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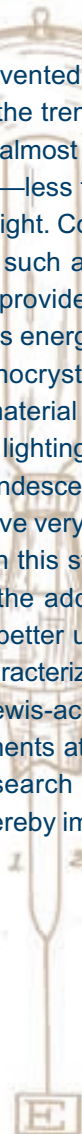
T. A. EDISON.
INCANDESCENT LAMP.

No. 425,761.

Patented Apr. 15, 1890.

TRANSFORMING HOW WE LIGHT THE WORLD

In 1879, Thomas Edison invented a commercially practical incandescent lightbulb. Despite the tremendous success of Edison's invention and the passage of almost 150 years, modern incandescent lightbulbs are not energy efficient—less than 10% of the energy supplied to the bulb is converted to visible light. Compared with incandescent lighting, however, solid-state lighting such as the light-emitting diode (LED) lasts about 50 times longer and provides three or more times the luminous efficacy while using 80% less energy. For the solid-state lighting application, a semiconductor nanocrystal ("quantum dot") of indium phosphide (InP) is a promising material because its properties have the potential to give blue LED-based lighting the appropriate color rendering to compete aesthetically with incandescent lighting. However, current synthesis methods of this material have very poor photoluminescence yields, less than 1%. The researchers in this study report achieving yields with InP particles of 10% to 50% by the addition of a Lewis acid (cadmium oleate or zinc oleate). To form a better understanding of the mechanism behind this improvement, they characterized the structure and composition of both the core and surface of Lewis-acid-modified InP quantum dots by using x-ray absorption measurements at the APS, as well as other characterization techniques. This research could lead to more widespread adoption of solid-state lighting, thereby improving global energy efficiency.



WITNESSES:

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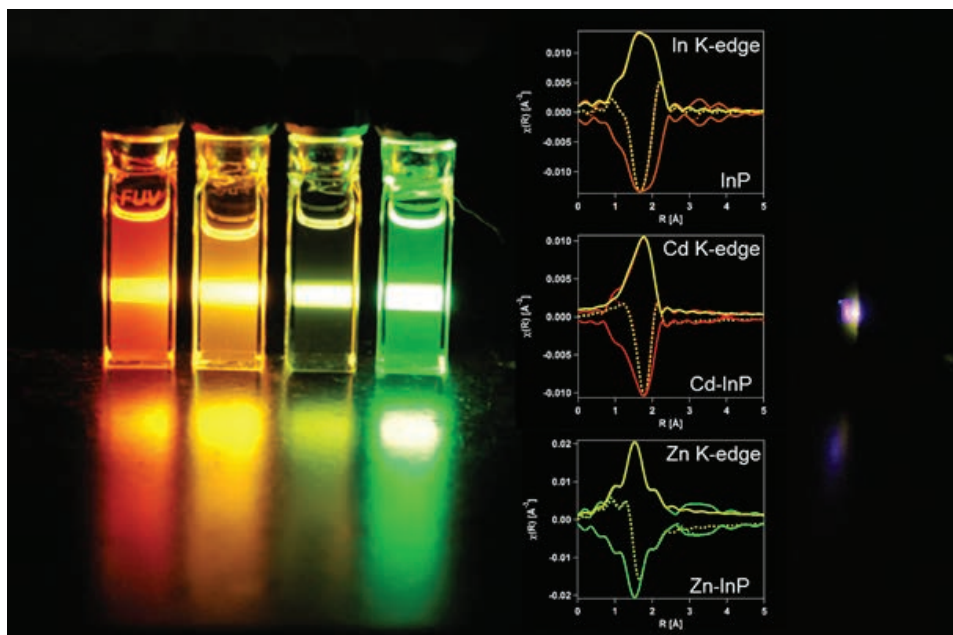


Fig. 1. Color tunability of modified InP quantum dots (left). The extended x-ray absorption fine structure spectra on the right show experimental and quantitative fits (yellow curves) of the first coordination shell. Spectra obtained at the APS.

For synthesis of the InP quantum dots, $P(\text{SiMe}_3)_3$ is injected into a hot solution (315°C) of indium oleate. Particle nucleation and growth occurs rapidly, where the continuous size increase is monitored by ultraviolet-visible spectroscopy. The InP solution is post-synthetically modified through thermal treatment with metal carboxylates. Heating zinc or cadmium oleate with InP quantum dots at 200°C for several hours resulted in photoluminescence quantum yields of 10%-20% with zinc and 20%-50% with cadmium, significant improvements over that with current synthesis methods. Notably, in addition to photoluminescence turn-on, the authors found that the absorbance and emission maxima blue-shifted with zinc, and red-shifted with cadmium.

The possibility of cadmium/zinc alloying or shell growth were considered as explanations for the perceived optical shifts, but structural characterization indicated that particle sizes were conserved post-modification. Additionally, the InP lattice was retained as indicated by powder x-ray diffraction. Purification of these luminescent particles revealed the presence of In_2O_3 by-products, indicating the likely displacement of surface indium carboxylates that could thermally decompose into In_2O_3 nanoparticles. Thus, the authors investigated a mechanism in which exogenous metals

exchanged with surface indium.

Transmission and fluorescence x-ray absorption measurements of the samples were acquired at the MR-CAT 10-BM-A,B beamline at the APS. Figure 1 shows examples of extended x-ray absorption fine structure spectra collected for each metal species in the quantum dots. The orange, red, and green curves, which represent indium, cadmium, and zinc, respectively, show the distance to the nearest neighbor atoms (x-axis) with contributions to peak shape from coordination number. Quantitative fitting (yellow curves) required a combined environment of metal oxygen and metal phosphide in order to accurately represent the experimental data, verifying the authors' hypothesis that Zn^{2+} and Cd^{2+} were coordinated to the particle surfaces (Fig. 1). In addition, chemical etching experiments demonstrated that metal carboxylates could be stripped from the surface, and the photoluminescence would be effectively quenched. These analyses indicate that cadmium and zinc carboxylates predominantly displace native In^{3+} from the quantum dot surface to bind to phosphide, and that this effect is largely responsible for the observed photoluminescence boost.

A key finding was the ability to tune the absorbance and emission profiles of the quantum dots with no apparent

change in particle size. Importantly, the ability to color tune the luminescence of InP quantum dots without an associated change in particle size may offer a versatile strategy to access novel materials for solid-state lighting. Further examination of other metal ions than Zn^{2+} and Cd^{2+} is essential to formulate a complete picture regarding the mechanism and scope of the improved yield and tunability. — *Joseph E. Harmon*

See: Jennifer L. Stein¹, Elizabeth A. Mader², and Brandi M. Cossairt^{1*}, "Luminescent InP Quantum Dots with Tunable Emission by Post-Synthetic Modification with Lewis Acids," *J. Phys. Chem. Lett.* **7**, 1315 (2016).

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