V^th ICONMO 20-23 March, 2019, **Borovetz Bulgaria**

COLLOIDAL NANOCRYSTALS AS NEXT GENERATION ENERGY MATERIALS

O. Kostadinova, S. Stankov, T. Stankulov, B. Banov, A. Momchilov

Institute of Electrochemistry and Energy Systems "Acad. E. Budevski",
Bulgarian Academy of Sciences, Sofia, Bulgaria

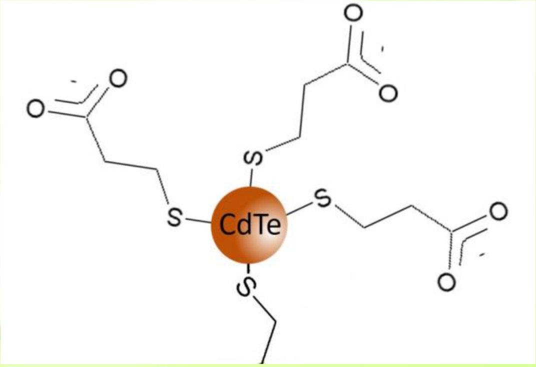
Content

- What is a quantum dot material
- Applications: energy production and storage
- Quantum confinement effect
- Synthesis
- Restrictions
- Compositions for eco-friendly PVs

Quantum dots?

A zero dimensional crystalline solid with size ≥ 10 nm

It has electronic and optical properties between those of much larger macro and microscale bulk semiconductor crystals, and much smaller atoms and molecules.



Quantum dots use

Use of QDs are expected to reach $27.5 billion of market share by 2030 according to Future Markets Inc

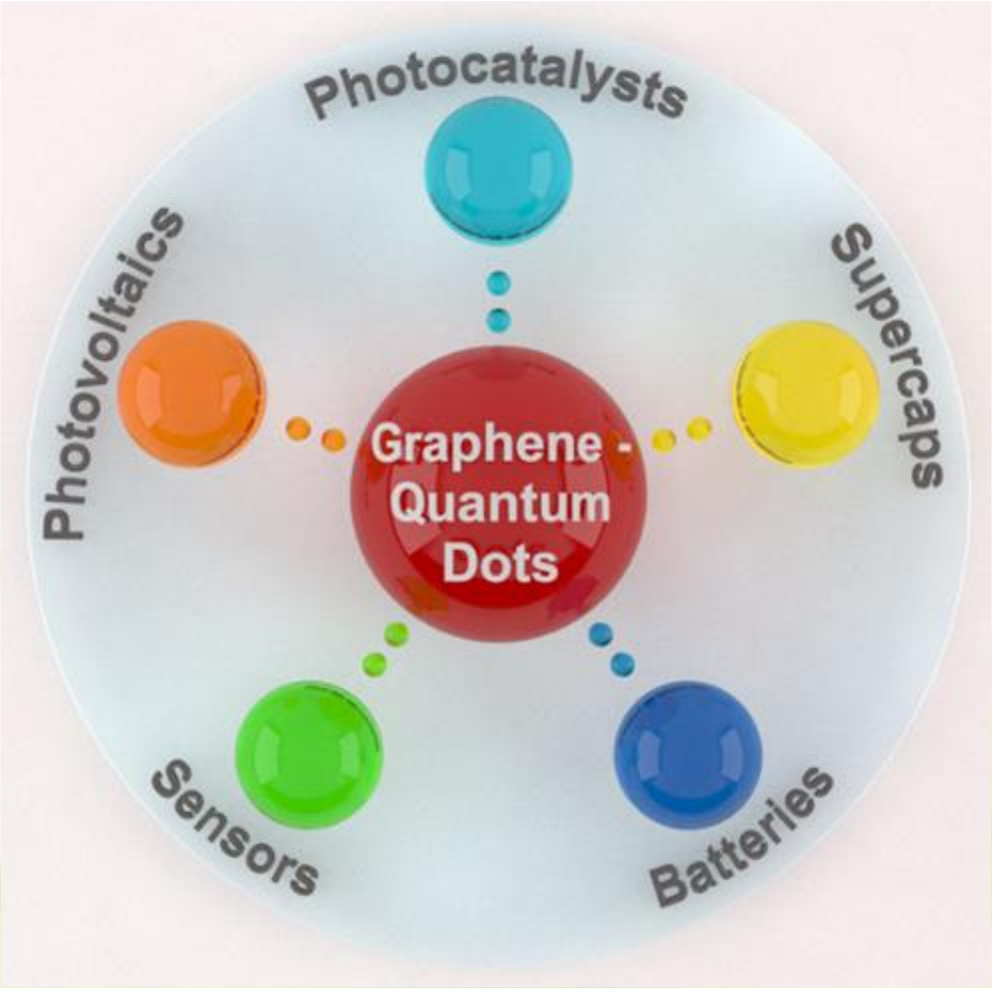
Potential application areas

TVs
smartphone screens
photovoltaics
security tags and inks
sensors
lasers
transistors

bio-imaging
solar windows
biomarkers
solid-material-based memories
thermoelectric materials
quantum dot computers
artificial photosynthesis
light emitting diodes (LEDs)
and more

The Global Market for Quantum Dots to 2030, Future Markets, Inc., July 2018, link: http://futuremarketsinc.com/the-global-market-for-quantum-dots-2/.

Energy applications



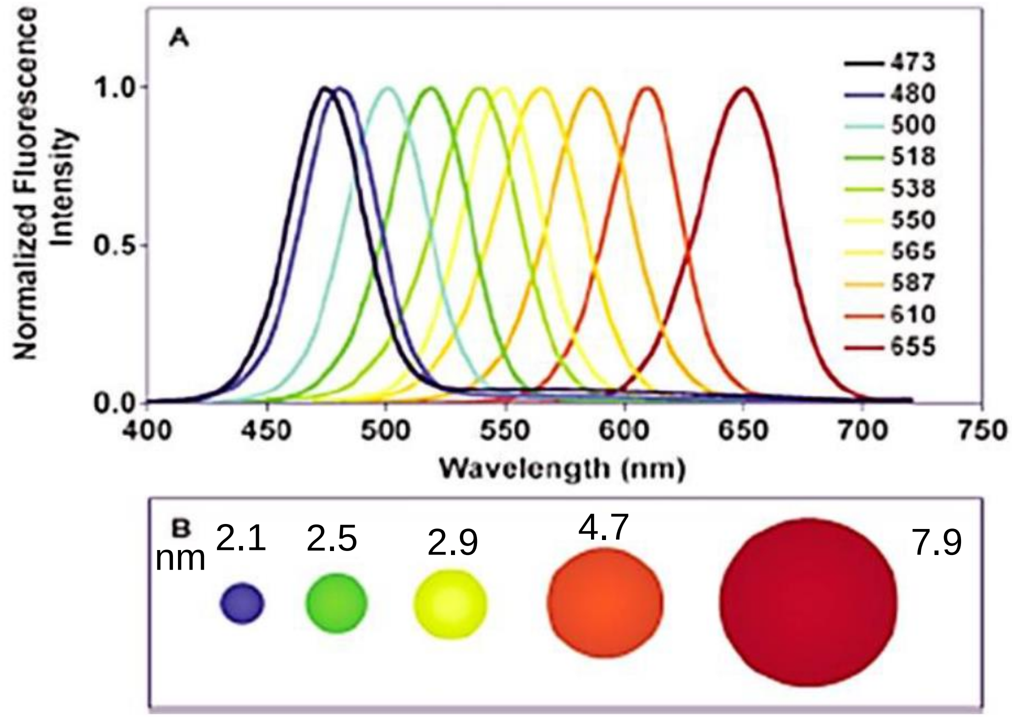
Quantum confinement effect

Quantum confinement effect: changes in the atomic structure as a result of direct influence of ultra-small length scale on the energy band structure.

When the size of a semiconductor crystal becomes small enough that it approaches the size of the material's Exciton Bohr Radius, the electron energy levels should be treated as discrete.

A decrease in the size of the QDs will result in a hypsochromic shift of the absorption and photoluminescence (PL) spectra by increasing the bandgap energy.

QDs with the same composition but different sizes can generate fluorescence of different wavelengths: size tunability



J.g Li, Jun-Jie Zhu, Analyst, 2013, 138, 2506;

Synthesis of quantum dots

Top-Down Synthesis Processes:

Electron beam lithography
Focused ion beam (FIB) techniques
Etching techniques

Bottom-up Approach

Wet-Chemical Methods:
sol-gel
hot-injection
Vapour-Phase Methods:
CVD
PVD
Molecular beam epitaxy

Other Synthetic Processes:

Ultrasonic or Microwave irradiation
Hydrothermal synthesis
Solvothermal synthesis

Traditional quantum dots

Group	Quantum dots
III–V	GaAs, InP, InAs, InGaAs, IrGaAs, AlGaAs
II–VI	CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, MgS, MgSe, MgTe
IV–VI	PbS, PbSe, PbTe
CdS/ZnSe, CdS/ZnS, CdSe/ZnS, CdSe/CdS, CdTe/ZnS, CdTe/CdS, PbSe/CdSe, CdSeTe/ZnS, CdHgTe/CdS	

LEDs, flat screens, biolabeling

J. Li, Jun-Jie Zhu, Analyst, 2013, 138, 2506, DOI: 10.1039/c3an36705c

Traditional QDs: restrictions

toxic and carcinogen

DIRECTIVE 2011/65/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment

Prohobition of Cd for TVs and displays sold in Europe after October 2019

http://www.nanocotechnologies.com/media/pressreleases

Multicomponent colloidal chalcogenide QDs for solar cells

Cu_2ZnSnS_4 (CZTS): solvothermal; kesternite structure; optimal direct band-gap 1.5 eV; large absorption coefficient over 10^4 cm^{-1};
I. Calvet, J. B. Carda et.al, Boletín Soc. Esp. Cerám. y vidrio 54 (2015) 175–180, http://dx.doi.org/10.1016/j.bsecv.2015.09.003

Cu_2NiSnS_4: hydrothermal;
S. Sarkar, B. Das, P. R.Midya, G. C. Das, K. K. Chattopadhyay, Mater. Lett.152(2015)155–158, http://dx.doi.org/10.1016/j.matlet.2015.03.083

Zn-Cu-In-Se: Solution processed;
H. Zhang, W. Fang, W. Wang, N. Qian, X. Ji, ACS Appl. Mater. Interfaces 2019, 10.1021/acsami.8b18033

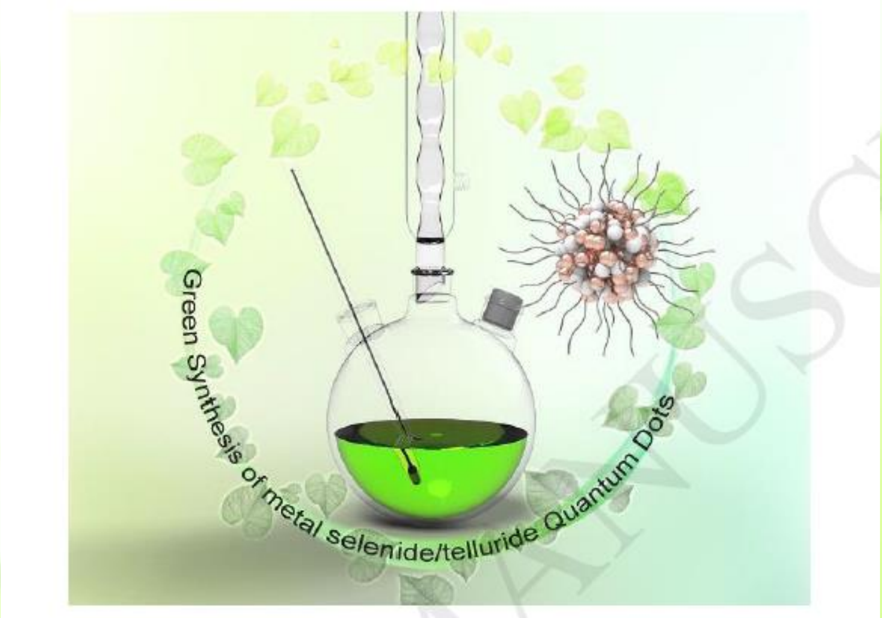
$Cu_2(Zn,Fe)SnS_4$: ball milling in ethanol;
C.L. Azanza Ricardo et.al. , J Power Sources 230 (2013), 70e75http://dx.doi.org/10.1016/j.jpowsour.2012.12.045

$Cu_2Zn_xNi_{1-x}SnS_4$: hydrothermal;
G. S. D. Babua, X. S. Shajan, et. al. , Mater ScinSemicond Process.63 (2017) 127–136, http://dx.doi.org/10.1016/j.mssp.2017.02.015

Summary

- The quantum dots scope of application areas expands - reaching $27.5 billion of market share by 2030 according to Future Markets Inc.;
- Restriction of EU for some heavy metals.

Research of new QD compounds



MULTIGRAPH

This research is supported by Bulgarian Science Fund with contract № КП-06-ОПР 04/2

Thank you very much

“Green” QDs

Eco-compatible compositions and synthesis

Colloidal nanocrystals are solution-grown, nanometre-sized, inorganic particles that are stabilized by a layer of surfactants attached to their surface. The inorganic cores possess useful properties that are controlled by their composition, size and shape, and the surfactant coating ensures that these structures are easy to fabricate and process further into more complex structures. This combination of features makes colloidal nanocrystals attractive and promising building blocks for advanced materials and devices.

A typical synthesis system for colloidal nanocrystals consists of three components: precursors, organic surfactants and solvents. In some cases, surfactants also serve as solvents. Upon heating a reaction medium to a sufficiently high temperature, the precursors chemically transform into active atomic or molecular species (monomers); these then form nanocrystals whose subsequent growth is greatly affected by the presence of surfactant molecules. The formation of the nanocrystals involves two steps: nucleation of an initial ‘seed’ and growth. In the

Daniel Oliveira, Fernando Menegatti de Melo, Henrique E. Toma, One-pot single step to label microtubule with MPA-capped CdTe quantum Dots, Micron, https://doi.org/10.1016/j.micron.2018.03.002

Other
problematic factors have also been suggested, such as the suitability of the capping agents, the retention of particles over a certain size, biological magnification, and importantly, the breakdown and decomposition products of these inorganic materials. Quantum dots are notoriously labile and the identity and ultimate destination of the inorganic decomposition products remains unclear

Cadmium and selenium, which are the major components of the majority of quantum dots, are known to be acutely and chronically toxic to cells and organisms. In cells, they are taken up into calcium membrane channels where they accumulate.[3,4] Cadmium inhibits the synthesis of DNA, RNA and proteins, as well as breaking up DNA strands and mutating chromosomes.[5–7] The toxic ions are commonly thought to be released from quantum dots when the surface of the nanoparticle is oxidised

Bohr radius of a particle is defined as
(Yoffe 1993),

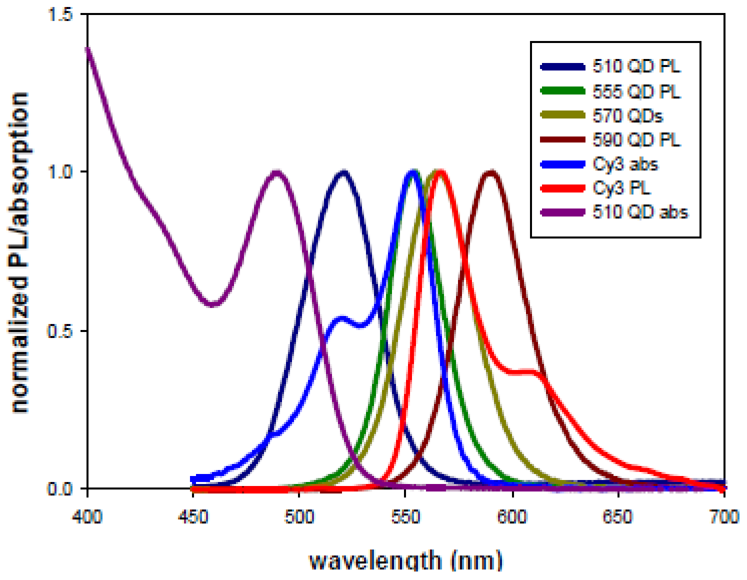
$$a_B = \varepsilon \frac{m}{m^*} a_o \qquad (1)$$

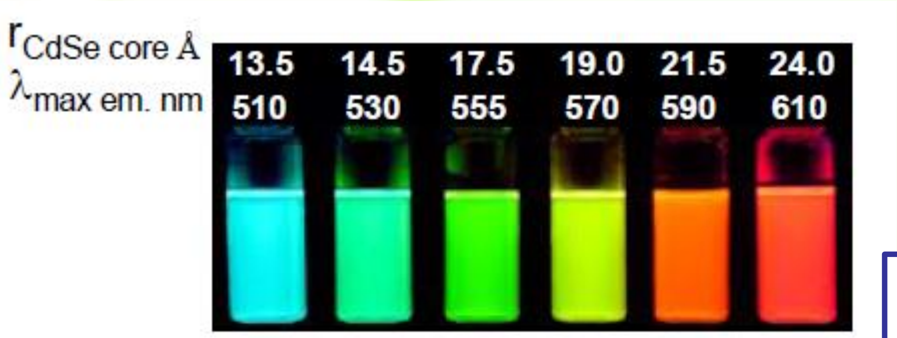
where ε is the dielectric constant of the material, m* is the mass of the particle, m is the rest mass of the electron, and ao is the Bohr radius of the hydrogen atom. When the particle size approaches Bohr exciton radius, the quantum confinement effect causes increasing of the excitonic transition energy and blue shift in the absorption and luminescence band gap energy (Yoffe 1993)

QDs optical properties, such as

tunable emission,

tobleaching,





J.g Li, Jun-Jie Zhu, Analyst, 2013, 138, 2506; K. E. Sapsford, T. Pons, I. L. Medintz, H. Mattoussi, Sensors 2006, 6, 925-953