Engineering Nanocrystal-Based Functional Materials

Engineered nanocrystals (NCs) are set to become the building blocks of a new generation of solar cells, light-emitting devices for displays and other applications, and catalysts that work when light shines on them. Extended x-ray absorption fine structure (EXAFS) measurements of manganese K-edge undertaken on the MR-CAT 10-ID-B and XSD 9-BM-B,C beamlines at the APS are helping scientists pin down the details and show the way to tuning the properties of engineered nanocrystals for specific applications.

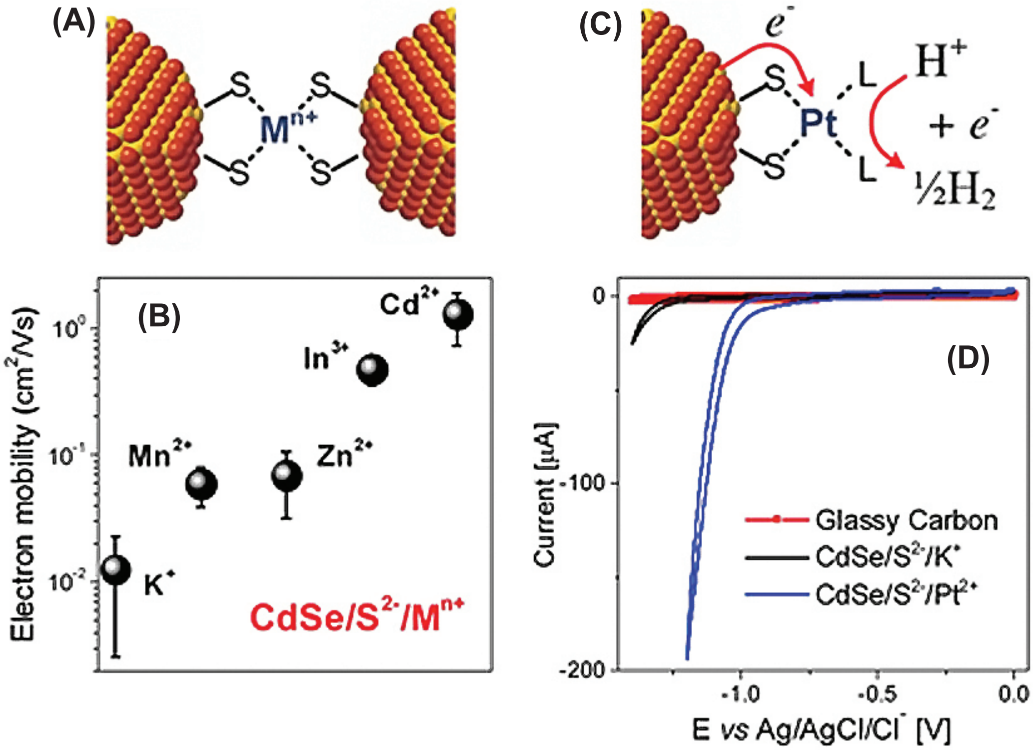

Fig. 1. (A) Semiconductor nanocrystals linked with metal ions. (B) The effect of different metal ions on the field-effect electron mobility in CdSe/S^{2-}nanocrystal films. (C) Schematics of CdSe/S^{2-} NC surface with coordinated Pt^{2+} ions showing that electrons supplied by NC can drive proton reduction. (D) Cyclic voltammograms measured for CdSe/S^{2-}/K^{+} and CdSe/S^{2-}/Pt^{2+} nanocrystals in aqueous solution at pH 6.5. The increase of current shows electrocatalytic reduction of water.

Nanocrystalline pieces of inorganic semiconductors, a few billionths of a meter across, can be stirred into a liquid to form a colloid suspension in which the particles never settle out. Such mixtures are ideal for evaporating the liquid to form thin films and layered structures. The layers left behind can be electrically active, respond to or generate light, or catalyze various chemical transformations.

The researchers from The University of Chicago and Argonne utilized a range of techniques, including EXAFS at the MR-CAT 10-ID-B beamline, sulfur K-edge XANES spectra measured at the XSD 9-BM-B,C beamline, electron paramagnetic resonance spectroscopy to characterize the materials, and SQUID magnetometry to investigate the nanocrystals' magnetic properties.

> These cations not only make fully inorganic systems but also provide a way to hook together individual nanocrystals in the lattice in a way that was not possible with previously utilized capping materials. The result is nanocrystals with increased luminescence efficiency, greater electron mobility, greater catalytic activity, and superparamagnetism.

The researchers demonstrated that by engineering these cations they can control almost every property of the nanocrystals including photoluminescence efficiency (how brightly they glow when a current is applied), electron mobility (how well they themselves conduct electricity), and their electrocatalytic performance (Fig. 1). The same approach to engineering the cations on the surface of a nanocrystal can also be used to adjust the type and concentration of free-charge carriers in the nanocrystal layer and the materials' magnetic susceptibility. Such fine control of the nanocrystals will allow scientists to tune their properties for specific applications, whether boosting solar energy conversion or adjusting the color of the light they produce in a display panel.

Until now, most research into inorganic semiconductor nanocrystals has faced a problem in that the surface of the nanocrystals must be “capped” with organic compounds. The team hoped to avoid this problem so that they could exercise greater control of their nanocrystals for the development of the particles into photovoltaic solar energy materials, thermoelectrics, light-emitting diodes, and photodetectors for light sensors.

The alternative is to find small and conductive inorganic molecules to cap the nanocrystals. So the use of sulfide, selenide, and telluride anions has been investigated as a way to provide an inorganic protective coating on nanocrystals. Of course, this brings its own problems in that the anions then give the surface an overall negative charge, making the nanocrystals repel each other, which is undesirable if the aim is to make them pack neatly together in a layer.

In previous work the researchers employed ammonium and hydrazinium cations to counteract this repulsive effect and to balance the surface charges. Those cations decomposed into gaseous fragments upon mild heating and could not be used to tailor the material properties. However, there has been one example of other researchers utilizing a more complex cation, didodecyldimethylammonium, to make the nanocrystals soluble in non-polar solvents. The researchers in this study have now simplified the concept and opened a whole new range of options by binding lead, calcium, potassium, manganese, or indium ions to their semiconductor nanocrystals. Platinum ions could also be utilized to create photocatalytic arrays of nanocrystals made from the semiconductor material cadmium selenide.

The team found that these cations not only allow them to make fully inorganic systems but also give them a way to hook together individual nanocrystals in the lattice in a way that was not possible with previously utilized capping materials. The result is nanocrystals with increased luminescence efficiency, greater electron mobility, greater catalytic activity, and superparamagnetism.

— David Bradley

See: Angshuman Nag[1], Dae Sung Chung[1], Dmitriy S. Dolzhnikov[1], Nada M. Dimitrijevic[2], Soma Chattopadhyay[2], Tomohiro Shibata[2], and Dmitri V. Talapin[1,2]*, “Effect of Metal Ions on Photoluminescence, Charge Transport, Magnetic and Catalytic Properties of All-Inorganic Colloidal Nanocrystals and Nanocrystal Solids,” J. Am. Chem. Soc. **134**, 13604 (2012). DOI:10.1021/ja301285x

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •

9-BM-B,C • XSD • Materials science, chemistry • X-ray absorption fine structure • 2.1-23 keV • On-siteAccepting general users •