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Self-assembly of fluorescent nanospheres on nanostructured azo molecular thin films and optical near-field excitation

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We demonstrate self-assembly of fluorescent polymer nanospheres on a nanostructured azobenzene molecular thin film, and evaluate optical near-field excitation of aligned nanospheres. Nanogratings on azo thin film optically fabricated utilizing standing evanescent waves were used for an alignment layer of nanospheres. After dropping and air-drying a solution of nanospheres, the nanospheres were aligned along the grooves of nanograting. The variations in distribution of nanospheres were observed for a choice of grating shape and dispersing solvent of nanospheres. The size ordered alignment of nanospheres was found by using spin coating. To evaluate the fundamental processes of optical near-field excitation of the nanospheres, the emission light from the fluorescent nanospheres periodically aligned on azo grating was observed. The angular distribution of emission lights at a prism side of the angles larger than critical angle was confirmed, which correspond to the near-field optical excitation mediated by evanescent waves radiated near nanospheres. © 2019 The Japan Society of Applied Physics

1. Introduction

Architecture of photoreactive materials at nano scale is significant for an operation of optical nanodevices utilizing optical signal transportation through the nanostructures constructed in the devices.¹⁻⁶⁾ Among many choices of material in a device design, the softmaterials open a novel functionality not only on an optical signal processing and but also on motion control needed for a biomimetic technology such as light driven soft robot.^{7–9)} In particular, the application of an intelligent optical device needs a shape deformability of softmaterials. The real time modification of the nanostructures during device operation provides many degrees of freedom in control of optical signals in softmaterial devices.

The nanosphere-based self-organization of nanostructures has been developed with many methods, for example, using bottom up fabrication, large area and higher-order construction with a help of prepared nanostructures for aligning the spheres.^{10–15)} Furthermore, the spheres have ability to manipulate the optical fields at micro and nano scale. The size scale at optical interactions of spheres provides a different kind of applications. An optical resonator and photonic crystal are typical examples of the use of microsize spheres. The optical fields with wavelength selectivity can be confined resonantly by a whispering gallery mode of electromagnetic waves circulating around the surface of microspheres.^{16,17)} The light transmissions to a desired direction are engineered by designing the photonic crystal structures^{18,19)} that can control interference phenomena in the microstructures including microspheres. A nano scale optical field with spatial resolution exceeding diffraction limit is manipulated by using nanospheres that can excite and transmit an optical near-field localizing near the nanospheres.^{20–22}) The optical energy at nano region can be transferred through the near-field optical interactions strongly dependent on the size and shape of the nanospheres.

In particular, a fluorescent nanosphere acts as a highperformance optical source at nano region. For example, wideband local fields can be generated with nano resolution, just by irradiating the nanospheres of broad fluorescence with a monochrome laser light. Furthermore, in the vicinity of fluorescent nanospheres, tunable large wavenumbers of optical near-fields are obtained, which can be modulated by its size and their distribution of the nasnospheres.²⁰⁾ Therefore, optically-deformable alignment control of fluorescent nanospheres is extremely important as an elemental technology for full operation of optical nanodevices driven by near-field optical signals at nano scale.

However, the traditional methods for aligning nanospheres have no optical controllability of their distribution after fabrication of the nanostructures. Here, we propose the use of the azobenzene films as an alignment layer of nanospheres. The azobenzene molecules have photoisomerization processes that cause the molecular migration and volume changes during optical interactions, so that the structures of azo materials can be optically fabricated through the photoisomerization of azo molecules.^{23–26)} The interference fringes of laser light have been used for inscribing a grating structure on azo thin films at micro scale. Furthermore, a nano-sized grating can be obtained utilizing standing evanescent waves generated by a total internal reflection of laser light on dielectric prism surface.^{27–30)} Despite of the usefulness of the optical deformability of azo thin film for optical nanodevices, the optical near-field excitation properties of fluorescent nanospheres aligned by nanostructured azo films have not been investigated yet.

In this study, we demonstrate self-assembly of fluorescent polymer nanospheres on nanograting structures of azo thin films fabricated by standing evanescent waves, and show the evaluation of near-field optical excitation at the nanospheres aligned on azo nanograting. Periodical and binary selfalignments were obtained after dipping and air-drying the water droplet dispersed with nanospheres on the azo nanograting. The size ordered alignment of nanospheres was observed by employing spin coating. Furthermore, the fundamental processes of near-field optical excitations using fluorescent nanospheres periodically aligned on the azo nanogratings were evaluated by observing an angular distribution of emission light from the samples. The prism coupling was utilized for the conversion of evanescent waves excited at fluorescent nanospheres into an observable transmission light in a far field. The strong dependences of polarization of emission light on the alignment of fluorescent nanospheres were confirmed.





Fig. 1. (Color online) (a) Self-assembly of fluorescent nanospheres using nanograting fabricated on azo thin film. (b) Optical setup for observing emission light from the nanospheres and (c) configuration of polarization direction and sample alignment for emission light measurements.

2. Experimental methods

Figure 1(a) shows sample setup for self-assembly of fluorescent nanospheres. The azobenzene films were preprocessed by standing evanescent waves excited on the prism surface.²⁷⁾ The azo copolymer of poly [(methyl methacrylate)-co-(Disperse Red 1 acrylate)] purchased from Sigma Aldrich was spin-coated on a glass substrate. The nanogratings on the azo thin films were fabricated by standing evanescent waves formed by p-polarized light with incident angle 45°. In this study, commercially available nanospheres of fluorescent polyethylene (Moritex, R100) were utilized. The average diameter of the spheres is 100 nm. The nanospheres contain red fluorescent dyes with the spectral peak of absorption and fluorescence at 530 and 610 nm respectively.³¹⁾ The water solution mixed with the fluorescent polymer nanospheres was dropped on the nanograting of azo thin film, and air-dried at room temperature. The surface morphologies of the samples were evaluated by atomic force microscopy (AFM). The periodicity and depth of the azo grating can be adjusted by the wavelength, incident angle and injection power of incident laser, which restrict the size of nanospheres to be aligned. The periodicity should be longer than the diameter of spheres at least. In this study, Ar^+ laser of wavelength 515 nm was used to fabricate the grating. The periodicity is theoretically estimated to be 240 nm for refractive index 1.522 of the sample substrate, which is enough to separately align the nanospheres of diameter 100 nm. The grating depth can be adjusted within several ten nanometer levels by controlling the injection power of the laser, so that the nanospheres can be confined at the nano groove of the grating after drying the solvent of the nanospheres.

The emission lights from the samples were analyzed for the fluorescent nanospheres aligned on the azo nanograting. Figure 1(b) shows schematic diagrams of optical setup and sample configurations for the measurements. In order to analyze the near-field excitation of the nanospheres, the sample substrate was attached to the semicylindrical prism of BK7 using matching oil with same refractive index of the prism. The far field lights scattered into the prism side were analyzed. It is well known that the optical near-fields localized around the nanospheres are represented by superposition of the evanescent waves.^{32–34)} Therefore, in this



Fig. 2. (Color online) AFM images of the surface of nanograting and fluorescent nanospheres. (a) Nanograting fabricated on azo thin film using standing evanescent waves, (b) nanospheres aligned using the solution of deionized water observed at the positon around center of sample, (c) observed at the position away from the center, (d) nanospheres aligned using ethanol solution.

optical setup, the prism acts as an optical coupler that converts evanescent wave components included in the nearfields into a transmission light propagating in a far field. In this study, the fluorescent nanosperes were excited by Ar⁺ laser with wavelength 488 nm from a normal direction to the sample surface. The emitted light from the fluorescent nanospheres were corrected using an optical fiber placed at the prism side, and the transmitted lights thorough the fiber were high sensitively detected by photon-counting systems using photomultiplier tube (PMT). The fluorescence components emitted from the nanospheres were extracted by utilizing sharp cut filter (SCF) which removes the incident light components included in the scattered light from the samples. The angular distribution of emission light was observed by rotating the input port of optical fiber using a precise rotational stage. The polarizations of the emission light were analyzed by using linear polarizer. The directions of polarization and alignment of the nanospheres on the nanograting were defined as indicated in Fig. 1(c).

3. Results and discussion

Figure 2 shows AFM images of the nanogratings fabricated on the azo thin film and aligned fluorescent nanospheres. The periodicity and depth of the nanograting after fabrication was typically 260 and 80 nm as shown in Fig. 2(a), where the thickness of azo film was 120 nm. The power and irradiation time of fabrication laser were 11 mW mm^{-2} and 10 min respectively. Nanometer sized gratings were fabricated on the azo films which clearly correspond to the intensity distribution of the interference fringes of counter propagating evanescent waves. Figure 2(b) shows AFM image of the nanospheres observed at the position around the center of the samples after air-drying the sample at room temperature. The nanospheres were dispersed in deionized water, and the droplet of the solution was dropped on the nanograting of azo thin film. The concentration of the nanospheres in water solution was 6.5×10^{11} particles ml⁻¹. The nanospheres of dimeter 100 nm were clearly aligned at the bottom of the groove of nanograting. The Fourier spectrum of the spatial distribution of the observed surface has a peak at 260 and 130 nm, approximately corresponding to the repetition frequencies of the grating and nanospheres. When the observation positon were away from the center of the droplet, the distributions were changed to high-order quasi grating structure with slight randomness as shown in Fig. 2(c). The periodicity reflecting the structures of nanograting can be seen. It is estimated that the nanospheres vertically stack and form a high-order structure on the aligned spheres at the groove. It is estimated that the majority of the nanoparticles were left near the edge of solvent dropped on the surface during the evaporation of the water. These alignment processes are restricted by the wettability, viscosity and evaporation speed of the solvent. Therefore, to obtain a desired distribution of the nanospheres, the solvent condition should be optimized.

As a comparison, we utilized an ethanol solution as a dispersion medium of the nanospheres. The result using ethanol dispersion medium is shown in Fig. 2(d). As a result



Fig. 3. (Color online) Effects of extra forces for nanosphere alignment using spin coating. (a) Spin coating of the sample, (b) nanospheres aligned after spin coating and (c) alignment in size order using mixture of nanospheres of diameters 50 and 100 nm.

of good wettability of ethanol than water on azo films of PMMA, the ethanol solutions including nanospheres were uniformly spread in almost all areas on the sample, and the nanospheres were aligned in a wide area on the nanograting. There were no significant differences in dispersion behavior of nanospheres at central and other areas as observed using water medium of Figs. 2(b) and 2(c). However, the multiple nanospheres were overlapped as compared with the results of Fig. 2(b). This possibly is caused by the faster evaporation speed of the ethanol than the water.

Next, we investigated the effect of the external forces using spin coating technique. The tangential forces can be acted on the nanospheres during the evaporation processes. In this study, the sample substrate was attached at the stage of the spin coater, and mounted approximately 1 cm away from the center of the stage as shown in Fig. 3(a). The samples were spin-coated with rotational speeds 1st- 1000 rpm/20 s and 2nd- 2000 rpm/20 s. Figure 3(b) shows the AFM image of nanospheres observed on nanograting of azo film using dispersion medium of water. The nanospheres were aligned even after the spin coating. The combinations of the several nanospheres can be confirmed along the grooves of the azo films; the length of aligned nanospheres was shortened compared with the case without spin coating as observed in Fig. 2(b). We speculate that the shortening is caused by blowing the nanospheres due to the mechanical effects of tangential forces acting on the nanospheres during spin coating. To confirm the further effects of the extra forces, we mixed the nanospheres of different sizes. The result of the mixture of the nanospheres of 50 and 100 nm diameters are shown in Fig. 3(c) after spin coating. The nanospheres of different size within manufacture's guaranteed size distribution were clearly arranged in size order. We speculate that the size selective arrangements are caused by the pinning of smaller nanospheres by the largest spheres stacked in the groove of nanograting during spin coating the samples. The largest spheres were located at the beginning of the rotation direction, and then the smaller nanospheres tend to be arranged in order of the size.

The distribution of the nanospheres can be adjusted by modifying the nanostructures of the azo grating. As a simple case, we fabricated a bamboo type structure on azo thin film. The surface structures of azo films were modified by two step of fabrication processing using standing evanescent waves. After 1st processing of nanograting, the sample was rotated at 90° and irradiated by standing evanescent waves again. In this study, at the 2nd processing, the center of laser beam totally reflected on prism was slightly replaced from the position of the 1st processing. The differences of intensity profiles of 2nd and 1st processing caused the bamboo structures. Figures 4(a) and 4(b) show the AFM images of the surface morphologies after 2nd processing. The straight lines of nanograting were distorted with the periodicity of the standing evanescent waves forming in the direction orthogonal to the grooves fabricated at 1st processing. Figure 4(c)shows the nanospheres after air-dring the water solution of the nanospheres. The nanospheres of 100 nm diameter were dispersed on the nanostructured azo thin films formed by two step fabrication. The digitalized distribution of the nanospheres was obtained which corresponds to the shape of the bamboo structures for an alignment layer as observed in Fig. 4(b). The small nanospheres locate close to the large nanospheres without being influenced by the nanostructures of azo films.

Furthermore, we evaluated a near-field optical excitation at the nanospheres periodically aligned on nanogratings of azo thin film. The emission light distributions from the samples were measured for the nanospheres. The direction of



Fig. 4. (Color online) Variations in distributions of nanospheres by modifying the shape of azo grating. (a) Bamboo structure formed by two step of fabrication processing using standing evanescent waves, (b) enlarged view of (a), and (c) digitalized distribution of nanospheres aligned on the bamboo structures.

polarization and alignment of nanospheres are defined as Cartesian coordinates indicated in Figs. 1(b) and 1(c). The samples attached to the semicylindrical prism were irradiated by 488 nm Ar⁺ laser light propagating in the direction normal to the surface. The intensity of incident light was set to be 50 μ W, which is extremely weak to suppress a photoisomerazation of azo thin films. The fluorescent nanospheres of diameter approximately 100 nm were periodically aligned on the nanogratings of azo thin film. The optical absorbance of the azo molecular film and nanospheres of film state were respectively less than 0.14 and 0.2 at wavelength 488 nm, when the sphere density was about 30 particles $\mu m^{-2.31}$ It is estimated that the incident light can pass through the azo films and excite the nanospheres. Figures 5(a)-5(d) show the intensity of the s- and p-polarization components of emission light from the samples, as a function of emission angle in the region of prism side. The E_x and E_y -polarized incident lights in propagation direction normal to the surface were irradiated to the nanospheres aligned in x-direction and y-direction. In all combination of incident polarization and sample alignment, the emission lights exist at the angle larger than the critical angle which is estimated to be 41° assuming the wavelength 610 nm of the light corresponding to the fluorescence peak of the nanospheres. This angle dependence shows the observation of evanescent waves excited at the fluorescent nanospheres. According to the angular spectrum representation of the scattered filed of nano object, optical near-fields near a nano-sized sphere are expressed as a superposition of evanescent waves propagating on an assuming planar boundary considered near the sphere.^{32–34)} Because the evanescent waves have a large wavenumber than that in free space, the excited evanescent waves can be coupled to the observable transmitted light in the prism region exceeding the critical angle to satisfy a wavenumber matching at the interface of prism surface.^{35–37)} The angular distribution of emission light corresponds to the wavenumber spectrum of the evanescent waves radiated from the fluorescent nanospheres.

The polarization components of the emission light were strongly dependent on the combination of the incident light polarization and the alignment of the samples. Figures 5(a) and 5(b) show the results of E_y -polarization excitation of fluorescent nanospheres aligned in *x*- and *y*-direction. The emission light observed in the region at prism side has a main component of p-polarization. Contrary to this, in case of E_x -polarization excitation, the polarization component of emission light was altered to s-polarization as shown in Figs. 5(c) and 5(d). Furthermore, the emission lights were enhanced when the alignments direction and polarization direction between alignment and polarization observed in Figs. 5(a)–5(d) are summarized as follows:

- (i) y-alignment enhances p-polarized emission light by E_{y} -polarized incident light
- (ii) x-alignment enhances s-polarized emission light by E_x -polarized incident light

It is thought that the polarization dependence and enhancement of optical near-fields in the nanospheres are provided by



Fig. 5. (Color online) Emission light distribution of fluorescent nanospheres aligned on nanograting of azo thin film observed for y-alignment (a) and x-alignment (b) excited by E_{x} -polarized incident light, and for y-alignment (c) and x-alignment (d) excited by E_{x} -polarized light.

the combination of polarization and alignment, and the optical resonance between the nanospheres. The polarizations of evanescent waves emitted from the fluorescent nanospheres coincide with those of emission light due to the boundary condition of the electromagnetic waves on the surface; E_x and E_y components of electric field vector of evanescent waves are respectively connected with the s and p-polarization of emission light. When the incident polarization coincided with the alignment direction, the optical near-fields are resonantly generated and enhanced at the gap between nanospheres, from which the strong emission lights are observed in a far field.

These phenomena of near-field optical excitation via evanescent waves of fluorescent nanospheres can be extended to the excitation of a surface plasmon that is localized optical near-field at metallic surface.^{38–41)} In order to confirm the direct excitation of surface plasmons with the aligned fluorescent nanospheres, we coated the samples with silver thin films using vacuum evaporation, and observed the emission lights from the sample as shown in Fig. 6(a). The metallic films act as a material for exciting the surface plasmon mode. The thickness of Ag layer was 50 nm. The pitch and depth of grating fabricated on azo thin film of 50 nm thick were 260 and 20 nm. The samples were excited

by E_{y} -polarized laser light in the direction normal to the sample surface. The polarizing elements were not used in front of PMT to obtain high signal to noise ratio. Figure 6(b)shows the spatial distribution of emission light as a function of emission angles. It is noted that any reflected lights on Ag film did not enter to the PMT photodetector, because the excitation laser was incident from the normal direction and the emission lights were observed at the angle larger than the critical angle. The scattered lights of wavelength 488 nm of incident light caused by nanospheres were removed using SCF so that the only fluorescence of nanospheres was extracted. The emission lights at the angle larger than the critical angle were observed with and without Ag film. In particular, in the presence of the Ag film, the obvious modulation on the curve was occurred at the angle 45°-55°. The intensity was higher than the case without metallic coating. These emission light distribution and modulation indicate the surface plasmon excitation through the optical near-filed excitation at fluorescent nanospheres. The enhancements of electromagnetic field due to surface plasmon excitation on the Ag film also cause the increasing of emission light.

To confirm the emission light phenomena due to the surface plasmon excitation, these results were complementally verified



Fig. 6. (Color online) Emission light observed for Ag coated fluorescent nanospheres aligned on nanograting. (a) Sample setup and optical system for measurement of emission light, (b) angle dependence of emission light from Ag coated fluorescent nanospheres on nanograting and (c) complemental measurement of ATR properties of Ag coated nanograting without nanospheres. The inset figures in (c) show AFM image of the Ag coated nanograting without nanospheres and optical system of ATR measurement.

with an attenuated total internal reflection (ATR) measurement of metallic coated nanograting. The illumination of evanescent waves formed by ATR on prism can directly excite the surface plasmon on the metallic samples. Figure 6(c) shows the ATR properties. As indicated in inset of Fig. 6(c), the nanograting without nanospheres was Ag coated, and the substrate was attached to the semicylindrical prism. The sample was irradiated by the totally reflected light of diode laser with wavelength 650 nm approximately corresponding to the peak wavelength of fluorescence of the nanoshperes. The intensity changes of the reflected light were observed as a function of incident angles of the laser. Two dips at 43° and 47° were observed only for p-polarization of incident light. The dip at 43° coincides with the surface plasmon excitation observed for the flat surface of Ag films. The dip at 47° is shifted than the case of 43°. We speculate that the dip shift was occurred by the nanograting-assisted plasmon excitation. In the presence of nanograting, larger wavenumbers than those of evanescent waves excited by incident light can be generated due to extra momentum exchanges provided by the nanogratings. The resonance angle can be shifted to satisfy the wavenumber matching of the surface plasmon even at off resonance angles of prism coupling on a flat surface.⁴²⁾ The characteristic profiles of emission light observed in Fig. 6(b) can be considered from the resultant multiple surface plasmon excitations due to molecular fluorescence with wideband spectra that provide further shifting and broadening of the resonance angle of surface plasmon excitation on the metallic surface. The modulation of optical near-field provided by such engineering of the surrounding system around the aligned nanospheres is significant for the controlling the optical energy transfer at nano scale.

4. Conclusions

The self-assembly of fluorescent nanospheres using nanograting of azo thin films was demonstrated. The nanospheres were periodically aligned depending on the dispersion solution and the extra forces during the evaporation of the solution of nanospheres. The digitalized distributions of the nanospheres were also obtained by modifying the shape of the azo grating. Furthermore, the fundamental processes of near-field optical excitations of fluorescent nanospheres periodically aligned on azo nanograting were evaluated from the distribution measurements of the emission light scattered in a far field via prism coupling of the evanescent waves excited near the nanospheres. The strong polarization dependence of emission lights was observed which is excited selectively by the alignment direction of the nanospheres on the grating. The direct excitation of surface plasmon was also demonstrated on metallic coated azo nanogratings. The further optimizations of the parameters for self-aligning nanospheres will be necessary to obtain desired nanostructures available to nanophotonic devices. Furthermore,

the local fabrication at nanoscale utilizing near-field optical probe will open the exploration of more precise and complex structures. Our method of self-assembly of fluorescent nanospheres can be extended to fully optical manipulation of the nanostructure because the photoreactivity of azo molecules can optically deform the nanostrucutres. The optically controllable nanostructures consisted of fluorescent nanosphres will be beneficial for feature optical devices utilizing novel signal control and softmaterial devices embedded in real life.

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