Metal nanocluster metamaterial fabricated by the colloidal self-assembly

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A new bottom-up approach for fabricating the optical metamaterial is reported. An array of metal nanoparticle clusters can provide both electric and magnetic activity in the optical frequency region through the excitation of the collective plasmon resonance. A two-dimensional square array of gold nanoparticle clusters (nanoclusters) was fabricated by using the template-directed colloidal self-assembly. The optical measurements showed strong extinction peaks in the near-infrared region owing to the electric resonance supported by the nanoclusters. The peak positions were in excellent agreement with the numerical simulations. The metal nanocluster metamaterial represents a promising new architecture for an optical metamaterial that can be fabricated by a scalable bottom-up fabrication technique. © 2009 Optical Society of America

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Optical metamaterial is a class of artificial material whose optical properties can be engineered by designing its subwavelength scale structural unit. The capability of designing optical properties in a metamaterial enables the realization of novel optical properties, such as a negative refractive index, which are not found in natural materials. Applications, such as superlensing and invisibility cloaks, have attracted much attention and are being investigated extensively [1–3]. So far, a split-ring resonator, a nanorod pair, and a fishnet structure have been the most successful in realizing optical metamaterials [4–6]. However, all of these structures require expensive and complicated fabrication techniques, such as electron-beam lithography and focused ion-beam milling. Recently, a new design for the optical metamaterial based on metal nanoclusters was reported [7]. A metal cluster composed of nanosized metallic units can support collective plasmon resonances that may be of an electric or a magnetic nature. Since the resonances are based on plasmons, they occur in the optical frequency region. It is thus possible to build optical metamaterial structures that are electrically or magnetically active. It is also possible to achieve a negative index by combining the magnetically active clusters with thin metal films or metal shells that provide negative permittivity [8]. This concept can be extended to a three-dimensional (3D) structure by assembling clusters of metal spheres. A theoretical study showed that an array of metal sphere clusters exhibits a negative permeability in the optical frequency region [9]. The most exciting aspect of this new design is that this structure can be fabricated by a simple and scalable bottom-up technique, such as the template-directed colloidal self-assembly. In this Letter, we report the experimental realization of the new optical metamaterial architecture based on metal nanoclusters for which we developed the template-directed colloidal self-assembly process.

The structure we aimed to fabricate is a two-dimensional (2D) periodic array of metal nanoparticles, which is shown schematically in Fig. 1. Metal nanoparticles are formed into cylindrical nanoclusters that in turn are arranged into a 2D square array. The nanoclusters can support electric and magnetic resonances, giving a resonant behavior in effective permittivity and permeability, respectively. To fabricate this kind of structure, we used the template-directed colloidal self-assembly. It has been demonstrated that this technique can control the colloidal particle deposition into a desired pattern with the aid of the template [10]. The template with a 2D square array of holes was fabricated by the laser (He–Cd laser, 325 nm) interference lithography using negative photoresist (SU-8) on a glass substrate. The periodicity and the hole diameter of the pattern can be controlled by adjusting the incident angle of laser beams and UV exposure time. The electron micrograph in Fig. 2(a) shows a square array of holes with a periodicity of 620 nm, a hole diameter of 420 nm, and a thickness of 300 nm. We synthesized gold nanoparticles (GNPs) by reducing tetrachloroauric acid (HAuCl₄) in the presence of sodium citrate [11] and then stabilized them with the nonionic surfactant (Tween 20). Subsequently, the GNPs were self-assembled on the patterned template by placing a confinement cell on top of the template into which a GNP colloidal solution was injected. As the GNP solution was dried inside the cell, GNPs were brought...
into each hole by the capillary force of solvent (water). The undesirable particle deposition on the outside of the holes was suppressed by the electrostatic repulsion between the negatively charged surfaces of GNPs and the template surface, which was also negatively charged by oxygen plasma treatment. Figure 2(b) shows an electron micrograph of a gold nanocluster array. GNPs are selectively deposited on the holes and are rarely deposited on the unpatterned region. The diameter of the gold nanocluster was 420 nm and the periodicity was 620 nm, as determined by the geometry of the patterned template. We also fabricated additional samples with various size (cluster diameter and periodicity) parameters using the same self-assembly procedure but with different templates. The results of different-sized gold nanocluster arrays are shown in Figs. 2(c) and 2(d).

We measured the optical properties of the gold nanocluster array using a microscope coupled to a fiber spectrometer. We chose three samples with different cluster diameters (390, 420, and 450 nm) but the same periodicity (620 nm). The optical measurement results are shown in Fig. 3. Clear extinction peaks were observed in the near-infrared region, indicating the presence of resonance supported by the clusters. The extinction peak was shifted according to the cluster size. The sample with a 390 nm cluster diameter shows the extinction peak at 1.05 μm, a 420 nm cluster diameter sample at 1.09 μm, and a 450 nm cluster diameter sample at 1.14 μm. To model the gold nanocluster, we first calculated effective parameters for a 3D array of GNPs and treated the gold nanocluster as a block of homogeneous effective medium. We believe this approach is justified because both the size and the spacing of GNPs within the nanoclusters are much smaller than the operating wavelengths. Using the extended Maxwell–Garnett formula, we calculated the effective permittivity of the GNP array in which the GNP diameter was 14 nm and the spacing was 3 nm and observed an electric resonance at a wavelength of 600 nm. Thereafter, we computed the extinction spectra of a cylindrical nanocluster array embedded in SU-8, and the results are shown in Fig. 4. The size parameters are the same as the samples used in the experiments. The blue square, green circle, and red triangle curves correspond to clusters with diameters of 390, 420, and 450 nm, respectively. The numerically calculated extinction spectra showed excellent agreement with the experimental results. The origin of the extinction peaks can be understood by examining the electromagnetic field patterns at the corresponding wavelength. The electric field pattern for a 420 nm diameter cluster at 1.08 μm shows a resonant mode oscillating along the incident electric field direction [Fig. 4(b)]. The electric field patterns of the other two cluster metamaterials also showed a similar field pattern, and the effective permittivity calculated by the retrieval method also showed resonant behavior at their respective resonant wavelengths. Thus, the coupling of the incident electric field with the electric resonance of the nanoclusters is responsible for the strong extinction peaks. The small deviation on the peak position between the simulation and the experimental results and the slight broadening of the extinction peaks in the experimental spectra are attributed to the nonuniformity of the GNP and
nanocluster size in our samples. The ratio of standard deviation to the average diameter of GNPs and nanoclusters was 17% and 11%, respectively. The theoretical study estimated an 11% size distribution in 390 nm clusters would cause the extinction peak to be broadened to a 146 nm width, which is comparable to the measured peak width (FWHM, 204 nm). This peak broadening also resulted in the lower extinction ratio in the measured spectrum at the resonant peak compared to the simulation result.

By forming a cluster with GNPs, we found that the electric resonance can be induced and tuned in frequency by simple controlling of the pattern size on the template. Optimizing the filling factor of the cluster can enhance the resonance of the effective permittivity of the metamaterial, which can be used to implement, for example, an epsilon-near-zero material [15]. On the other hand, magnetic resonance can occur by properly designing the size of the clusters. Our simulations indicated that a smaller-sized cluster could exhibit magnetic resonance and can thus be used to create magnetic metamaterials or negative index metamaterials at optical frequencies. Owing to the cylindrical shape of the gold nanocluster and the square symmetry of the array, the optical properties of the gold nanocluster array corresponding to two orthogonally oriented polarized lights were almost the same (data not shown). Therefore, this structure can also be used to create polarization insensitive metamaterial, and it is an advantage over other metamaterial structures, which are often anisotropic.

In conclusion, we report a new type of optical metamaterial that is compatible with a simple and scalable bottom-up fabrication technique, the template-directed colloidal self-assembly. Using the patterned templates fabricated by the laser interference lithography, we successfully self-assembled high-quality gold nanocluster metamaterials composed of a 2D square array of GNP clusters. We experimentally observed a strong extinction peak in the near-infrared region, which agreed well with the numerical results. Based on the simulations, we conclude that the observed extinction peaks were due to electric resonances supported by the gold nanoclusters. The ability to exhibit both electric and magnetic resonance and the potential for large-scale manufacturing makes the nanocluster metamaterial a highly promising architecture for optical metamaterials.

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