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Alivisatos, A. Paul

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

In the first phase, hyperbranched nanocrystals of Cadmium Selenide [CdSe] were synthesized, isolated, and characterized. During active research on CdSe nanostructure-based solar cells, toxicity and processing complexity issues were encountered. The research was redirected to find non-toxic and abundant materials. It was determined that copper (I) sulfide and iron disulfide pyrite generated a much broader impact for photovoltaic solar cell applications. First, a simple low temperature solution phase synthesis of copper (I) sulfide nanocrystals was demonstrated. An all-inorganic bilayered solar cell device based on these nanocrystals and CdS nanorods demonstrated power efficiencies of about 1.6%. Second a novel single source precursor approach was established to synthesize pure phase iron disulfide pyrite nanocrystals with high purity through a surfactant-assisted hydrothermal reaction. These nanocrystals represent new groups of well-defined nanoscale structures for high-performance photovoltaic solar cells based on non-toxic and earth abundant materials.

15. SUBJECT TERMS

cadmium selenide nanocrystals, hyperbranched nanocrystals, high-performance photovoltaic solar cells

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a. REPORT	b. ABSTRACT	c. THIS PAGE			A. Paul Alivisatos
unclassified	unclassified	unclassified			19b. TELEPHONE NUMBER: 510-643-7371

Final Report

Hierarchical Junction Solar Cells Based on Hyper-Branched Semiconductor Nanocrystals
AFOSR Grant No. FA9550-06-1-0488
7/15/06 – 6/30/09

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Statement of Objectives

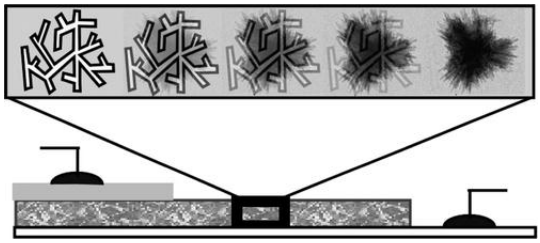
Demonstrate concept of hierarchical junction solar cells	March 2007
Prepare hyper-branched nanocrystals of CdSe – control branch lengths/widths	June 2007
Prepare hyper-branched nanocrystals of CdTe – control branch lengths/widths	June 2007
Fabricate hybrid nanocrystal/polymer solar cells with the hyper-branched CdSe and CdTe nanocrystals	December 2007
Compare nanorod/polymer and hyper-branched/polymer solar cell performance	December 2007
Prepare dual-nanocrystal all-inorganic solar cells with hyper-branched nanocrystals paired with spherical and rod-shaped nanocrystals	December 2008
Compare dual nanocrystal solar cells fabricated with rods only to dual nanocrystal solar cells containing hyper-branched nanocrystals	December 2008
Prepare core-shell hyper-branched nanocrystals	December 2009
Fabricate solar cells with the core-shell hyper-branched nanocrystals	December 2009

Program Summary:

In this three-year program, we met most of our objectives as stated in our proposal and established a more innovative research based on the existing results. In the initial research, we, for the first time, synthesized, isolated, and characterized hyperbranched nanocrystals of CdSe. By using P_3HT as the companion hole transporter, these CdSe hyperbranched nanocrystals were incorporated into bulk heterojunction solar cells with power efficiencies of about 3%. During the active research on CdSe nanostructure-based solar cells, we started to realize the toxicity and processing complexity issues of CdSe nanomaterials. These scientific problems drove us to re-shape our research to find non-toxic and abundant materials for solar cells and indeed we received an immediate success and generated a much broader impact by showing copper (I) sulfide (Cu_2S) and iron disulfide pyrite (FeS_2) for photovoltaic solar cell application. First, we demonstrated a simple low temperature solution phase synthesis of Cu_2S nanocrystals and the all-inorganic bilayered solar cell device based on Cu_2S nanocrystals and CdS nanorods with power efficiencies of about 1.6%. Second, we established a novel single source precursor approach to synthesize pure phase FeS_2 nanocrystals with high purity through a surfactant-assisted hydrothermal reaction under optimum pH value. These Cu_2S and FeS_2 nanocrystals represent new groups of well-defined nanoscale structures for high-performance photovoltaic solar cells based on non-toxic and earth abundant materials. In addition, we studied the photochemical formation of metal–semiconductor heterostructures by photodeposition of metals on semiconductors nanorods. This study can be used to understand how factors such as nanocrystal composition, shape, carrier dynamics, and surface chemistry influence the photochemical properties of semiconductor nanocrystals.

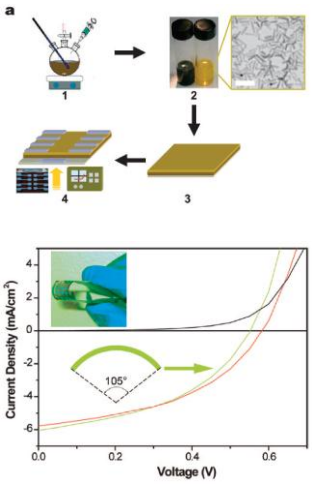
Accomplishments/New Findings:

1. Hyperbranched CdSe nanocrystal-based bulk heterojunction solar cells.



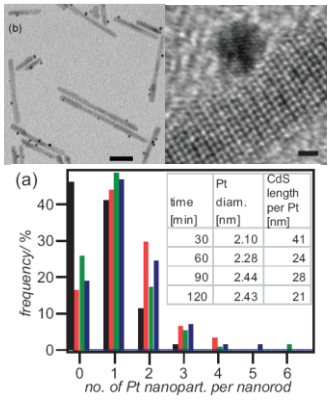
Bulk Heterojunction Solar Cells are a new type of device geometry under active consideration for use in nanoscale solar cells. It is useful in cases where solution processing of the solar cell active medium results in low charge mobilities. Ordinarily, these solution processed solar films rely on the formation of a percolation network of electron and hole transporting media during the solvent casting. Using pre-formed hyperbranched nanocrystals, we were able to create percolation networks independent of the film casting conditions. As a result the processing of these devices is extremely forgiving, while the performance is superior to that achieved previously using nanorod-polymer networks.

2. Cu_2S-CdS all-inorganic nanocrystal solar cells.



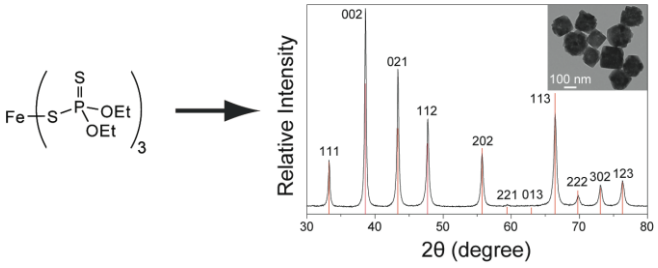
We demonstrated the rational synthesis of colloidal copper (I) sulfide nanocrystals and their application as an active light absorbing component in combination with CdS nanorods. This combination was used to make a solution-processed solar cell with 1.6% power conversion efficiency on both conventional glass substrate and flexible plastic substrate and stability over a 4 month testing period.

3. Photodeposition of Pt on Colloidal CdS and CdSe/CdS Semiconductor Nanostructures.



We demonstrated the growth of Pt on colloidal CdS and CdSe/CdS core/shell nanorods through the photoexcitation of CdS and CdSe/CdS in the presence of an organometallic Pt precursor. Stark differences are observed in the Pt nanoparticle location on the two substrates, and the photodeposition can be completely inhibited by the modification of the semiconductor surface. Our results suggest that tuning of the semiconductor band structure, spatial organization, and surface chemistry should be crucial in the design of photocatalytic nanostructures.

4. Surfactant-assisted Hydrothermal Synthesis of Single Phase Pyrite FeS_2 Nanocrystals.



We demonstrated a single-source molecular precursor that can be used for the synthesis of single phase pyrite FeS_2 nanocrystals. Characterization confirms an indirect transition and a bandgap of 0.95 eV. The reaction temperature, pH value, precursor, and surfactant were found to play important roles in the control of material purity. These single-phase pyrite FeS_2 nanocrystals represent a good candidate material for studies of nanoscale photovoltaic solar cells based on non-toxic and earth abundant materials.

Personnel Supported: List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

Principal Investigator: Paul Alivisatos
Graduate Student: James Nelson, Jessy Baker (fellowship), Cyrus Wadia (fellowship), Steven Hughes
Postdoc: Wanli Ma, Yue Wu (fellowship)

Publications: List peer-reviewed publications submitted and/or accepted during the 12-month period starting the previous 1 October (or since start for new contracts).

I. Gur, N. A. Fromer, A. P. Alivisatos, "Controlled Assembly of Hybrid Bulk-Heterojunction Solar Cells by Sequential Deposition," *Journal of Physical Chemistry B,* **110** (50):25543-25546 (December 2006).

I. Gur, N. A. Fromer, C.-P. Chen, A. G. Kanaras, and A. P. Alivisatos, "Hybrid Solar Cells with Prescribed Nanoscale Morphologies Based on Hyperbranched Semiconductor Nanocrystals," *Nano Letters,* **7**(2): 409-414 (January 2007).

S. M. Hughes, "Advanced Branching Control and Characterization of Inorganic Semiconducting Nanocrystals", Ph. D. thesis, 2007

G. Dukovic, M. G. Merkle, J. H. Nelson, S. M. Hughes, and A. P. Alivisatos, "Photodeposition of Pt on Colloidal CdS and CdSe/CdS Semiconductor Nanostructures," *Advanced Materials,* (2008), 20(22), 4306.

Y. Wu, C. Wadia, W. Ma, B. Sadtler, A. P. Alivisatos, "Synthesis of Copper (I) Sulfide Nanocrystals for Photovoltaic Application" *Nano Letters,* (2008), 8(8), 2551.

C. Wadia, Y. Wu, S. Gul, S. K. Volkman, J. Guo, A. P. Alivisatos, "Surfactant-assisted Hydrothermal Synthesis of Single Phase Pyrite FeS_2 Nanocrystals", *Chemistry of Materials,* in press.

Interactions/Transitions:

a. Participation/presentations at meetings, conferences, seminars, etc.

July 2-5, 2007, Plenary Lecture in Nanotechnology at the Materials Chemistry Conference, Royal Society of Chemistry, University College London, UK

July 19, 2007, Bay Area Science & Innovation Consortium - Innovative Energy Solutions from the San Francisco Bay Area: Fueling a Clean Energy Future," San Francisco, California.

August 20-22, 2008, "Plasmonic Rulers for Measuring the Kinetics of Macromolecular Assembly," and "Plasmon Rulers for Measuring Dynamical Distance Changes in Biological Macromolecular Assemblies," Fall, ACS Meeting, Boston, Massachusetts.

August 26-29, 2007, Plenary Speaker, 12th Annual IUPAC International Symposium, Fukuoka, Japan.

September 28-30, 2007, Chair, Session - Other One-Dimensional Systems and Thermal Properties, Keynote Speaker," Development of New Nanocrystal Molecules for Biological Sensing and Detecting," at the Annual Nanowire Symposium and International Conference on One-Dimensional Nanomaterials, Malmo/Lund, Sweden.

October 22-23, 2007, "Nanocrystals with Applications in Biological Imaging and Renewable Energy," IGERT Seminar at Levich Institute, City College of CUNY, New York, and invited talk at Yale University, New Haven, Connecticut.

October 30-31, 2007, Nieuwland Lecture, University of Notre Dame, South Bend, Indiana.

November 15, 2007, MNSS Seminar Speaker, MIT, Cambridge, Massachusetts.

November 26-27, 2007, invited speaker in the symposium, Quantum Dot and Nanoparticle-Bioconjugates: Tools for Sensing and Biomedical Imaging, and co-chair of session on Nanoparticle-Nanoparticle and Nanoparticle-Bioreceptor Interactions, and presentor,"Plasma Rulers for Measuring Dynamical Distance Changes in Biological Macromolecular Assemblies," MRS 2007, Boston, Massachusetts.)

February 4-7, 2008, Invited Speaker, "Organic-Inorganic Hybrid Solar Cells, ORGAPVNET, Linz, Austria.

March 2-6, 2008, Invited Speaker, "Development of New Nanocrystal Molecules for Biological Sensing and Detecting," PITTCON, New Orleans, Louisiana .

March 25-27, 2008, "Molecular Mechanistic Studies of the Synthesis of Colloidal II-VI Semiconductor Nanocrystals, " in the symposium, Nanostructures in Molecular Solvents;

the Fred Kavli Distinguished Lectureship in Nanoscience, "Nanocrystals as Model Systems for Understanding Structural and Chemical Transportations in Solid State;" and "Chemical Transformations of Nanocrystals," in the symposium, Crystal-Shape Control and Shape-Dependent Properties--Methods, Mechanism, Theory, and Simulation, Spring 2008 MRS conference, San Francisco, California.

April 6, 2008, Invited Speaker, "Nanocrystal Based Solar Cells," and "Colloidal Nanocrystals with Complex Shapes and Topologies," ACS, New Orleans, Louisiana.

April 30-May 1, 2008, Invited Speaker, "Nanoscale Materials for Solar Fuel Generation," Al Gore and Climate Crisis Panel Discussions, New York City.

May 2, 2008, Invited Speaker, Economic Summit, Oakland Mayor Dellums, Oakland, California.

May 18-19, 2008, Invited Speaker, "Artificial Molecules built from Colloidal Nanocrystals, IMM Symposium, the Netherlands.

May 21-23, 2008, Invited Speaker, Nanocrystal conference, NANAX3, Lecce, Italy.

June 2-4, 2008, Invited Talk, "Nanocrystal Molecules with Application in Single Molecule Biological Imaging," Nobel Foundation Symposium on Single Molecule Spectroscopy, Stockholm, Sweden.

July 8, 2008 -- Invited Speaker, "Mechanism of Colloidal Semiconductor Nanocrystal Growth and Surface Modification," Symposium: Organometallic Chemistry, Gordon Research Conference, Newport, Rhode Island.

July 24-28, 2008 -- Invited Speaker, "Nanocrystals as Model Systems for Understanding Structural and Chemical Transformations in the Solid State," in the coupled Nanosystems Workshop, Max Planck Institute, Stuttgart, Germany and "Optical Properties of Individual DNA – Assembled Nanocrystal Molecules," in workshop at Dresden, Germany.

August 20, 2008 – Invited Speaker, "Optical Properties of Plasmon Coupled Single Nanocrystal Molecules," Symposium: Single Molecule Approaches to Biology, Gordon Research Conference, New London, Connecticutt.

August 30, 2008 – Invited participant in Laser Cooling Single Molecule Biophysics and Energy Symposium, Lawrence Berkeley National Laboratory, Berkeley, California.

September 5, 2008 – Invited Speaker, "Nanocrystals as Model Systems for Understanding Structural and Chemical Transformations in the Solid State, in a seminar at the Stanford Linear Accelerator Center.

September 9, 2008 – Rohm and Haas Lecture, "Development of New Nanocrystal Molecules for Biological Sensing and Detecting," University of North Carolina, Chapel Hill, North Carolina.

September 22, 2008 – Keynote Speaker, "Practical Applications of Nanocrystals for Renewable Energy," in Session on Nanomaterials for Renewable Energy, Nanotech Northern Europe 2008, Copenhagen, Denmark.

October 1, 2008 – Debye Lectures, "Nanocrystal Molecules with Application in Single Molecule Biological Imaging," and "Nanocrystals as Model Systems for Understanding Structural and Chemical Transformations in the Solid State, Cornell University, Ithaca, New York.

October 30-31, 2008 – Invited Speaker, "Nanocrystal Based Solar Cells, NanoBio 2008, Seoul, Korea.

November 8, 2008 – Plenary Speaker, "Nanocrystal Based Solar Cells," 25th Anniversary of FORTH [Foundation for Research and Technology, Hellas] in Heraklion, Crete, Greece.

November 15, 2008 – Opening remarks, "Helios Project: from Photon to Fuel," Nano High, Lawrence Berkeley National Laboratory.

January 21, 2009 – Invited Speaker, "Artificial Molecules Built from Colloidal Nanocrystals," the Royal Swedish Academy of Engineering Sciences, Stockholm, Sweden

January 22, 2009 – Invited Speaker, Chalmers University of Technology, Gothenburg, Sweden.

February 13, 2009 – Invited Speaker, "Nanoscale Materials for Solar Fuel Generation," American Academy of Arts and Sciences Symposium, Chicago, Illinois.

March 2, 2009 – Keynote Speaker, Energy and the Environment Session, Summit on the National Academy of Engineers Grand Challenges, Duke University, Durham, North Carolina.

March 12, 2009 – Edgar Fahs Smith Lecture, "Nanocrystal Molecules with Application in Single Molecule biological Imaging," Pennsylvania State University, University Park, Pennsylvania.

March 30, 2009 – Invited Speaker, "Nanocrystal Based Solar Cells," NanoIsraael 2009, Jerusalem, Israel.

April 1, 2009 – Invited Presentor, 2009 Science Fair, Balboa Park, University of California, San Diego, California.

April 7-8, 2009 – Keynote Lecturer, "Artificial Molecules Built from Colloidal Nanocrystals," in the Symposium, Frontiers at the Nanoscale, (a symposium in honor of Prof. Alivisatos) and part of the 37th John Stauffer Distinguished Lecture in the Sciences series, University of Southern California, Los Angeles, California.

b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories

April 2, 2008 Democratic Senator's Steering Committee Forum, and the Science Coalition Media Roundtable, U.S. Capitol, Washington, D.C.

c. Technology Assists, Transitions and Transfers: None.

New discoveries, inventions, or patent disclosures:
1. Layered Inorganic Photovoltaic Devices (filed as a provisional patent in March 2008)

Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel Prize, honorary doctorates, and society fellowships prior to this effort.

-MRS Fellow, 2009
- Nanoscience Prize, International Society for Nanoscale Science, Computation, and Engineering 2009
- Kavli Distinguished Lectureship in Nanoscience, MRS, 2008
-Ernest Orlando Lawrence Award, 2007
-Eni Italgas Prize for Energy and Environment, 2006
-Larry and Diane Bock Chair in Nanotechnology, 2006
-University of Chicago Distinguished Alumni Award, 2006
-Rank Prize for Optoelectronics Award, 2006

Lifetime Achievement Awards:
-Elected to the National Academy of Sciences, 2004
-Elected to the American Academy of Arts and Sciences, 2004
-Fellow, American Association for the Advancement of Science, 2000
-Chancellor's Professor, University of California, Berkeley, 1998-2001
-Fellow, American Physical Society, 1996