Self-Assembly and Optical Characterization of Semiconductor and Metallic Nanocrystal Monolayers and Multilayers

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Abstract

Interactions between semiconductor and metallic nanocrystals are the subject of intensive investigations. Enhanced photoluminescence (PL) yield of quantum dots in the presence of notable nanoparticles or nanohole arrays has potential applications in light-emitting diodes (LED) and sensors. Surface plasmon resonances (SPR) are believed to either increase the PL efficiency by enhancing the local exciting field or cause nonradiative damping due to energy transfer through an inverse route.

Introduction

We studied the collective interactions, in terms of linear and nonlinear optical properties, between cadmium selenide (CdSe) quantum dots, rods, cadmium telluride (CdTe) tetrapods and gold (Au) nanoparticles (NPs), comprised in monolayers and multilayers. Ultra thin films that incorporated NPs with a size of several nanometers were successfully created via an interfacial evaporation induced self-assembly (EISA) process. These films assembled on the surface of water within a polymethyl-methacrylate (PMMA) polymer matrix and were then transferred to desired substrates. Similarly, ultra thin films of pure PMMA were assembled, acting as a dielectric spacer between the two parallel layers of semiconductor and metallic NPs. Atomic layer deposition (ALD) was also utilized, allowing us to achieve precise control on the thickness of spacing layers. Finally, patterning of PMMA supported nanocrystal monolayer thin films was demonstrated. Our results indicate that the PL is affected by the distance between the semiconductor and Au nanoparticles.

Fabrication of Thin Films

Solutions of PMMA, CdSe nanocrystals or quantum dots, and Au nanocrystals, in an appropriate ratio, were dissolved in toluene. One drop of the solution was carefully released over a deionized water surface sitting in a Petri dish. The suspension of nanocrystals spread out over the surface and a thin film formed through interfacial evaporation-induced self-assembly as shown in Figure 1. The thin films consisted of the nanoparticles embedded in the PMMA polymer matrix. After the toluene evaporated, the thin film was captured on a substrate of our choice by submerging the substrate and bringing it up through the thin film. The sample was then left to dry undisturbed. The weight fraction of CdSe to Au nanocrystals within the solution was varied to explore the effect on photoluminescence. We also prepared multilayer thin films of the ratio-varied solutions to explore how stacking the layers would affect the PL.

First, we attempted to fabricate a binary nanocrystal superlattice from CdSe and Au nanocrystals dispersed with PMMA in toluene and let them co-assemble on the interfacial surface. However, the transmission electron microscopy (TEM) image in Figure 2 clearly indicates that isolated islands of nanocrystals with severe overlapping formed instead of a homogeneous monolayer thin film. Nevertheless, significant PL quenching was observed due to appropinquity of the two different types of nanocrystals when compared to the PL readings from a solution and monolayer thin film comprised solely of CdSe quantum dots.

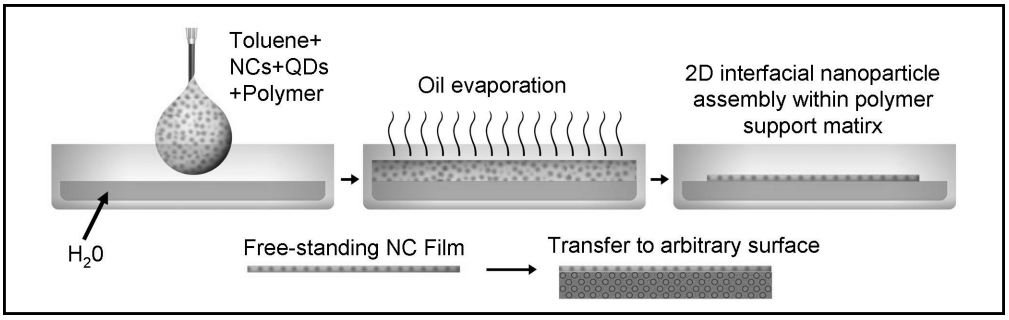


Figure 1: Schematic detailing evaporation induced self-assembly (EISA). A) Solution dropped onto surface, B) Oil evaporation, C) 2D interfacial nanoparticle assembly within polymer support matrix, D) Free-standing thin film, and E) Transfer to arbitrary surface.

Believing that the close proximity of the Au nanocrystals to the CdSe nanocrystals caused the quenching effect, we redesigned our experiment to further distance the two NPs by placing a dielectric spacing layer between a thin film composed of Au NPs and another thin film of CdSe NPs. In addition, this new strategy allowed us to tune the width of the spacing layer and this distance became the independent variable in our experiments.

Thin Films with Dielectric Spacing Layer

One thin film, composed of Au NPs, was transferred onto a glass substrate. Figure 3 shows how the solution composed solely of Au nanocrystals and PMMA creates a monolayer thin film, where the Au NPs do not coagulate, but spread out into a thin even film. Thin films composed solely of PMMA polymer were then captured on top of the Au nanocrystal layer until the desired thickness was obtained. Finally, the last thin film layer composed of CdSe NPs and PMMA was captured on top of all the other thin films. As the thin film layers were added to the sample, the surface of the sample became increasingly uneven. When the surfaces of the samples were scanned with a laser, the photoluminescence readings had no correlation to the number of PMMA spacing layers.

Seeking to better control the thickness and quality of the dielectric spacing layer, we utilized atomic layer deposition (ALD) to deposit a layer of amorphous SiO_2. We prepared 15 samples of 2 cm^2 silicon wafer chips by capturing a single Au ultra thin film layer on each wafer through EISA. The samples were then plasma-etched in order to render the surface hydrophilic and placed within the ALD instrument. All samples, heated to 50°C, were exposed to alternating cycles of vaporized $SiCl_4$ and H_2O in order to build up a dielectric spacing layer. One sample was removed from the instrument after every 30 cycles of deposition. A final thin film layer of CdSe and PMMA was captured on top of the amorphous SiO_2 to form a sandwich structure.

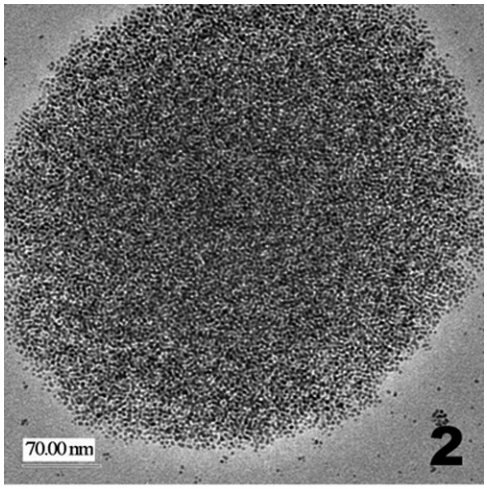
Electron beam lithographic patterning of Au and PMMA monolayer thin films has also been demonstrated. As a positive photoresist, PMMA can be washed away in the developer when exposed to light. Figure 4 shows an optical microscopy image of a patterned thin film. The diameter of the wheel is approximately 40 μm and the width of the lines is about 1 μm. Our patterning of these thin films suggests the ability to use interfacial assembly in device fabrication.

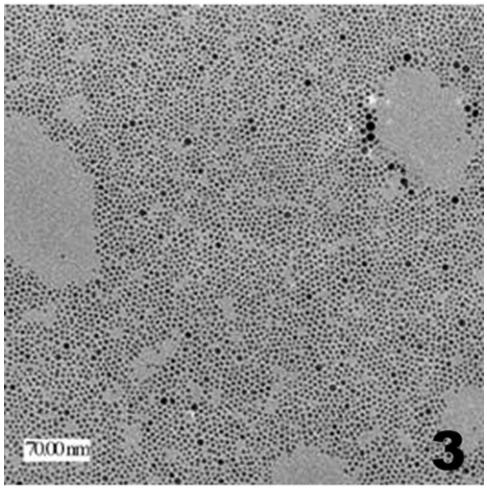
Results

We were able to successfully use interfacial assembly to create mono and multilayer thin films that incorporated semiconductor and noble nanocrystals. We also explored novel methods to create spacing layers between the two parallel thin films of CdSe and Au nanocrystals. Our results indicate that the photoluminescence of semiconductor nanocrystals can be affected by the appropinquity of noble metallic nanocrystals.

Acknowledgments

I would like to sincerely thank Professor Jeff Brinker and my mentor, Shisheng Xiong, for their guidance and support. Special thanks are also extended to the Brinker and Boyle Groups, the UNM coordinators, the National Science Foundation, and the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program.





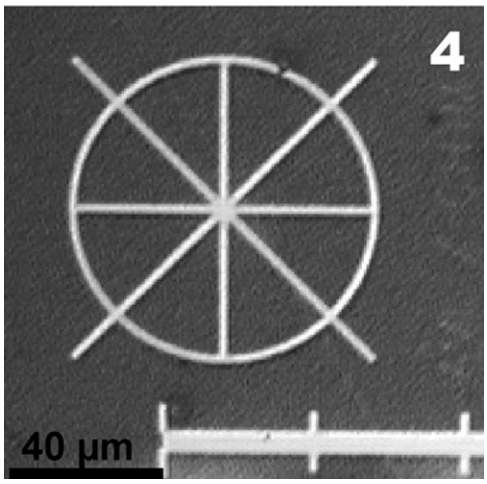


Figure 2, top: TEM image of CdSe / Au NP thin film supported by a PMMA polymer matrix.

Figure 3, middle: Ultra thin monolayer of Au NPs supported by PMMA polymer matrix.

Figure 4, bottom: Optical microscope image of patterned Au monolayer thin film.