Colloidal quantum dots for mid-IR detection

Philippe Guyot-Sionnest, Sean Keuleyan, Heng Liu, and Emmanuel Lhuillier

Liquid inks made of quantum dots show promise for a number of uses, including biological fluorescent markers, precursor inks for roll-to-roll solar cells, and now IR detection.

Thermal imaging is a key technology for applications such as safety, night vision, and defense. The technology relies on IR detection, which owes its success to materials such as crystalline mercury cadmium telluride (MCT). This alloy with a precise composition has been developed over the past 50 years. An elaborate growth technique produces the high-quality single-crystalline wafer required for IR detection. Subsequent lithography processing allows pixellation and multiple wavelength detection, which are essential in identifying small temperature differences. However, compared with the very cheap silicon-CCD cameras in the visible range, the materials cost and cooling requirements of IR technology largely restrict the use of thermal imaging to scientific or military applications.

Consequently, several alternatives to MCT have been investigated. Indium arsenide and gallium antimonide semiconductor quantum wells of nanometer thicknesses enable single-crystal materials that approach the quality and spectral response of MCT while potentially lowering fabrication costs and raising the operating temperature. With much lower performance but greatly reduced cost and with no need for cooling, microchip bolometer cameras (a type of thermal detector) have also entered the market as high-end consumer electronics, where they are used, for example, in diagnostics for home insulation, engine trouble, and water leakage.

To retain the higher-sensitivity advantage of photoconduction and photovoltaic mechanisms while lowering the cost and reducing cooling requirements, we explored the potential of colloidal quantum dots. These have emerged in the last decade as promising materials for several applications, including biological fluorescent markers, fluorescent visible materials in phosphors or LEDs, and also as precursor inks for roll-to-roll solar cells. In the past few years, colloidal quantum dot inks have been deposited as thin photoconductive or photovoltaic films in the visible and near-IR. The major property of colloidal quantum dots is the ease with which the optical absorption is controlled.

To make colloidal quantum dots responsive in the mid-IR, we have used the semiconductor mercury telluride (HgTe). In bulk, HgTe is a semimetal because the conduction band minimum and the valence band maximum overlap, and it has no useful photoresponse. In MCTs, HgTe is alloyed with cadmium to tune the absorption gap to any wavelength from the long-wave IR to the near-IR. With a nanocrystal of pure HgTe, we achieve the same tuning range simply by using quantum confinement. With HgTe nanocrystals, a gap opens between the lowest-energy electron state and the highest energy-hole (positive charge carrier) state, and the gap increases as the quantum dot gets smaller. This gap corresponds to the longest wavelength of absorption or emission of the nanocrystal. The colloidal nanocrystals can be...
deposited on any substrate by many techniques. The inset in Figure 1 shows a HgTe quantum dot thin film dried on a glass substrate.

We have shown that HgTe nanocrystals can be synthesized with good size control such that they have a well-defined absorption edge. The colloidal solution inks are then dried as thin films on planar electrodes. As the nanocrystals in a film absorb IR light, electrons are excited from the valence state to the conduction state, and both the electron and the hole can hop from nanocrystal to nanocrystal until they are collected at the metal electrodes, leading to a photocurrent that is measurable at room temperature. By controlling the nanocrystal sizes in the inks from 7 to 14nm, we demonstrated a photoresponse with cut-offs from 2 to 7 µm (see Figure 1). The response time of the detector is much faster than milliseconds and therefore fast enough for imaging applications. The nanocrystal inks are well suited for pixelleted printing on an underlying silicon thin-film transistor matrix. At present, the detectivity of the material is lower than bulk single-crystalline MCT by a couple of orders of magnitude. However, we have literally just started to scratch the surface, in that most of the material is surface and accessible to chemical modification.

There is still basic research to be done and several milestones to pass before commercial applications can be developed. Extending the wavelength to the long-wave IR is important for thermal detection and will require larger nanocrystals of 20–25nm dimensions or different composition. Improving the detectivity of the materials for imaging applications will mostly require reducing the large 1/f noise, an important issue that we are currently investigating. Maximize detectivity will require photovoltaic sensing. We have already investigated n- and p-type HgTe quantum dots and found that the p-type has a better photoresponse.

Another unusual property of colloidal quantum dots is their potential for efficient IR luminescence. We have demonstrated luminescence in relatively narrow bands up to 5 µm, but with still very low quantum yields. The right surface chemistry will lead to brighter nanocrystals that may find other applications as tagging inks in the mid-IR. Infrared technology has made great progress in the past by perfecting single-crystal growth, but costs have remained high. Using inks of colloidal nanocrystals is a promising new approach that has now been demonstrated in the mid-IR.

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Author Information

Philippe Guyot-Sionnest, Sean Keuleyan, Heng Liu, and Emmanuel Lhuillier
The University of Chicago
Chicago, IL

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