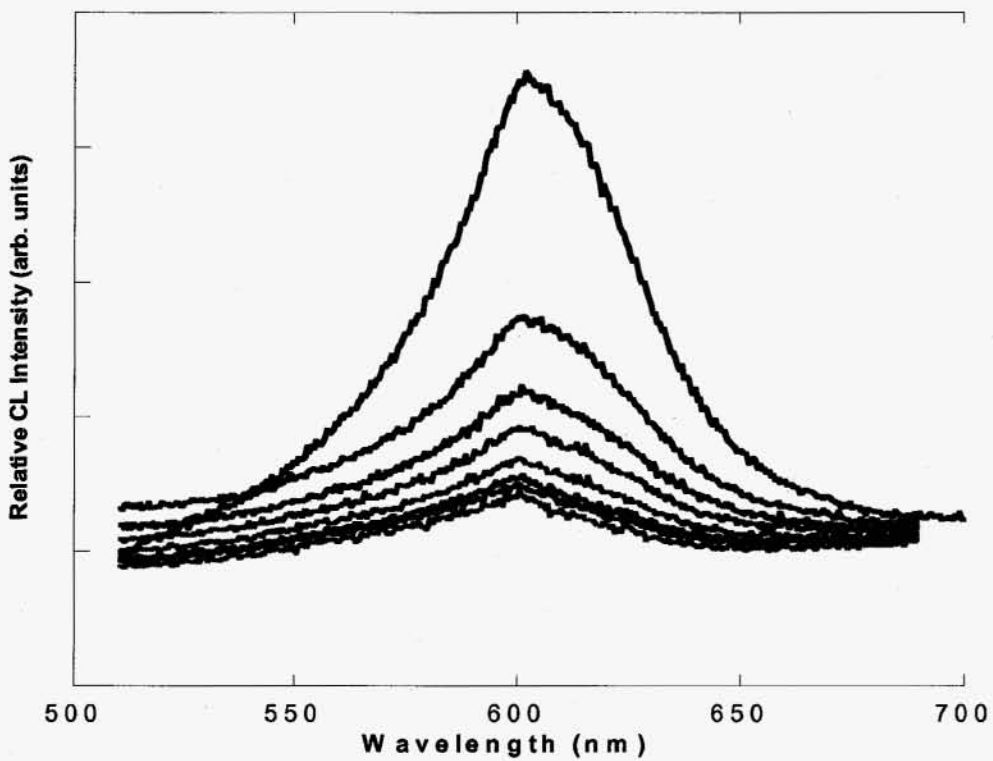


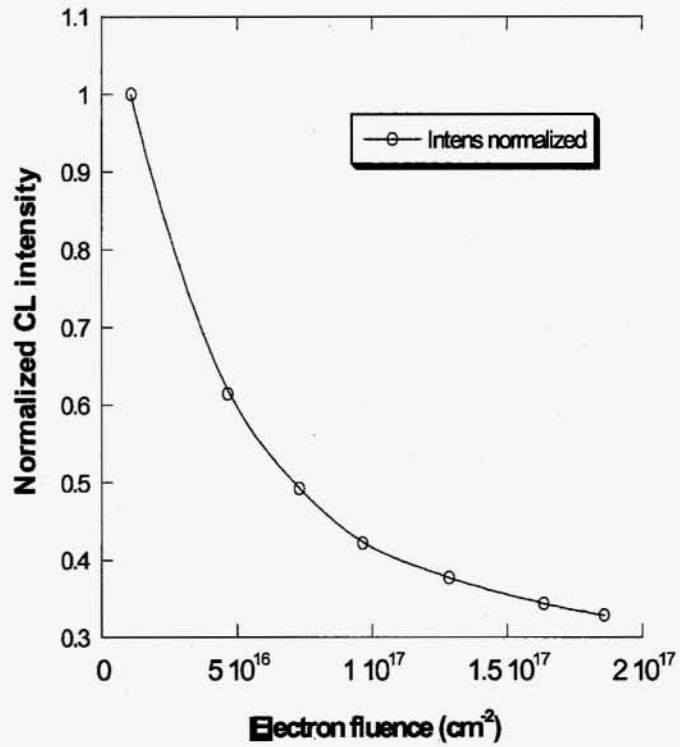
Effects of TOPO include passivation of the surface of the QDs, reducing surface states and enhancing the luminescence emission. However, these colloidal nanoparticles are only soluble in non-polar solvents.



Substitution of the TOPO coating with MAA allows solubilization in polar solvents, like water or saline, and it also allows binding organic molecules to the external surface of the QDs. Hence, the role of MAA is to make these quantum dots biologically compatible.

Cathodoluminescence signal intensity diminishes with successive spectra

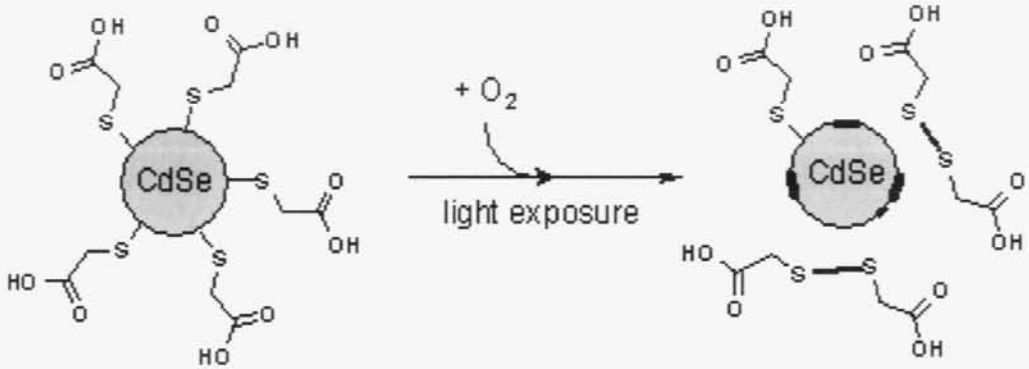




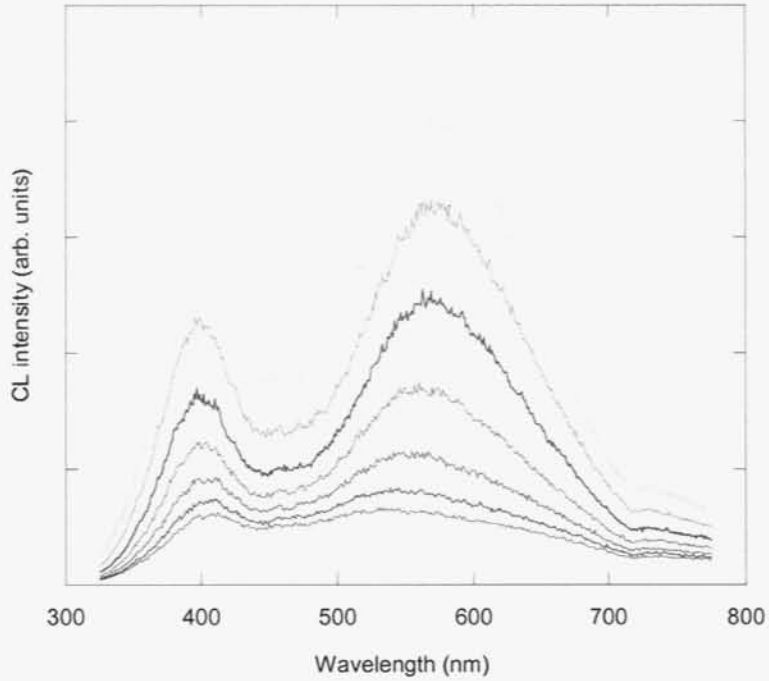
The broad emission from CdSe - TOPO originates from slight variations in the nanocrystal sizes. The closer the size calibration, the narrower the luminescence emission spectra will be from these QD. In these nanocrystals, the PL signal intensity from the nanocrystals increases linearly with excitation and they show bi-exponential decay dynamics.

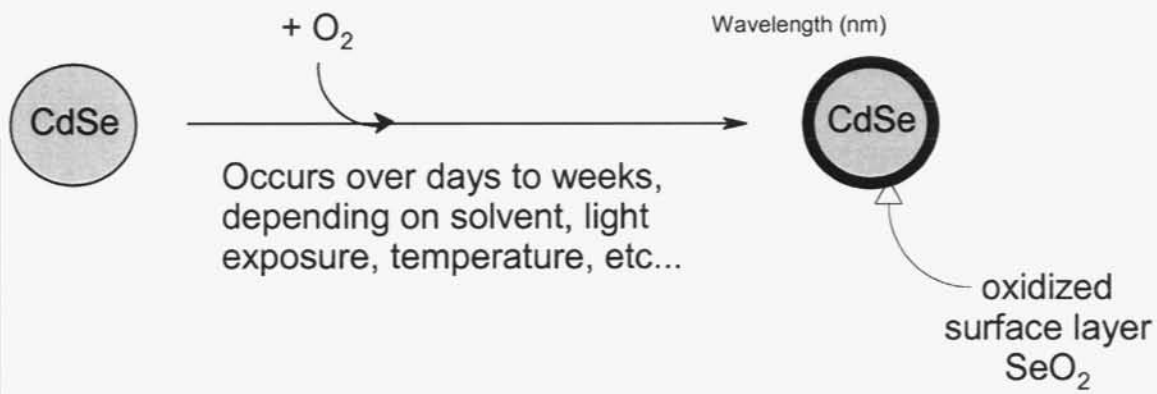
Graphs show cathodoluminescence spectra for CdSe quantum dot nanocrystals coated in TOPO. Curve set shows successive scans taken at the same spot, showing the effect of 30 keV electron beam on the CL intensity. CL emission degradation with electron dose was quantified by measuring the beam current, recording the irradiated area and timing the exposure. After such analysis, intensity degradation plots as shown can be obtained.

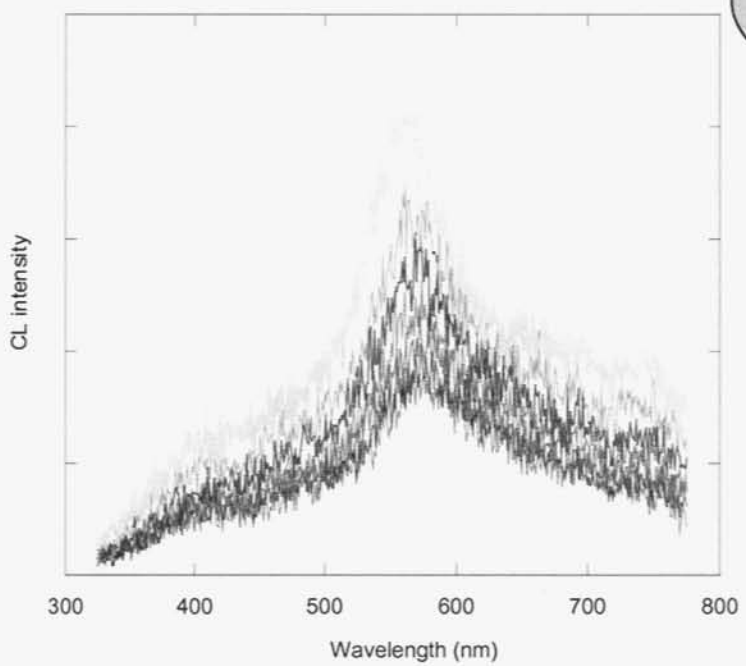
Bio-compatible nanocrystal emission



(CdSe)MAA



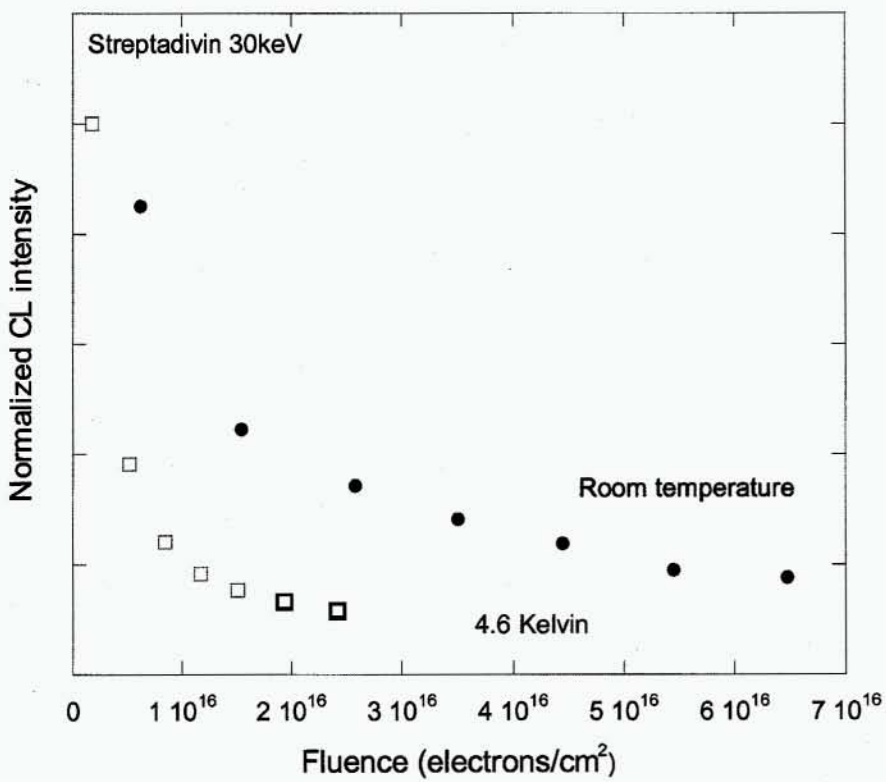


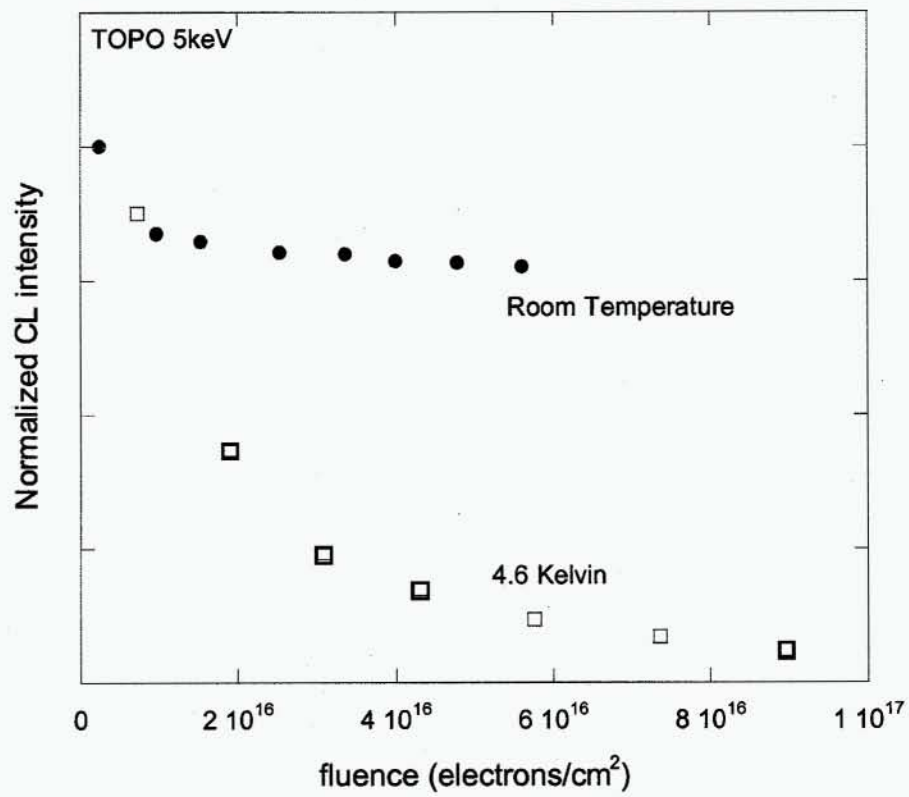


MAA has a quenching effect on the luminescence which improves with nanocrystal surface oxidation

Weak intensities are one of the problems in some of these biological application

Cryogenic effects in e beam response of protein conjugated and inorganic nanocrystals

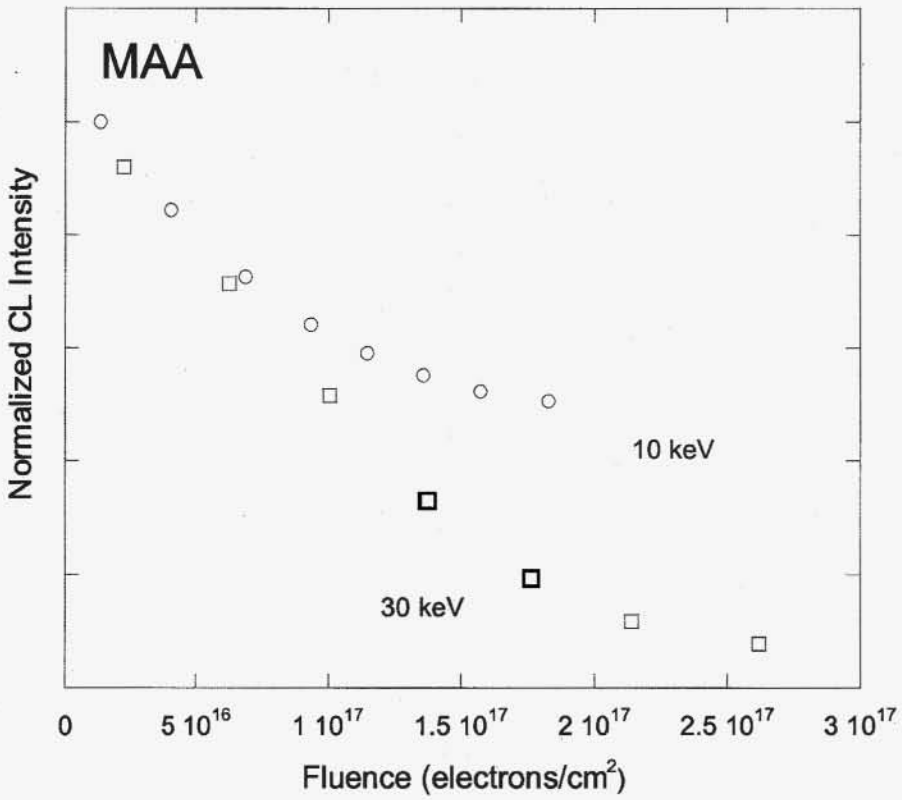


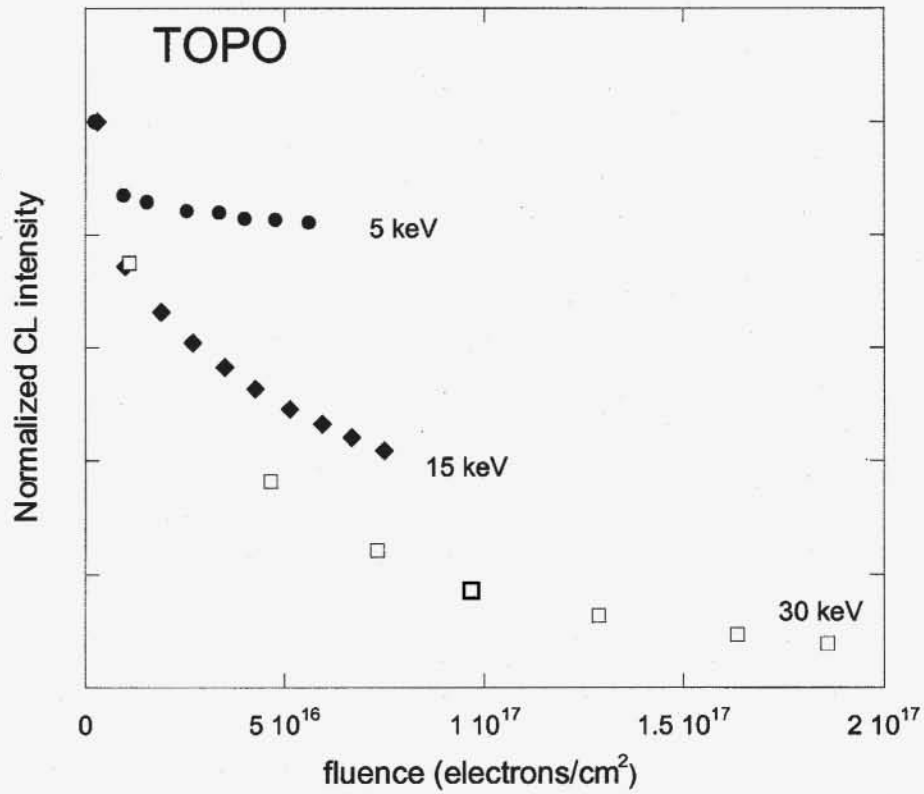


30 keV electron irradiation induced degradation at room temperature and 4.6 K for CdSe nanocrystals conjugated with streptadivin.

5 keV electron irradiation induced degradation at room temperature and 4.6 K for CdSe nanocrystals coated in TOPO.

electron induced degradation – dependence on beam energies

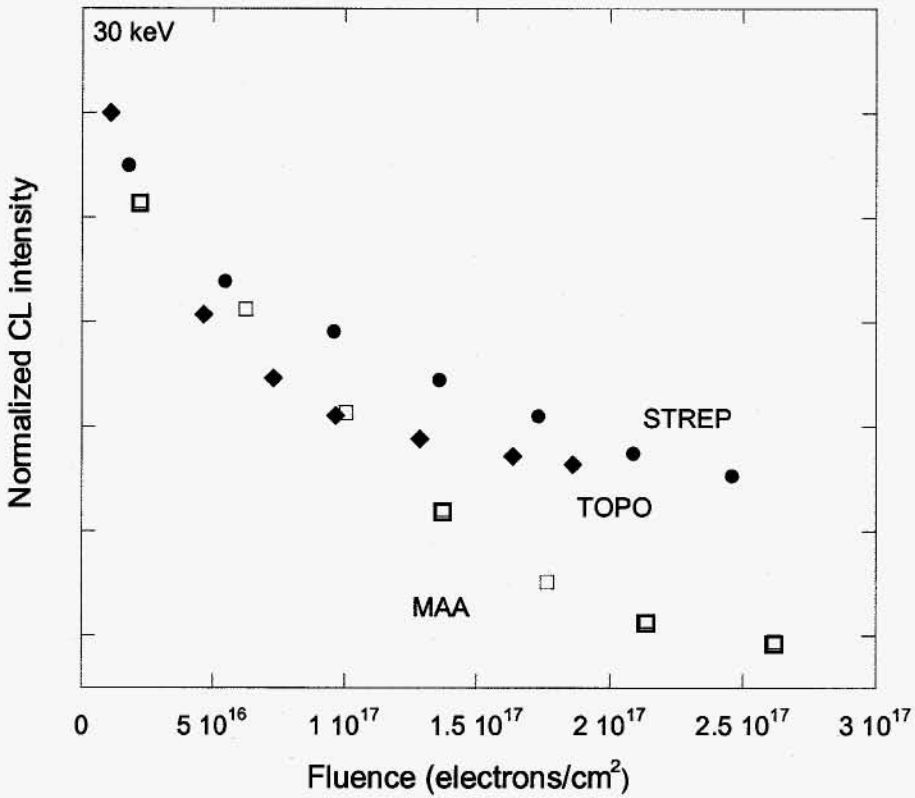


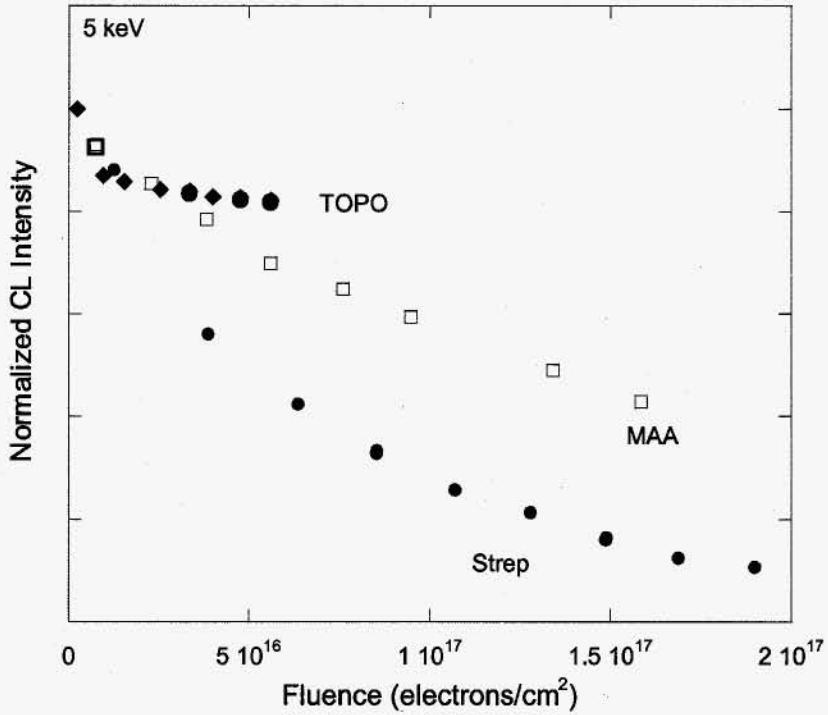


Comparison of degradation in CdSe nanocrystals in MAA and in TOPO under different beam energies (5, 10, 15 and 30 keV) at room temperature

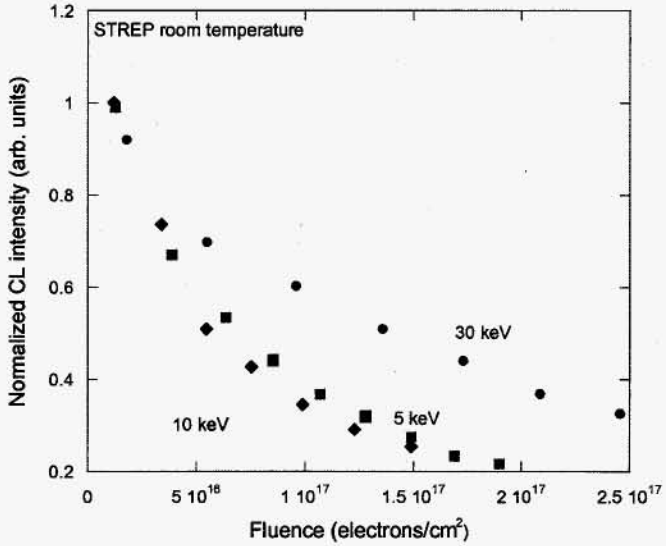
Strep (protein conjugated sample) exhibits reverse e-beam energy response

Sample response (QD type) to different e beam energies





Comparison between nanocrystal types in e beam response for 30 keV and 5 keV for inorganic nanocrystals (CdSe in TOPO) and biologically compatible 'bare' nanocrystals (CdSe in MAA) and the Streptadivin protein conjugated CdSe nanocrystals.



Discussion

electron irradiation has been shown to alter the properties of many semiconductor materials – but - this rapid degradation can be surprising in light or earlier results that showed epitaxial quantum dots to be highly tolerant to proton induced damage [1]

First report of CL of biologically compatible QDs.
Several other CL studies using CdSe QDs grown by MBE, resulting in visualization of excitons and biexcitons, and a recent one reporting changes in the CL spectra from 12 keV e-beam effects during MBE growth [2]

Three factors must be considered to understand these results:

(a) the displacement damage threshold in II-VI materials is known to be considerable lower than in other commonly used semiconductor materials [3],

(b) the radiation conditions and geometries in these nanocrystal QDs are completely different since the nanocrystals in this present study are bare, without the benefit of a large volume of large bandgap semiconductor cladding or surrounding the quantum dots.

(c) Surface effects play an important role on the optical properties of these nanocrystals. Surface modification can be achieved for lower beam energies, as oxides, weak protein links and weaker bonding is at play in the TOPO and MAA coatings.

1. R. Leon et al., IEEE Trans. Nucl. Sci. **49**, 2844 (2002).
2. V. I. Kozlovsky et al., Phys. C 16, S133 (2004).
3. H. Morkoç et al., J. Appl. Phys. 76, 1363 (1994).

The differences observed with cryogenic conditions in the relative effects of electron beam irradiation on the semiconductor quantum dots are probably related to the lack of thermal annealing of Frenkel pairs under cryogenic conditions.

These results show the potential of using CL to investigate electron induced degradation

CL can also be a valuable tool investigating environmental effects, and in understanding how electron radiation effects can change at cryogenic temperatures.

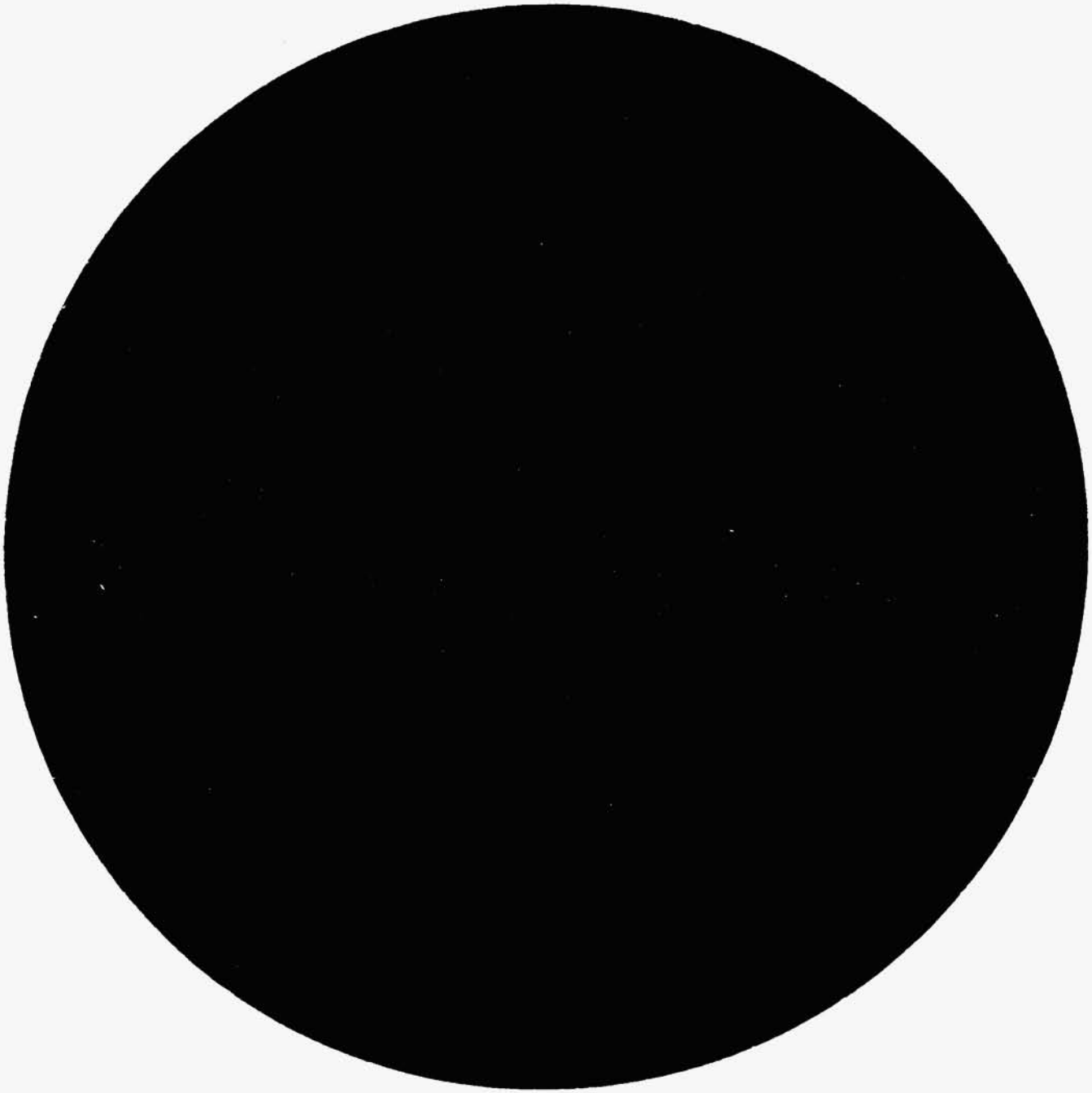
Summary/Conclusions

- This technique of cathodoluminescence was applied to the study of nanocrystal quantum dots with inorganic passivation, bio-compatible passivation and conjugated with organic molecules.

- We have shown that the technique of cathodoluminescence can be successfully utilized as a quantitative tool for *in-situ* monitoring of electron damage in materials.

- Our results show significant degradation in the luminescence emission from nanocrystals after electron beam exposure in the KeV ranges.

- We observe higher sensitivity to keV for bio compatible nanocrystals

- In bio compatible nanocrystals cryogenic temperatures enhance degradation, and faster degradation is also seen in TOPO nanocrystals at low keV

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