

2D Ceramics Nanopatterning and 3D Particle Assembly

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2D ceramics nano/micropatterning and 3D particle assembly were realized using self-assembly processes. Site-selective deposition of UV- and visible-light-emitting ZnO crystals was successfully achieved in an aqueous solution at low temperature. Molecular recognition was effectively utilized for patterning of ZnO crystals on self-assembled monolayers. Crystalline ZnO was further controlled to have different morphologies such as cylindrical hexagonal rods, ellipse or multi-needle shape by changing the solution conditions to improve the photoluminescence properties. All of the morphologies emitted strong photoluminescence in UV and visible regions with different emission spectra. The novel process shows the high ability of solution processes for fabricating nano/micro-devices constructed from crystalline materials for visible-light-emitting devices. We further proposed a novel process to fabricate micropatterns of spherical particle assemblies. Hydrophilic regions of a patterned self-assembled monolayer were covered with methanol solution containing SiO₂ particles and immersed in decalin to control the shape of droplets and gradually dissolve the methanol into decalin. Particles were assembled to form spherical shapes on hydrophilic regions of an SAM and consequently, micropatterns of spherical particle assemblies were successfully fabricated through self-assembly. This patterned two-solution process has the advantages of both a drying process having meniscus force and a static solution process having high controllability.

Key words: Ceramics, Patterning, Particle, Self-assembly, self-assembled monolayer

1. INTRODUCTION

Self-assembly processes were proposed for fabrication of future nano/micro devices. Synthesis of crystalline ceramics in an aqueous solution and their 2D nano/micro patterning has especially attracted much attention in ceramics field. Additionally, self-assembly process of nano/micro particles has been proposed to fabricate nano/micro periodic structures. We proposed novel self-assembly processes for 2D ceramics patterning and 3D particle assembly based on interface chemistry, solution chemistry and colloid chemistry.

2D Patterning of ZnO crystals. ZnO has attracted much attention as a luminescence material in various applications such as vacuum fluorescent displays (VFD)[1], field emission displays (FED)[2, 3], electroluminescent displays (ELD)[4], and UV light-emitting diodes and laser diodes[5-7] due to its wide gap of 3.37 eV at room temperature. The use of ZnO has also been explored in gas sensors[8], varistors[9], piezoelectric devices[10], electroacoustic transducers[11], and highly transparent conducting windows for solar cells, and displays[12, 13]. ZnO micropatterns are prepared for devices by an etching process using photoresist and lithography techniques. However, high resolution etching is difficult to achieve without damaging the substrate. Additionally, the morphologies need to be controlled in order to improve luminescence properties. To solve such problems, site-selective deposition of ceramic was proposed in 2001[14] for the first time and site-selective deposition techniques have recently been developed for micropatterning of ceramic

thin films[14-18] or particles[19-22] by using knowledge of the ceramic synthesis in solution systems[23, 24]. The solution process has the advantage that ZnO crystals having high crystallinity can be synthesized and their crystallinity and morphology can be controlled to improve luminescence properties.

In this study, we propose a novel process to fabricate micropatterns of UV- and visible-light-emitting ZnO crystals in an aqueous solution without the use of the annealing process or catalyst such as Pd.

3D Particle Assembly. Particles show various interesting properties[25-28] such as photonic band gap[29], electronic energy transfer in close-packed CdSe[30] or InP[31], or metal-insulator transition in silver quantum dot[32] that are not observed in the bulk form of a material. Various scientific and engineering applications, such as control of spontaneous emission, zero-threshold lasing, sharp bending of light, and so on, are expected to become possible by using the photonic band gap and the artificially introduced defect states and/or light-emitters. Recently, monodispersed particles have been synthesized by various methods. Thus, particles may be treated as if they were atoms, and one-, two- or three-dimensional arrangement of particles has been studied by many researchers. Materials with micron- and submicron-scale patterns are expected to be applied to the desirable devices.

We have developed several patterning methods, without the use of a template, having microstructures such as molds or grooves in static solution systems[19, 33, 34] or in drying

processes[35, 36] to apply them for photonic crystals. These self-assembly solution processes do not need preprocessing of micromolds or grooves. However, each patterning system has its own advantages and disadvantages, and further progress based on novel concepts is strongly required.

Here, we developed a novel process to realize spherical particle assembly and their micropatterning using droplets of colloidal solution and a patterned SAM. This two-solution process was developed to have the advantages of both the static solution process and the drying process.

2. 2D PATTERNING OF ZINC OXIDE CRYSTALS.

Preparation of ZnO crystals. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$, Kishida Chemical Co., Ltd.) was dissolved into water to be 15 mM at 50°C, and ammonia (28% solution, Kishida) was then added to be 30, 60 or 90 mM ($[\text{NH}_3] / [\text{Zn}] = 2.0, 4.0$ or 6.0) with stirring as complexing agent. These solutions showed pH = 7.04, 7.50 or 8.93, respectively. Zinc ions reacted with ammonium ions (NH_4^+) formed from ammonia to form tetra amine zinc(II)[37] $[\text{Zn}(\text{NH}_3)_4]^{2+}$. ZnO was crystallized from the reaction between $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and OH^- . The solution became clouded shortly after adding ammonia due to homogeneous nucleation of ZnO crystals. Morphology of ZnO crystals was controlled by the ratio of ammonia to zinc acetate, i.e., super-saturation degree for crystallization.

Self-assembly patterning of ZnO crystals. Patterned OTS-SAMs were immersed downward into the solution containing zinc acetate (15 mM) and ammonia (30 mM) as complexing agent ($[\text{NH}_3] / [\text{Zn}] = 2.0$) at 50°C for 3 h (Fig. 1). After having been immersed in the solution, SAMs were rinsed with distilled water and dried in air. Patterns of ZnO crystals were evaluated with a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.), an X-ray diffractometer (XRD; RINT-2100, Rigaku, in-plane x-ray diffraction profiles) with $\text{CuK}\alpha$ radiation (40 kV, 30 mA) and Ni filter plus a graphite monochromator, an optical- and photoluminescence-microscope (BX51WI Microscope, excitation wavelength for photoluminescence image 330–385 nm, Olympus

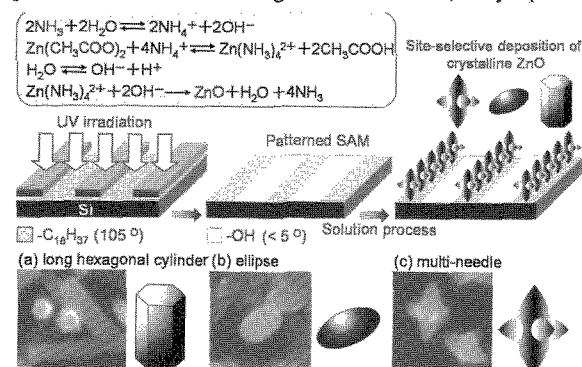


Fig. 1. Conceptual process for self-assembly patterning of light-emitting crystalline ZnO nanoparticles in an aqueous solution.

Optical Co., Ltd.) with a digital camera (DP50, 5.8 megapixels, Olympus Optical Co., Ltd.) and a computer for capturing data, and a fluorescence spectrometer (F-4500, excitation wavelength 350 nm, Xe lamp, Hitachi, Ltd.).

Site-selective deposition of ZnO crystals and their morphology control. ZnO crystals having long hexagonal cylinder shape (inset of Fig. 2b) were homogeneously nucleated to make the solution turbid shortly after adding ammonia. Crystals showed sharp hexagonal facets of about 100 nm in diameter and larger than 500 nm in length. The morphology indicated high crystallinity of ZnO nanoparticles. The nanoparticles were deposited and further grown on hydrophobic octadecyl group regions of a patterned SAM selectively (Fig. 2). Consequently, a micropattern of light-emitting ZnO crystals was successfully fabricated in an aqueous solution without Pd catalyst. This showed that the method is highly versatile and offers good potential for the fabrication of devices.

Patterned SAMs were also immersed into the solution containing zinc acetate (15 mM) and ammonia (60 mM or 90 mM) as complexing agent ($[\text{NH}_3] / [\text{Zn}] = 4.0$ or 6.0) for 3 h. ZnO crystals having ellipse or multi-needle shape (two large needles and four small needles) were homogeneously nucleated to make the solution turbid shortly after adding ammonia. Nucleation and deposition of ZnO crystals were accelerated by addition of ammonia. Each ZnO crystal was about 500 nm in size. The crystals were deposited and further grown on hydrophobic regions of patterned SAMs selectively. Micropatterns of light-emitting ZnO crystals having ellipse or multi-needle shape were fabricated on patterned SAMs in aqueous solutions.

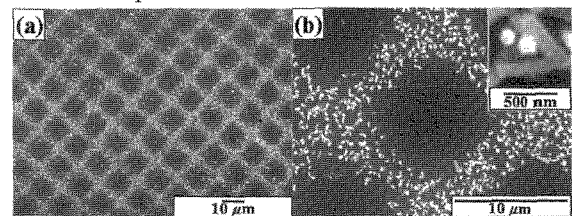


Fig. 2. SEM micrographs of (a) patterned crystalline ZnO (long hexagonal cylinder) and (b) magnified area of (a).

XRD spectra of ZnO crystals having ellipse or multi-needle shape showed dominant peaks corresponding to ZnO (0002) planes revealing that ZnO crystals were deposited with a high degree of orientation of their c-axes perpendicular to the substrate. Enhanced (0002) and (1010) peaks from ZnO crystals having long hexagonal cylinder shape showed that crystals were deposited to make (0002) or (1010) planes parallel to the substrate. Crystals having high crystallinity and high purity with no additional phase were shown to be prepared in an aqueous solution with precise control of their morphologies without the use of Pd catalyst. The aqueous solution system showed high ability for fabricating nano/micro devices

composed of crystalline materials. ZnO crystals are well known to grow along the c-axis. The c-axes of ZnO crystals can be deduced from their shapes and the deposited directions were estimated by XRD spectra. The orientations evaluated from XRD patterns were consistent with SEM observations and were shown to be controlled precisely by the solution conditions.

Photoluminescence of ZnO crystals.

Photoluminescence properties of ZnO crystal patterns were further evaluated. Micropatterns of ZnO crystals were observed by an optical microscope and strong visible-luminescence from ZnO crystals excited by 330–385 nm light was observed by a photoluminescence microscope. ZnO crystals showed strong UV luminescence (around 390 nm) attributed to band-edge luminescence and visible-light luminescence caused from oxygen vacancy (450–600 nm)[38, 39]. All of the crystals showed photoluminescence (Fig. 3) due to high purity and high crystallinity with optimal oxygen vacancy, and this caused the bright visible-photoluminescence image. ZnO crystals deposited from an aqueous solution were shown to have high visible-light-emitting properties. Luminescence properties can be controlled by changing the crystalline morphologies. Photoluminescence intensity of (b) ellipse and (c) multi-needle was stronger than that of (a) long hexagonal cylinder. This difference would be caused by the increase of oxygen vacancy, and the increase of oxygen vacancy would be caused by the increase of super saturation degree of the solution by addition of ammonia. The stoichiometrical change is likely to occur under non-equilibrium vacuum conditions. However, an oxygen concentration was shown to be controllable even in equilibrium condition such as a solution system in this study. The phenomenon shown in Figure 3 is thus worthy of attention and has high scientific value. This study would contribute to the development of this field.

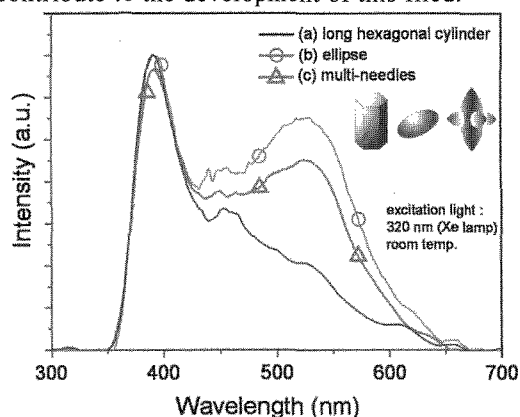


Fig. 3. Photoluminescence properties for ZnO crystals; (a) long hexagonal cylinder, (b) ellipse. (c) multi-needles.

3. 3D PARTICLE ASSEMBLY

Self-assembly into spherical particle assembly. SiO₂ particles (1.13 μmφ, Hipresica UF N3N, CV: 3.57 %, specific gravity: 1.8 ± 0.1 g/cm³, Ube-Nitto Kasei Co., Ltd.) (0.2 mg, 1.5 ×

10¹⁰ particles) were thoroughly dispersed in water (20 μl) and dropped on a hydrophobic OTS(octadecyltrichlorosilane)-SAM (Fig. 4 (Top)). The OTS-SAM with droplets was then immersed in hexane (20 ml, solubility of hexane in water at 20°C: 0.0013 g / 100 ml, specific gravity: 0.7) and ultrasonicated for 1 min. Large water droplets containing SiO₂ particles were separated into many small emulsions that kept them spherical on hydrophobic OTS-SAM. Water in the emulsions was gradually extracted to hexane to reduce the size of emulsions forming spherical particle assemblies[40]. After having been immersed for 12 h, spherical particle assemblies with different diameters were observed on OTS-SAM; it was also observed that the assemblies were constructed from various numbers of particles such as 3, 5, 6, 8 or many particles (Fig. 4). Quantities of 3, 5, 6 or 8 particles were assembled into triangular, pyramidal, octahedral or decahedral particle clusters, respectively. The number of particles in spheres can be controlled by the change of emulsion size or particle concentration in water[40]. The spherical shape of particle assemblies was caused by the high contact angle of water emulsion on hydrophobic OTS-SAM in hexane. Consequently, various sizes of spherical particle assemblies can be prepared using this emulsion process.

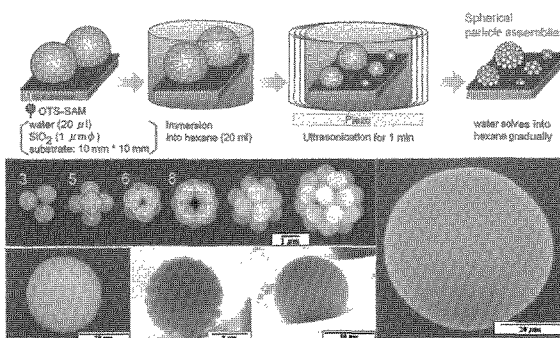


Fig. 4. Conceptual process and SEM micrographs of spherical particle assemblies.

Micropatterning of spherical particle assemblies. SiO₂ particles (1.13 μmφ, 1 g/l) were thoroughly dispersed in methanol solution (10 μl) and dropped onto a patterned HFDTS(heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane)-SAM[16] having hydrophobic HFDTS-SAM regions and hydrophilic silanol regions, photopatterned using a mesh for transmission electron microscopy as a photomask (Fig. 5). The patterned SAM covered with the solution was then carefully immersed in decalin so as not to remove the solution because the density of methanol (0.79) is lower than that of decalin (0.88) causing methanol to float on decalin. The patterned SAM was then gently vibrated to remove additional methanol solution and assist the movement of droplets to silanol regions. The methanol solution was selectively contacted on hydrophilic regions to form a micropattern of the solution, which became clearer after immersion for a few hours. The methanol solution containing

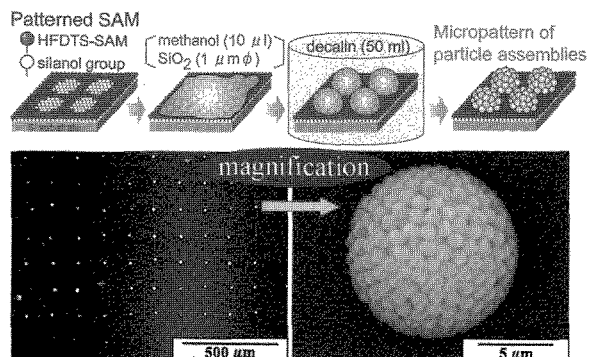


Fig. 5. Conceptual process and SEM micrographs of micropattern of spherical particle assemblies.

particles formed a spherical shape because of the surface interaction between methanol, decalin and surface of a SAM and the buoyant force of methanol in decalin. Methanol in emulsions was gradually dissolved into exterior decalin phase to form particle assemblies. After having been immersed for 12 h, particle assemblies having a dome shape were formed at the center of each silanol region (Fig. 5). The distance between the centers of each spherical particle assembly was same to the distance between holes of a mesh. The diameter of spherical particle assemblies was about $18 \mu\text{m}$. Consequently, the dot array of spherical particle assemblies was successfully fabricated by this self-assembly process.

4. CONCLUSIONS

We proposed a novel concept for site-selective deposition and micropatterning of crystalline materials in an aqueous solution without the use of catalyst or annealing. Micropatterns of ZnO crystals were successfully fabricated on patterned SAMs and ZnO crystals emitted strong UV- and visible-light photoluminescence. Furthermore, we proposed a novel self-assembly process to fabricate 3D particle assembly and successfully fabricated spherical particle assembly and micropatterns of particle assemblies, without the use of a template, having microstructures such as molds or grooves. These showed the high ability of self-assembly processes to prepare nano/microstructures for future devices.

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