Solution-Processed Light Sensors and Photovoltaics

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(Invited Paper)

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Abstract: Solution processed solar cells and photodetectors have been investigated extensively due to their potential for low-cost, high throughput fabrication. Colloidal quantum dots (CQDs) and conjugated polymers are two of the most promising materials systems for these applications, due to their processibility and their tunability, the latter achieved by varying their size or molecular structure. Several breakthroughs in the past year highlight the rapid progress that continues to be made in understanding these materials and engineering devices to realize their full potential. CQD photodiodes, which had already shown greater detectivity than commercially available photodetectors, have now reached MHz bandwidths. Polymer solar cells with near-perfect internal quantum efficiencies have been realized, and improved 3-D imaging of these systems has allowed theorists to link structure and function quantitatively. Organic photodetectors with sensitivities at wavelengths longer than 1 μm have been achieved, and multiexciton generation has been unambiguously observed in a functioning CQD device, indicating its viability in further improving detector sensitivity.

Solution-processed semiconductors are fabricated with ease, at low cost, and on any reasonable substrate including a flexible one. Both polymer and colloidal quantum-dot-based devices continue to show promise to replace current commercially available technologies, and a number of breakthroughs in the past year have brought them significantly closer to that goal by advancing our understanding of device operation and by highlighting ways to harness absorbed photons more efficiently.

Photodetectors, which underpin the sensitive capture of digital images, saw several major leaps forward in the past year. First, 2009 saw the advent of the first sensitive megahertz-bandwidth solution-processed photodetectors [1]. Earlier years had seen huge advances in sensitivity but, by exploiting photoconductivity, often did so at the expense of speed [2]. The realization of a fully depleted Schottky photodiode employing 1.55-um-bandgap colloidal quantum dots overcame slow diffusive transport in these materials. The resultant devices exhibited D^* (normalized detectivity) in the 10^{12} Jones, competing with sensitivities achieved by room-temperature InGaAs detectors. The colloidal quantum dot devices provided light sensing across the entire spectrum spanning 400 nm to 1.6 um (see Fig. 1).

A new avenue to even further-enhanced sensitivity—one distinctive to quantum solids—was proven in device form. Multiple-exciton generation (MEG), a process in which a single photon creates more than one excited electron-hole pair, has gained attention due to its potential for increasing the sensitivity and efficiency of photodetectors and photovoltaics. Despite this interest, evidence for MEG has so far been confined to spectroscopic signatures in ultrafast experiments which probe the relaxation dynamics of excitons in order to infer the presence of MEG [3]. An optoelectronic device

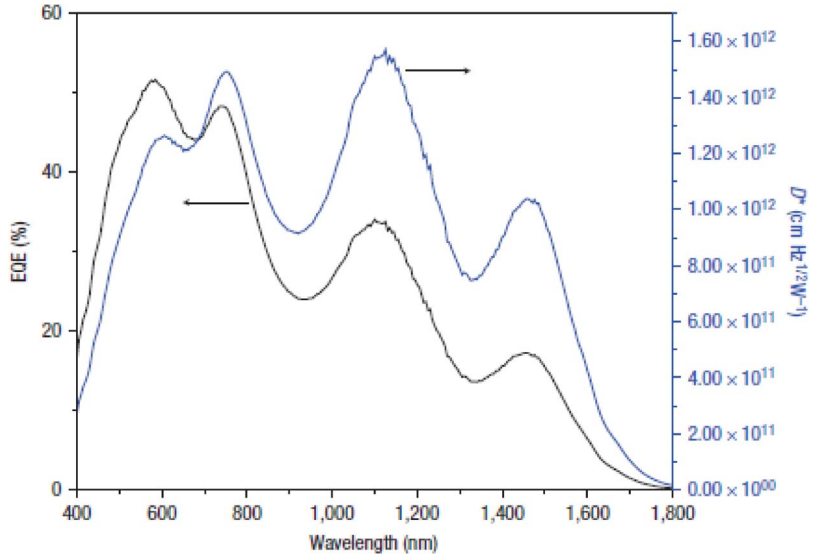

Fig. 1. Spectral responsivity of a solution processed quantum dot photodetector.

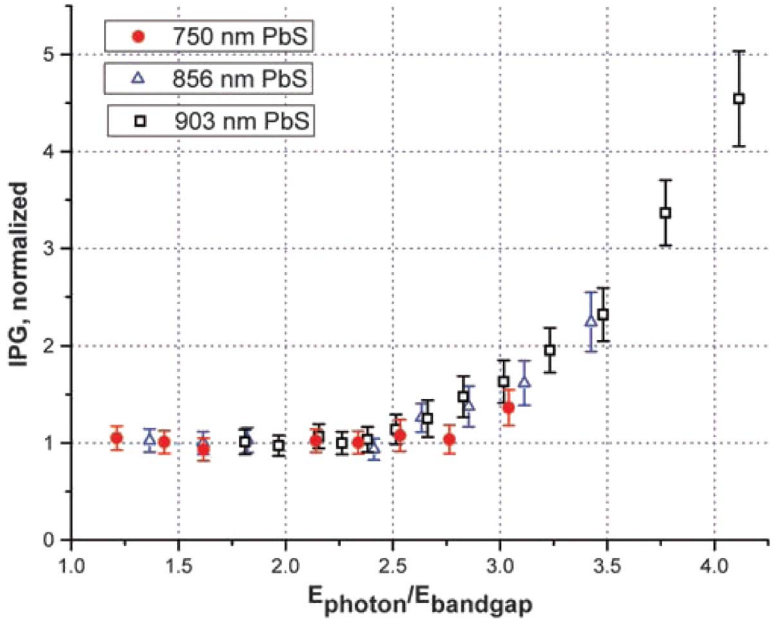

Fig. 2. Internal photoconductive gain as a function of photon energy for CQDs of three different sizes, showing increased sensitivity for photon energies above $2.7E_g$ as a result of MEG.

showing increased photocurrent at photon energies of more than twice the bandgap $(2E_g)$ could help prove not only the existence of MEG but its usefulness in enhancing device performance as well. 2009 saw the arrival of such a device in the form of a solution-processed photoconductive photodetector [4]. Consisting of a film of infrared-bandgap colloidal quantum dots addressed using coplanar electrical contacts, the device showed constant internal photoconductive gain as a function of photon energy for photon energies below $2E_g$. As the photon energy was increased to $2.7E_g$ and beyond, which is the MEG threshold in these materials, the internal gain grew significantly, reaching nearly four times the long-wavelength value when the photon energy reached $4.1E_g$ (see Fig. 2). MEG was thus harnessed to create a more sensitive photodetector.

Because they offer convenient integration combined with exceptional sensitivity and speed, these materials became poised for incorporation into commercial imaging arrays. This dream became a reality [5], with a multimegapixel light imager being created based on a CMOS silicon integrated circuit providing pixel read-out and a continuous 100%-fill-factor top-surface colloidal quantum dot layer providing high-performance low-light imaging.

Photovoltaics for energy conversion saw major advances as well. Polymer bulk heterojunction solar cells had seen many years of rapid progress, reaching 5% solar-power-conversion efficiencies in 2008. In 2009, three separate groups reported a significant further advance, creating bulk heterojunction solar cells with efficiencies above 6% [6]–[8]. All of the groups exercised careful control over nanoscale separation between electron-donating and electron-accepting phases to achieve optimal exciton dissociation and charge transport, *emphasizing the crucial role these two processes play in efficient device operation*. The best devices achieved near-perfect internal quantum efficiency (electrons collected for every photon absorbed). Combined with careful manipulation of the optical field in the device by the introduction of a transparent TiO_x spacer layer, this resulted in impressive short-circuit current densities greater than 10 mA/cm^2.

These findings put an even sharper focus on the critical importance of nanoscale morphology in polymer photovoltaics—and as such mandated further advances in its detailed characterization. Rough estimates of morphology from AFM [9], [10], TEM [11], or various photocurrent mapping techniques [12]–[14] are instructive, but the direct morphological information obtained from these techniques tends to be confined to surface or in-plane morphology of the films, while both exciton dissociation and carrier transport depend sensitively on the bulk and out-of-plane domain morphology as well. 2009 heralded nanometer-scale mapping of the 3-D morphology of polymer/ZnO bulk heterojunction solar cells, enabling quantitative correlation of device performance with nanoscale morphology [15]. The roles of transport and exciton dissociation in limiting device performance are today much better quantified.

Colloidal quantum dot photovoltaics saw a similarly brisk pace of progress. These materials offer the potential to absorb not only the visible but the infrared half of the sun's spectrum reaching the earth [16] as well. These devices, which were first reported in 2005 with subpercent efficiencies, [17] rose to multipercent efficiencies in 2009 [18]–[20].

In both polymers and colloidal quantum dots, one of the major outstanding questions is the stability of devices and materials. It is known that, with rigorous encapsulation, commercially relevant device lifetimes may be achieved in organic semiconductor materials and devices [21], [22]. *Polymer solar cells already have shown illumination stability over hundreds of hours, but degrade quickly on exposure to moisture or oxygen,* [23] *while early quantum dot devices exhibited exceptionally short lifetimes upon exposure to air* [24]. It is of interest to build materials that are amenable to processing in minimally controlled environments (ideally room air) and that survive either under ambient conditions or with low-cost encapsulation. One recent report [25] introduces a new concept: the idea of building active photovoltaic semiconductor materials that—rather than being resistant to oxidation—are tolerant of oxidation. Specifically, the materials employed cation-rich surfaces that form oxides that produced shallow, rather than deep, traps, enabling the extension of photocarrier lifetimes without excessively compromising their extraction times [26].

In sum, optoelectronic devices based on printable materials advanced in 2009 both in concept and in quantitative performance. Light sensors achieved photodetection capability comparable with that of their single-crystal counterparts, and photovoltaics made significant progress toward the 10% solar power conversion efficiency often touted as the threshold for commercial competitiveness of low-cost solar technologies. *There remains a great deal of work to do to reach this goal, including understanding and controlling degradation mechanisms to achieve long-term device stability and making devices that absorb fully, and convert efficiently, the IR portion of the spectrum. Finally*, two important issues have shown recent promise and demand further development. Colloidal quantum dots based on heavy-metal-free constituents have shown encouraging initial performance [27] and merit further optimization. In addition, there are initial indications that organic semiconductors can harness infrared light at wavelengths not previously addressed by such materials [28], potentially paving the way to polymer solar cells converting a greater fraction of the sun's broad spectrum.

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