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Optical properties of surface-patterned nanostructures

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Abstract

This concepts article describes our developments in nanopatterning related to photonics. We have a nanopatterning toolkit that can generate functional, nanostructured surfaces at nm-length scales and over cm^2-areas in a single (or small number of) step(s). This paper will focus on three examples of surface-patterned nanostructures and their optical properties: (i) one-dimensional arrays of metallic nanoparticles; (ii) arrays of small-diameter ZnO nanowires; (iii) mesoscale structures of CdSe/ZnS nanocrystals. The potential for advances in nanopatterning to contribute to a broad range of light-based applications will be discussed.

Keywords: Soft lithography; Nanofabrication; Semiconducting nanowires; Metallic nanoparticles; Near field scanning optical microscopy; Photoluminescence

1. Introduction

Rational engineering of the physical and structural properties of surfaces has enabled many exciting observations, from the measurements of single bio-molecule behavior to the significant enhancements of molecular properties. The detailed folding of ribozyme molecules immobilized on substrates and the enhanced Raman spectra of molecules adsorbed on metallic particles are such examples [1,2]. The construction of patterned surfaces—substrates with functional areas that are arranged in an ordered manner—with feature sizes similar to relevant chemical and materials structures is critical for innovative studies and applications.

The controlled growth and assembly of optically active nanoscale materials is important to many interesting scientific problems, including two-dimensional photonic crystals, single nanowire lasers and chemical and light-based sensors [3–5]. The ability to define the position, density and size of nanostructures on surfaces enables detailed studies not only of the properties of single particles but also the collective properties of their assemblies. For example, one-dimensional (1D) arrays of metallic nanoparticles are predicted to exhibit intense and extremely narrow plasmon resonances compared to individual or disordered arrays of nanoparticles [6–8]. Nanoscale fabrication techniques are well-suited for manipulating nanostructures on surfaces because the critical feature sizes are of the same magnitude. In particular, soft lithographic nanopatterning has been used to template the growth of small (20 nm) inorganic salt crystals in ordered periodic arrays of 100 nm wells and to generate feature sizes as small as 30 nm in photoresist and metal over areas covering 1 $in.^2$ [9]. Laser-assisted embossing has also successfully generated nanowells in silicon with zL-volumes; these nano-"beakers" have been used to grow individual semiconducting nanocrystals and metallic colloids [10].

This paper will describe our developments in nanopatterning to address important problems in chemistry, materials and photonics. The broad application of unconventional nanofabrication techniques has significant promise for the discovery of new fundamental principles in physical chemistry and the advancement of sensitive and powerful analytical techniques. We have a nanopatterning toolkit that can generate nanostructured surfaces with three-dimensional features at nm-length scales and over cm^2-areas in a single (or small number of) step(s); moreover, these patterns exhibit hierarchical order and selective chemical functionality from which to build or assemble new types of mesoscale (100–1000 nm) structures. In this concepts article, we will discuss three examples of surface-patterned nanostructures and their optical properties: (i) 1D arrays of metallic nanoparticles; (ii) arrays of small-diameter ZnO nanowires; (iii) mesoscale

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structures of CdSe/ZnS nanocrystals. These investigations exploit nanopatterning to control nm-sized components and employ local scanning probe methods to explore the detailed properties of nanomaterials.

2. Experimental

2.1. Nanofabrication using soft lithographic techniques

(i) *Preparation of the PDMS mask*: Nanoscale patterns in photoresist (the master) were generated by phase-shifting photolithography (PSP) [9] using composite PDMS masks [11]. Feature sizes 100–500 nm were produced in positive-tone resist (Shipley 1805) by exposing UV-light through a PDMS mask patterned with lines, and then rotating the mask and performing a second exposure. If the second exposure was through the same mask but rotated by 90° (60°), square (hexagonal) patterns were formed. If the second exposure was through a mask patterned with lines having a different spacing but rotated by 90°, rectangular or 1D lattices were formed [12]. A modified PDMS pre-polymer was spin-cast onto the nanopatterned master and cured at 70 ° C for 1 h to produce a nanopatterned elastomeric mask.

(ii) *Preparation of photoresist templates*: Composite PDMS masks with bas-relief features (50–500 nm posts; 3 μm posts and 5 μm lines spaced by 5 μm) were placed in conformal contact with a layer of negative-tone photoresist (ma-405, MicroResist Technology) supported on different substrates (sapphire, indium tin oxide (ITO)/glass and cleaned glass coverslips). This assembly was exposed to a broadband UV source for 4–8 s. The samples were then developed in Remover PG for ∼1 min to form photoresist templates of recessed patterns with critical feature sizes as small as 100 nm.

2.2. Nanopatterning arrays of metallic nanoparticles

(i) 1D arrays of silver nanoparticles were formed by evaporating 30 nm of Ag onto photoresist templates of 250 nm × 450 nm holes spaced by ∼500 nm (long axis) patterned on ITO-coated glass slides. These 1D arrays of holes were separated by 10 μm from other 1D arrays of holes. Following lift-off in acetone, 1D arrays of silver nanoparticles covered a square centimetre area. (ii) Arrays of gold nanoparticles were prepared by: (1) deposition of 15 nm of gold onto sapphire substrates; (2) patterning photoresist posts (200–500 nm in diameter) on the gold film in square, hexagonal and rectangular arrays by PSP using a nanopatterned PDMS mask; (3) etching the patterned substrates with a wet chemical etchant; (4) lifting-off the photoresist in acetone. The gold dots were then placed in a 1-in. tube furnace to catalyze the growth of ZnO nanowires.

2.3. Optical characterization of surface-patterned nanostructures

Near-field scanning optical microscopy (NSOM) topographic and optical images were acquired using an Aurora-3 NSOM operated in transmission mode. In this mode, samples are illuminated by a point source of light from the optical fiber tip, and the light transmitted through the sample is focused onto a detector. The 1D arrays of silver nanoparticles were illuminated by a white light source through an Al-coated tip; CdSe/ZnS quantum dot mesostructures were excited using 488 nm light. The photoluminescence (PL) of ZnO nanowires was measured using a cw He–Cd laser (325 nm). The PL was dispersed through a SPEX Triax 500 spectrometer with a 600 lines/mm grating and detected by a nitrogen-cooled CCD camera.

3. Results and discussion

3.1. One dimensional arrays of metallic nanoparticles

Metallic nanoparticles can amplify and confine light through the optical excitation of their localized surface plasmon resonance [13]. The assembly or patterning of nanoparticles into 1D or two-dimensional (2D) arrays has promise for plasmon-based applications, including plasmonic waveguides, switches, modulators and molecular sensors [8,14,15]. The most common method to fabricate 1D arrays of metallic (usually silver or gold) nanoparticles is electron-beam lithography because it can easily generate patterns with feature sizes less than 100 nm; however, this serial technique is limited to writing small (10–100 μm) areas in a typical patterning step. Using tools from our suite of nanopatterning methods, we can fabricate 1D arrays of metallic nanoparticles in a single exposure step over large (cm^2) areas. NSOM is an ideal scanning probe technique to investigate the optical properties of metallic nanostructures because of its high spatial and optical resolution capabilities.

We patterned 1D arrays of silver nanoparticles to study their collective behavior in the near-field. NSOM topographical and optical images were measured simultaneously on chains of 250 nm × 450 nm oblong silver nanoparticles (Fig. 1). The raw optical images collected through the sample exhibited a complicated pattern because of a combination of blocked, scattered and transmitted light through the sample (Fig. 1B). To discriminate among these effects, we inserted a combination of bandpass filters (bandwidth ±20 nm) between the sample and the detector and polarizers between the light source and the sample. Different bandpass filters (centered at 600, 650 and 700 nm) produced different optical images. In particular, when the wavelength of the filter was centered near the plasmon resonance for the silver particles, an enhancement in the optical image appeared *in-between* the patterned silver nanoparticles (Fig. 1C). Also, the enhancement between the metallic particles was present

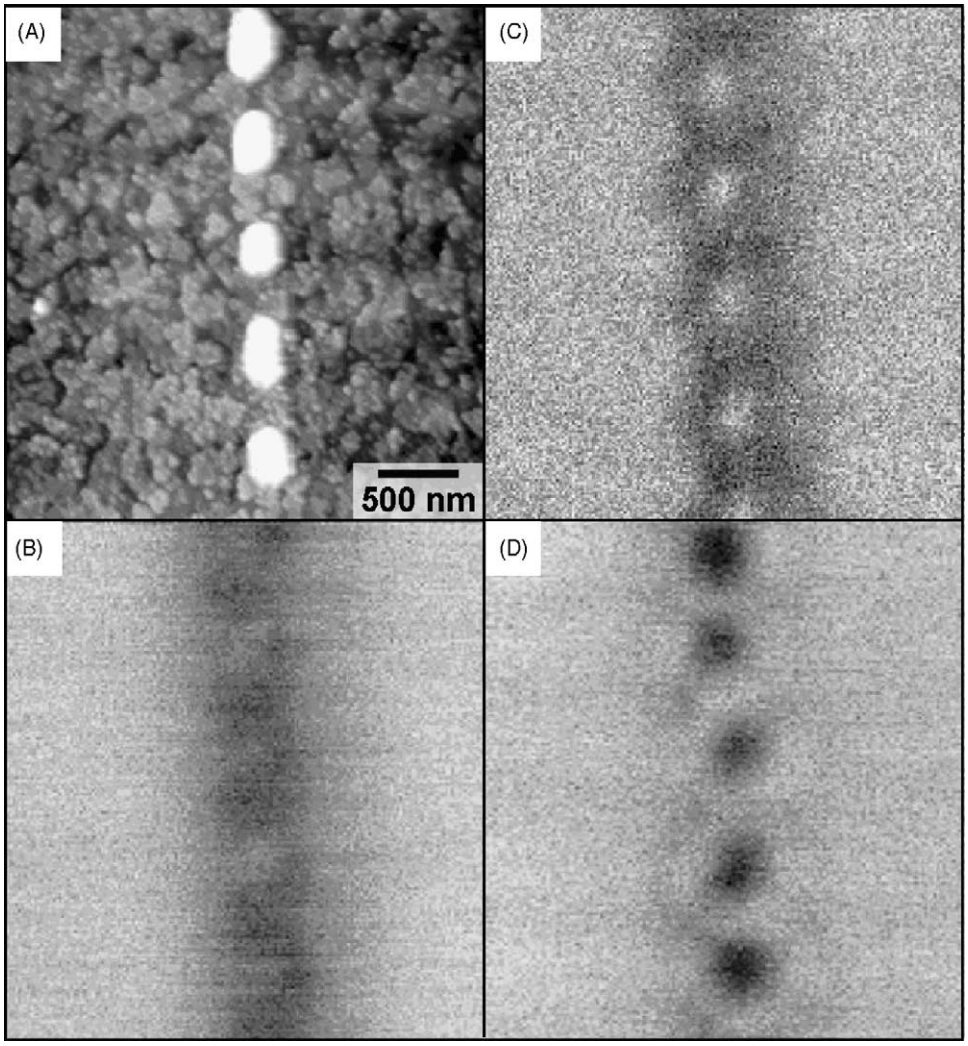

Fig. 1. NSOM topograph (A) and optical images (B–D) of a portion of a 1D array of silver nanoparticles. Optical images were acquired in transmission mode (B) without filters; (C) with a bandpass filter centered at 650 nm; (D) with a bandpass filter centered at 700 nm. All of the image sizes are the same.

only when the light source was polarized perpendicular to the long axis of the arrays. This phenomenon was observed for other 1D arrays of silver nanoparticles of different heights/widths, and the optical images acquired in constant force and height modes showed similar effects. Besides exhibiting interesting collective optical properties as shown by these preliminary investigations, arrays of metallic nanoparticles can also be used as catalysts to direct the growth of semiconducting nanostructures.

3.2. Directed growth of small-diameter ZnO nanowires

ZnO nanostructures are important materials because of their emission in the near-UV [3,16,17], strong absorption in the UV [18] and field-emission capabilities [19]. ZnO nanowires have been grown from μm^2-sized gold patterns on a variety of substrates using vapor–liquid–solid (VLS) methods; moreover, epitaxial growth on *a*-sapphire substrates resulted in aligned ZnO nanowires [3,20,21]. The ability to direct the growth of 1D ZnO nanowires at specific locations—with periodic order, variable spacing and symmetry—has promise for applications in nanoscale sensor arrays and optoelectronic devices.

We grew small diameter ZnO nanowires from patterned gold dots on sapphire substrates using a VLS process [12]. The source materials (ZnO and graphite powders) were ground and placed inside a quartz tube furnace held at 900 °C, while the patterned substrate was placed downstream. Scanning electron microscopy (SEM) images revealed that arrays of ZnO nanowires grew from the patterned gold dots in square and quasi-1D lattices (Fig. 2). These nanowires are very narrow in diameter (10–15 nm), are relatively long in length (2–10 μm) and often exhibit slight curvature, which we attribute to their high aspect ratios (1:1000) and small diameters. High resolution transmission electron microscopy images (Fig. 2B, left inset) revealed crystalline nanowires with growth along the [0 0 1] direction.

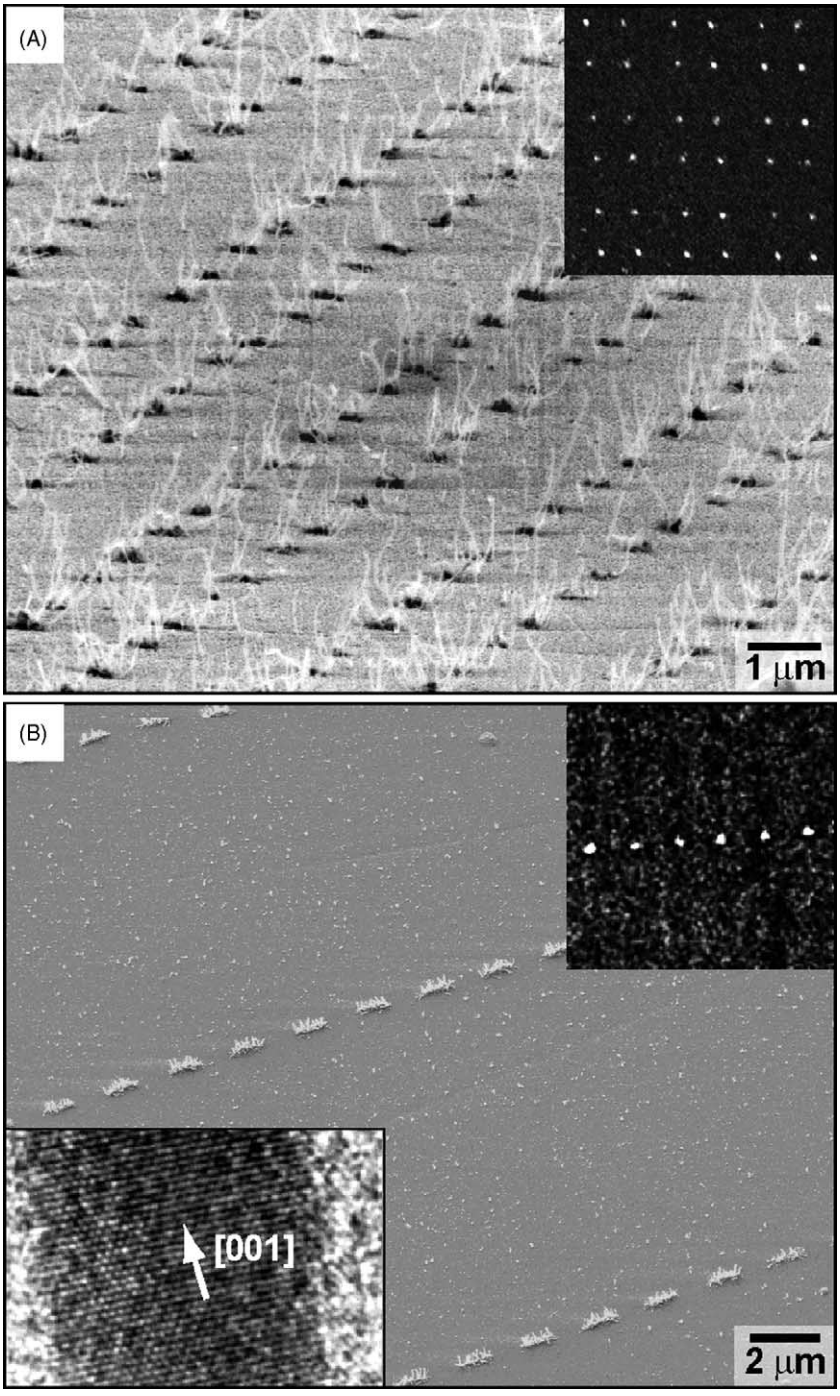

Fig. 2. SEM images of (A) square arrays and (B) 1D arrays of ZnO nanowires grown from gold dots of the same symmetry (top insets). (B, bottom inset) High resolution TEM image of a ZnO nanowire, whose growth direction is along [0 0 1]. Adapted from Ref. [12].

The optical properties of these patterned ZnO nanowire arrays were measured using UV–vis absorption and PL measurements. The PL of ordered ZnO nanowire arrays was obtained using a He–Cd laser (325 nm) as the excitation source. Fig. 3 shows strong room-temperature emission [17] ~374 nm for arrays of ZnO nanowires arranged in a square lattice pattern. The narrow (15 nm) full-width at half-maximum PL peak is another indication of the uniformity of diameters in the arrays of ZnO nanowires. Also, because of the small diameters of the patterned ZnO nanowires, the absorption band edge (Fig. 3, inset) is shifted towards a shorter wavelength (~355 nm) compared to other ZnO nanorods [22,23]. The directed growth strategy to pattern semiconducting nanostructures is quite versatile for materials that can form an alloy with the catalytic metallic nanoparticles. To organize other types of optically active

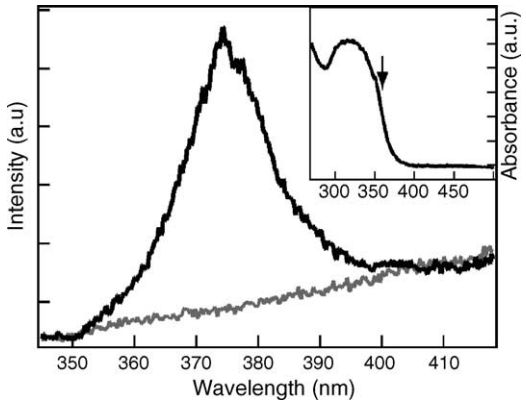

Fig. 3. Photoluminescence spectrum acquired from square arrays of patterned ZnO nanowires. (inset) UV–vis absorption spectrum. The arrow highlights a blue-shift of the absorption band edge. Adapted from Ref. [12].

materials without pre-patterning catalyst, we have developed an approach called template-based assembly, which involves two separate steps: (i) nanomaterials growth and (ii) solution assembly of nanomaterials into a patterned template.

3.3. Template-based assembly of semiconducting quantum dots into mesostructures

Colloidal semiconducting nanocrystals can self-assemble into close-packed solids on thin films, which are interesting for their cooperative physical properties and application in quantum dot lasers and conducting thin films [24,25]. For example, the band-edge PL peak of CdSe quantum dot solids have been observed to red-shift compared to the PL peak of dots dispersed in solution because of dipole-dipole inter-dot interactions [24,25]. Other studies have reported that the absorption edge of CdSe dots red-shifted in solution and in

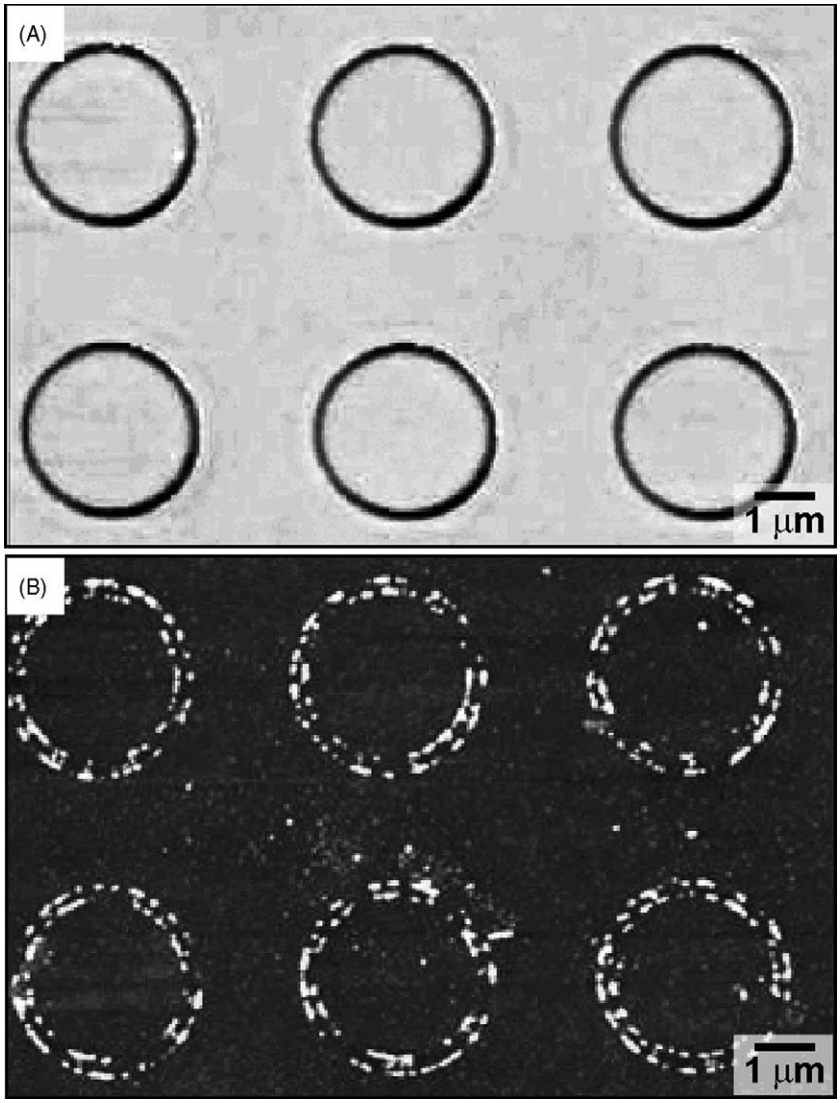

Fig. 4. Atomic force microscopy images of (A) rings formed in negative tone photoresist using phase-shifting photolithography and (B) quantum dots patterned into rings using the template in (A). The height of the quantum dot structures varied between 15 and 50 nm. Adapted from Ref. [27].

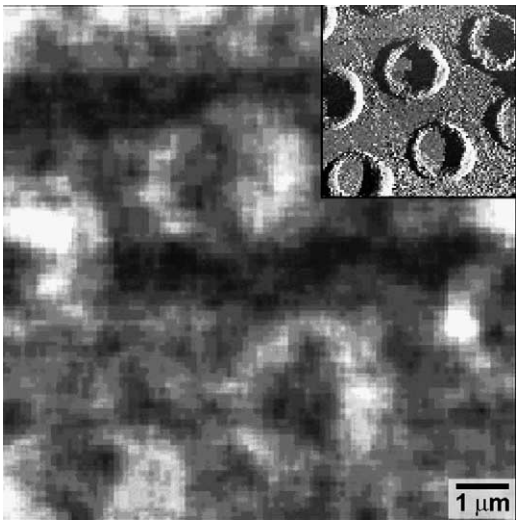

Fig. 5. Fluorescence NSOM image of arrays of quantum dots patterned into ring structures. (Inset) Amplitude image of rings of CdSe/ZnS dots acquired in constant force mode. Adapted from Ref. [27].

close-packed films because of changes in the external dielectric environment [26].

We have used photoresist templates to assemble CdSe/ZnS quantum dots into patterned mesostructures to investigate the optical properties of the nanoscale materials (Fig. 4A and B) [27]. Different sizes of water-soluble quantum dots were assembled into the template by immersing the patterned template in a concentrated solution of highly crystalline nanocrystals for 12–36 h. After removal of the photoresist template by rinsing with acetone, the patterned CdSe/ZnS mesostructures were 15–50 nm tall with critical lateral dimensions ∼100 nm. The patterned structures exhibited PL spectra that were red-shifted (by 5–7 nm) compared to spectra acquired in solution [27]. Using template-based assembly, we achieved a hierarchical patterning of nanostructures—organization over nm^2 (self-assembly of quantum dots), over μm^2 (template shape) and over cm^2 (arrays of template pattern).

The localized emission was characterized from individual quantum dot mesostructures using NSOM. The quantum dots were excited through the NSOM tip with the 488 nm line from a cw Ar-ion laser, and the emission was measured using transmission mode. The light was collected through a holographic edge filter at 488 nm and was focused onto an avalanche photodiode. Fig. 5 shows the spatially resolved emission of the patterned quantum dots; the inset depicts the amplitude image. As expected, the emission from the CdSe/ZnS mesostructures is strongest when the density of the dots and widths of the lines of the patterned CdSe quantum dots is widest.

4. Conclusion

In summary, we have demonstrated how simple nanofabrication techniques can be used to (i) pattern 1D arrays of metallic nanoparticles; (ii) generate catalytic patterns to direct the growth of ZnO nanomaterials; (iii) assemble pre-formed nanocrystals into mesoscale structures. Soft lithographic nanopatterning offers a versatile and general approach for the generation of optically functional, surface-patterned nanostructures. Our preliminary and continuing studies of patterned arrays will focus on how coupling between neighboring nanowires, quantum dots and metallic particles can produce collective optical properties [28]. Such interesting behavior can be exploited in emerging photonic-based applications including arrays of nanoscale light sources, detectors and sensors operating at wavelengths ranging from the UV to near-IR.

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