Colloidal quantum dot photodetectors enhanced by self-assembled plasmonic nanoparticles

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Self-assembled colloidal plasmonic silver nanoparticles monolayers were integrated into solution-processed colloidal quantum dot (QD) photodetectors. We observed plasmon enhancement of photodetector responsivity over a board spectrum range (400–600 nm), with a 1.2–1.6 fold enhancement for a 440-nm-thick QD film device and a 2.4–3.3 fold enhancement for a 100-nm-thick QD device. The enhancement behavior was wavelength dependent with higher enhancement factor at longer wavelengths. The origins of responsivity enhancement were discussed. © *2011 American Institute of Physics*. [doi:10.1063/1.3567514]

The pursuit of higher efficiency and lower cost is a constant theme in the field of light-absorbing optoelectronic devices such as photodetectors and photovoltaics. Among various approaches to enhance efficiency and reduce cost, plasmonic structures have received much attention in the recent years. As the result of strong interaction between surface-confined charge oscillations and light, surface plasmons generate strongly enhanced optical power density in the close vicinity of plasmonic structures.[1] By incorporating these plasmon structures into light-absorbing devices, the absorption efficiency of the active material can be increased or the same amount of absorption can be achieved with less volume of material required, which translates to higher efficiency and lower cost.

A plasmon-optoelectronic system can be categorized by the two main parts of such systems, the plasmonic component and the optoelectronic device component, and various combinations of the two have been studied. For the side of plasmonic component, structures explored include sputtered, evaporated, or annealed metal islands,[2–5] colloidal metal nanoparticles (NPs),[6,7] and e-beam or focused ion-beam lithographically patterned nanoantennas.[8,9] The control over the spectral position and line width of the plasmon resonance increases with each method, but the cost of e-beam or focused ion-beam lithography is significantly higher and not practical for large scale production (optical lithography is also used for plasmonic components but the application is constrained to infrared wavelength range[10]). For the side of light-absorbing optoelectronic device component, also quite a few materials and structures have been explored, including bulk and epitaxially grown thin-film semiconductors,[2,3,8–10] PN junction diodes,[6,7] and organic photovoltaics.[4,5] As the individual components as well as the integration structures differ from one another, each of these works offers important insights on the characteristic influence that plasmons have on the particular devices and implications for future application.

In this letter, we studied the integration of colloidal plasmonic particles into colloidal quantum dot (QD)-film photodetectors. We chose this system not only because, as a very promising material for photodetectors and photovoltaics,[11–14] the effect of plasmons on a colloidal QD film device had not been explored yet, but also because the combination of colloidal metal NPs and colloidal QD film was a very desirable one in many ways. First, both colloidal metal NPs and colloidal QD are made by solution-based synthesis which is well suited for large scale production. Second, they can be easily deposited though processes such as self assembly, drop-cast, spin-cast, or spray-on methods. Third, due to the result of versatile deposition method, they can be integrated on a wide variety of substrates ranging from Si wafers, glass substrates, to flexible polymer substrates. Therefore, the integration of colloidal metal NPs and colloidal QD film proffers a promising candidate for future solutions of mass-production scalable low cost light-absorbing optoelectronic devices.

The device structure is based on the prior works on nanoscale QD photodetectors,[13,14] which involves drop-casting nanocrystal QDs between electrodes. The 3D top view and cross-section side view schematic drawings of the device are shown in Figs. 1(a) and 1(b). An Ag NP layer is introduced between the QD layer and the glass substrate as the plasmonic enhancer. As the character of the fabrication approach we adopted here is long-range uniformity rather than precise controlling of individual particle positions, we used 40 μm wide-gap electrodes to ensure that the measurement results represent large-scale average effect.

To fabricate the device, the electrode-patterned substrate was first cleaned by oxygen plasma and treated with 3-aminopropyltriethoxylsilane (APTES). Then a monolayer of carboxylated Ag NPs, with a nominal diameter of 80 nm and an extinction peak at ~480 nm in solution, was self-assembled to the substrate. We found that using a high concentration colloidal solution (1 mg/ml) with relatively short assembly time (10 min) was critical to obtaining uniformly distributed high density Ag NP monolayers. The optimized recipe yielded an average density of 42 particles/μm^2 on glass substrate. Figures 2(a) and 2(b) show the dark-field microscope images of electrode-patterned substrate before and after the Ag NP deposition, respectively. The scattering spectrum peak of Ag NPs self-assembled on glass substrate was determined to be at 415 nm [Fig. 2(c)]. Following the QD photodetector fabrication procedures described in Ref. 14, partially ligand-removed CdSe/ZnS QDs with photolumi-

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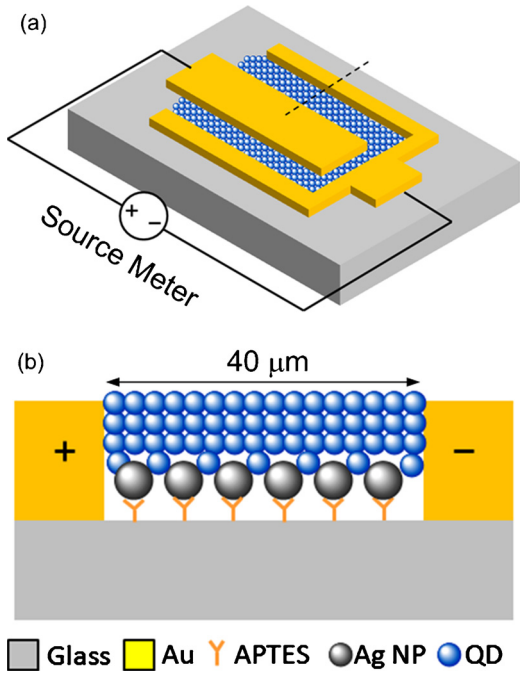

FIG. 1. (Color online) Schematic drawings of a plasmonic QD photodetector. (a) 3D top view schematics, and (b) cross-section view along the dash line in Fig. 1(a).

nescence at 640 nm were drop-cast onto the substrate. By using different precast QD solution concentrations, devices with different film thickness were fabricated.

To investigate how Ag NPs influence the performance of QD photodetectors, photocurrents generated at different wavelengths of illumination was measured and the result was

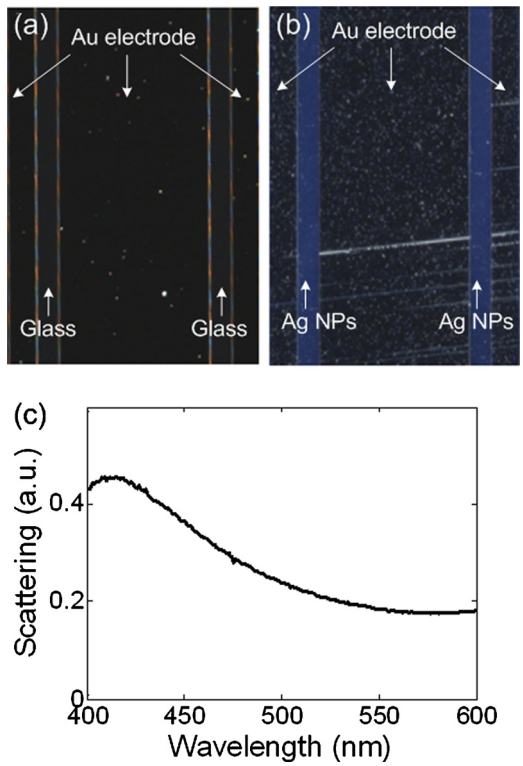

FIG. 2. (Color online) Plasmonic Ag NP deposition by self-assembly process. Dark field images of an electrode-patterned substrate (a) before, and (b) after Ag NP deposition. (c) Dark field scattering spectrum of Ag NPs on glass substrate. A resonance is shown at 415 nm.

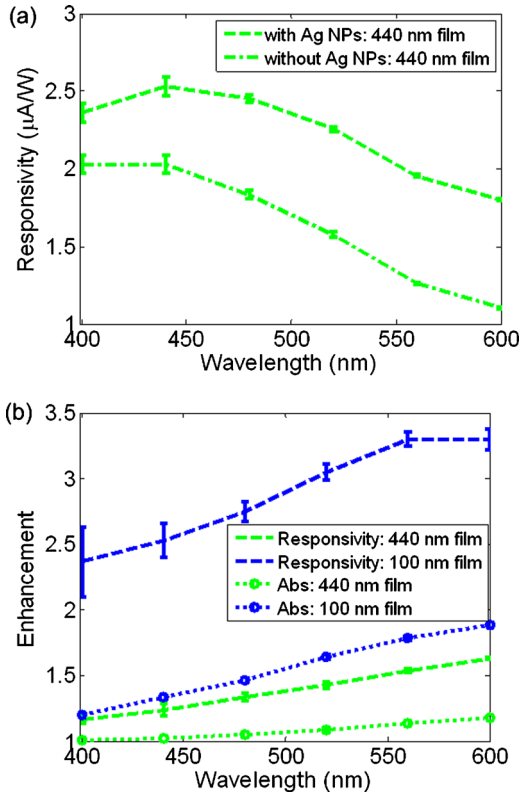

FIG. 3. (Color online) Device responsivity and enhancement results. (a) Responsivity for two QD photodetectors of 440 nm film thickness with (dashed line) and without (dashed-dotted line) Ag NPs. (b) Dashed lines: responsivity enhancement for devices with 440 nm [gray (green online)] and 100 nm [black (blue online)] film thicknesses. Dotted lines: absorption enhancement of QD film with 440 nm [gray (green online)] and 100 nm [black (blue online)] film thicknesses. Devices were biased at 20 V for responsivity measurement results in Figs. 3(a) and 3(b).

compared with QD photodetectors processed from the same QD solution on the same substrate but without Ag NP integration. The incident light came from a halogen lamp which was then passed through a monochromator with proper focusing optics and projected onto the sample surface. For each wavelength, about 200 data points for photocurrent were collected in a duration of 120 s with the device biased at 20 V and the average was used to represent the photocurrent at that wavelength. It is worth mentioning that careful comparison of dark currents was made between devices with Ag NPs and that without Ag NPs before QD deposition as well as after QD deposition. No consistent difference was measured in both cases which indicated that the Ag NPs did not cause noticeable leakage current at present particle density level. Device responsivity was calculated based on the average photocurrent and the power of light incident upon the active area of the device. Figure 3(a) shows the responsivity of two devices, one with Ag NPs and one without, over the spectral range from 400 to 600 nm. Film thickness measurement by a profilometer confirmed that both QD photodetector devices had a film thickness of ~440 nm. The responsivity of the device with Ag NPs was higher than that without Ag NPs over the entire measured spectral range. Responsivity enhancement, which is defined as the ratio of responsivity of a device with Ag NPs to one that without Ag NPs, was plotted (green dash line) in Fig. 3(b). It was noticed that the responsivity enhancement increased with wavelengths. This phenomenon was expected due to two factors.

First, as indicated by both simulation (Ref. 15) and film absorption measurement, the plasmon resonance of Ag NPs shifted to above 700 nm region (with the exact spectral positions to be 720 nm experimentally and 750 nm theoretically) after the QD deposition due to the dielectric constant change of the environment materials. As a result, the longer wavelength part of the measured spectrum lay closer to plasmon resonance and was enhanced more. Second, the wavelength-dependent absorption of QD film allowed more longer-wavelength portion of the incident spectrum to reach the plasmonic particles, and therefore relatively increased the input to plasmonic components at the longer wavelength. This effect of QD-film altered input spectrum for plasmon NPs was further confirmed when we measured the enhancement of a set of devices with thinner QD films. As shown in Fig. 3(b), the responsivity enhancement for a 100 nm QD film (blue dashed line) was higher across the spectrum as the thinner QD film allowed more input power to transmit to plasmon particles.

In a recent study of individual epitaxially grown QD-metal NP complex, enhanced optical near field and the resulting absorption enhancement has been identified as the sole cause of QD photoluminescence enhancement.[16] This absorption enhancement is also the most often accounted-for mechanism in studies on various plasmonic light-absorbing optoelectronic devices.[2–9] It would be interesting to investigate how the absorption enhancement compares with responsivity enhancement in the case of plasmonic QD photodetectors. To do this, we measured the absorption of QD films with and without Ag NP integration and the absorption enhancement was plotted in Fig. 3(b) (dotted lines). As expected, the absorption enhancement for both film thicknesses lay above 1 and increased with wavelength. However, there was a noticeable difference between absorption enhancement and responsivity enhancement, especially for the thinner 100 nm QD film. Considering that the film absorption includes the absorption from Ag NPs which does not contribute to photocurrent, the difference between device responsivity enhancement and effective absorption enchantment of QDs is even bigger. The higher enhancement of responsivity suggested that, for plasmonic QD photodetector devices, there were additional performance enhancement mechanisms besides the enhancement of QD film absorption. One possibility is that the Ag NPs layer also facilitates the transportation of photoexcited carriers in such devices by introducing additional conduction paths between QDs—the thinner QD film device exhibiting a bigger difference likely due to a bigger portion of QD film within the vicinity of Ag NPs.

In summary, we fabricated solution-processed QD photodetector integrated with a self-assembled plasmonic NP layer and studied the effect of plasmon NPs on the performance of QD photodetector. Enhancement of responsivity for a spectrum range from 400 to 600 nm was observed and the enhancement factor increased with wavelength. The wavelength dependent behavior of responsivity enhancement was caused by (1) the relative position of measured spectrum to that of plasmon resonance of Ag NPs, and (2) the altered effective input spectrum for plasmonic NPs due to wavelength dependent absorption of QD film. As expected, QD photodetector devices with thinner film thickness exhibited larger responsivity enhancement. Increased absorption of QD film due to enhanced optical near field by plasmonic NPs was identified as one of the enhancement mechanisms. Additional enhancement mechanism was possibly due to the metal NP-assisted photoexcited carrier transportation during the device operation. Our highly industry-transferable all-solution-processed device design suggests a way plasmon enhancement can be implemented in commercial light-absorbing optoelectronic products.

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