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Fabrication of single-crystalline microspheres with high sphericity from anisotropic materials

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Microspheres with high sphericity exhibit unique functionalities. In particular, their high symmetry makes them excellent omnidirectional optical resonators. As such perfect micrometre-sized spheres are known to be formed by surface tension, melt cooling is a popular method for fabricating microspheres. However, it is extremely difficult to produce crystalline microspheres using this method because their surfaces are normally faceted. Only microspheres of polymers, glass, or ceramics have been available, while single-crystalline microspheres, which should be useful in optical applications, have been awaiting successful production. Here we report the fabrication of single-crystalline semiconductor microspheres that have surfaces with atomic-level smoothness. These microspheres were formed by performing laser ablation in superfluid helium to create and moderately cool a melt of the anisotropic semiconductor material. This novel method provides cooling conditions that are exceptionally suited for the fabrication of single-crystalline microspheres. This finding opens a pathway for studying the hidden mechanism of anisotropy-free crystal growth and its applications.

Microcavities with high Q values and small mode volumes have attracted much attention because of their potential application in nonlinear optical devices or quantum optics[1]. Among these microcavities, whispering-gallery-mode (WGM) microresonators of microspheres provide the highest Q values when compared with other structures such as microdisks and Fabry-Perot cavities. Since the versatility of dye-doped polymers allows us to fabricate microspheres with high-sphericity, the production of WGMs by three-dimensional confinement have been intensively studied[2]. However, the available light frequency range is usually limited because of the difficulty in fabricating high-quality spheres with small size or high refractivity when using polymers. Even though the WGMs in semiconductor materials overcome this difficulty[3], single-crystalline microspheres are extremely difficult to fabricate because faceted surfaces normally appear, reflecting the atomic arrangements. Recently, the pulsed heating method was invented to fabricate aggregated submicron-sized spheres of semiconductors and metals in large numbers[4]. This pioneering method is useful for efficient fabrication of many spherical particles with a narrow distribution of sizes. However, obtaining particles with high sphericity and micron sizes, which are crucial for optical purposes in highly efficient lasing and so on, remains a challenge. In the present study, we discovered single-crystalline micrometre-sized spheres of materials with anisotropic crystal structures that tend to grow in shapes with low symmetry, such as ZnO and CdSe, after laser ablation in superfluid helium. These microspheres possessed surfaces with atomic-level smoothness and stability in ambient condition. Furthermore, the microspheres showed very high sphericity, which means that melts of the material that were generated initially, whose shapes were determined by surface tension, were ideally cooled to grow in crystalline form, thus preserving the highly spherical shapes.

Extreme conditions such as high pressure or high temperature are keys to fabricating novel materials[5]. Laser ablation in fluids, a method that involves both ultrahigh pressure and ultrahigh temperature, has been used to create new nanostructures[6]. Superfluid helium exhibits low temperatures, ultralow viscosity, high thermal conductivity, and good transparency in the visible region. It is also chemically inactive and can be used to provide a neutral environment for laser ablation[7,8]. Thus, we expect fabrication of unique structures to be feasible under such extreme conditions. We first tried the technique on anisotropic materials, whose nanostructures usually
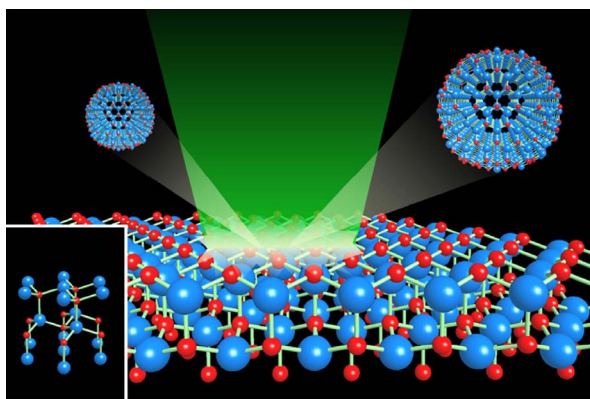
Figure 1 | Illustration of fabrication of single-crystalline semiconductor microspheres for materials with wurtzite crystal structures. The inset shows anisotropic crystal growth of material with a hexagonal structure. On the other hand, the melts generated under strong light irradiation in superfluid helium finally transform into particles with highly spherical shapes while retaining the crystal structure.

exhibit rod shapes with facets, as shown in the inset of Fig. 1. After they underwent laser ablation in superfluid helium, we found many spheres with a wide distribution of sizes in the range of several tens of nanometres to several micrometres with very high sphericity. Surprisingly, the spheres were single crystals, as shown in Fig. 1. It appeared impossible to accommodate an atomic arrangement with anisotropic lattice constants in the spheres, however. Details of the results are described below.

Results

Fabrication of ZnO single-crystalline microspheres. Laser ablation in superfluid helium of ZnO, a well-known wide-bandgap semiconductor with a wurtzite crystal structure which tends to grow in a rod-like manner[9], produces many spheres with typical sizes in the range of several tens of nanometres to around 3 μm, as shown in Fig. 2. The spheres were extracted from a He cryostat and released into the air. They were then observed using electron microscopes. Therefore, they

were stable in air and vacuum at room temperature. Moreover, their morphology and optical properties remained unchanged for at least one month. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of isolated fabricated ZnO particles (Fig. 2) prove that they were highly spherical and that no facets, which are characteristic of ZnO crystals[9,10], were present on their surfaces. The TEM image in Fig. 2b of one such microsphere was taken along the [001] zone axis; it shows that the cross section of the microsphere was circular, unlike the hexagonal microstructure of ZnO single crystals. Furthermore, the ZnO microspheres, as seen in Fig. 2b and c, which were submicron in size, showed uniform diffraction contrasts. Fringes of equal thickness were also observed along the outlines of the microspheres. These results indicate that the ZnO microspheres had very few dislocations or defects. On the other hand, the electron diffraction pattern in Fig. 2b', which corresponds to the ZnO microsphere in Fig. 2b, clearly proves that the fabricated ZnO microspheres were single crystals, with all the diffraction spots being attributable to those of a ZnO bulk crystal along the [001] zone axis[11]. In addition, the image in Fig. 2c' further confirms that uniform lattice fringes were present around the edge of the ZnO microsphere (Fig. 2c) as well. This means that the fabricated ZnO microspheres were indeed single crystals and the crystalline quality was good even near their surfaces. The interplanar spacing of the lattice fringes in Fig. 2c' was measured and found to be approximately 0.25 nm; this value corresponds to that of the {101} planes of a ZnO bulk crystal. These findings indicate that the fabricated microspheres, which were wide ranging in size, were single crystals with high surface smoothness.

Using this fabrication method, we were able to obtain large microspheres measuring >1 μm in diameter, which are suitable for optical applications. In the case of larger microspheres, such as the one shown in Fig. 2a, detailed TEM analysis could not be obtained. Hence, we performed micro-photoluminescence (micro-PL) measurements on one of these ZnO microspheres to determine its sphericity, based on the premise that a completely spherical microsphere acts as a WGM resonator[1–3]. We observed many WGMs very clearly (these WGMs could be perfectly reproduced in a simulation) and achieved efficient lasing in the visible region owing to the relatively high Q value (of the order of one thousand) of the fabricated microsphere, which shows its high sphericity (Supplementary Fig. S3).
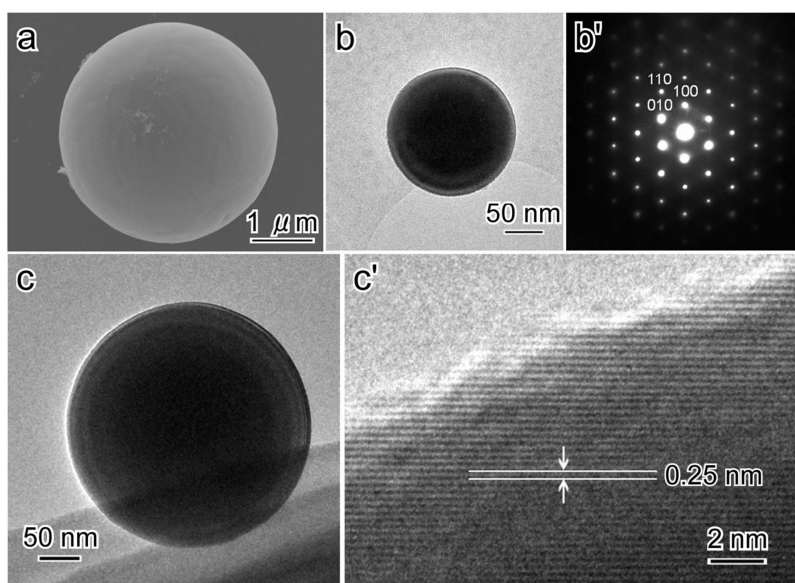

Figure 2 | Images and diffraction patterns of fabricated ZnO microspheres. (a) Typical SEM image of one of the larger microspheres fabricated in the study. (b, c) TEM images of a ZnO microsphere that was smaller in size and placed on a TEM grid substrate. (b') Electron diffraction pattern of the ZnO sphere shown in (b), taken along the [001] zone axis. (c') High-resolution TEM image of the sphere shown in (c). Uniform lattice fringes are clearly observable even on the surface.
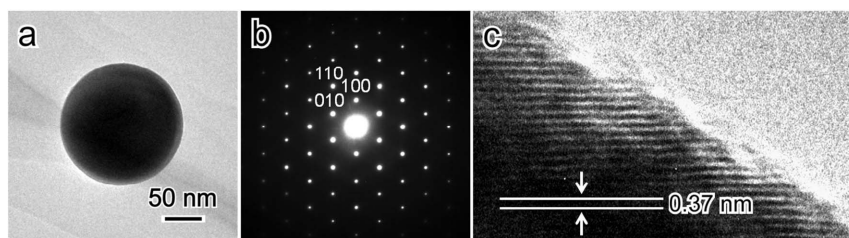
Figure 3 | **TEM images and diffraction pattern of a fabricated CdSe microsphere.** (a) Typical TEM image of a CdSe microsphere. (b) Electron diffraction pattern of the CdSe microsphere shown in (a) taken along the [001] zone axis. (c) High-resolution TEM image of the sphere shown in (a).

Furthermore, this means that the microspheres we fabricate using the proposed method are promising for various optical applications such as omnidirectional lasing and optical quantum information technology requiring high Q resonators.

Fabrication of CdSe, ZnSe, and CeO$_2$ single-crystalline microspheres. We successfully fabricated microspheres of CdSe, a well-known semiconductor with a wurtzite structure for nanophotonics in the visible region. The submicron-sized CdSe spheres had high sphericity and crystalline quality as well as good stability under ambient condition. The diameters of the fabricated spheres widely ranged from several tens of nanometres to around 2 μm. Figure 3a shows a typical TEM image of a submicron-sized CdSe sphere. It can be seen that the particle had high sphericity and no faceted structures. Furthermore, the submicron-sized sphere was uniform, and a strain contrast attributable to dislocations and lattice defects is not visible in Fig. 3a. In addition, the electron diffraction pattern in Fig. 3b, which corresponds to the CdSe microsphere in Fig. 3a, clearly proves that the fabricated CdSe microsphere was a single crystal, with all the diffraction spots being attributable to those of a CdSe bulk crystal along the [001] zone axis[12]. Figure 3c shows a high-resolution TEM image of the surface of the CdSe microsphere in Fig. 3a. The presence of uniform lattice fringes proves the good crystalline nature of the CdSe microsphere even at the surface. The interplanar spacing of the lattice fringes in Fig. 3c was measured and found to be approximately 0.37 nm; this value corresponds to that of the {100} planes of a CdSe bulk crystal.

On the other hand, in the case of laser ablation in superfluid helium of ZnSe, which exhibits a zinc blende structure under ambient condition, microspheres with a different crystal structure were fabricated. A typical TEM image of a fabricated ZnSe microsphere, shown in Fig. 4a, indicates that the particle had high sphericity and very few dislocations. Figure 4b shows the electron diffraction pattern taken from the ZnSe microsphere in Fig. 4a. All spots could be indexed by those of a ZnSe bulk crystal with a hexagonal wurtzite structure from the [-12-1] zone axis[13], showing that the fabricated ZnSe microspheres were also single crystals and that the transformation from a cubic structure to a hexagonal wurtzite structure occurred in the ablation process. It should be noted that this transformation was observed even in the laser ablation process in vacuum

that did not produce microspheres with high sphericity. This means that the transformation in crystal structure was caused by quenching. Our ability to obtain single crystals of ZnSe with high sphericity suggests that laser ablation in superfluid helium could fabricate microspheres of novel materials or structures where other methods have failed. In addition, the uniform lattice fringes, which can be clearly observed in Fig. 4c, demonstrate the good crystalline nature of the ZnSe microsphere even around its edge. The interplanar spacing of the lattice fringes in Fig. 4c was measured and found to be approximately 0.31 nm; this value corresponds to that of the {10-1} planes of a ZnSe bulk crystal with the wurtzite structure.

Finally, we tried to fabricate microspheres of CeO$_2$ with a cubic structure, which has attracted much attention as an efficient catalyst. Figure 5a shows a typical TEM image of a CeO$_2$ sphere. Furthermore, the electron diffraction pattern in Fig. 5b, which corresponds to the CeO$_2$ microsphere in Fig. 5a, clearly proves that the fabricated CeO$_2$ microspheres were single crystals, with all the diffraction spots being attributable to those of a CeO$_2$ bulk crystal along the [011] zone axis[14].

Thus, we obtained single-crystalline microspheres with high sphericity of many materials by laser ablation in superfluid helium regardless of their crystal structures, although it has been well understood that single-crystalline microstructures naturally possess facets. The extremely high sphericity of the fabricated microspheres was verified by TEM observation and a comparison of the experimental and calculated emission spectra of single microspheres. Furthermore, the detailed TEM analysis clearly proved that the microspheres were single crystals with very few dislocations despite the highly spherical shape. Detailed investigations on the mechanism[15] underlying the fabrication of these microspheres as well as the possibility of using this method with other materials are under way. The anticipated findings will not only extend application of this novel fabrication method, but will also help us better understand the crystallisation mechanism of solids.

Discussion

This fabrication method allows us to obtain large microspheres, which have potential application as WGM resonators with high Q value, because of the three-dimensionally efficient light confinement. In order to fabricate ZnO microspheres with extremely high spheri-
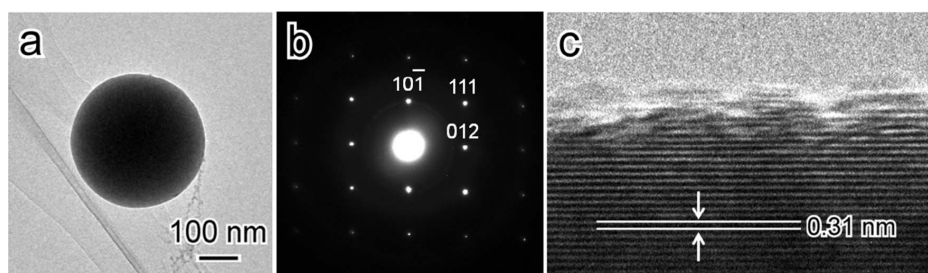

Figure 4 | **TEM images and diffraction pattern of a fabricated ZnSe microsphere.** (a) Typical TEM image of a ZnSe microsphere. (b) Electron diffraction pattern of the ZnSe microsphere shown in (a) taken along the [-12-1] zone axis. (c) High-resolution TEM image of the sphere shown in (a).
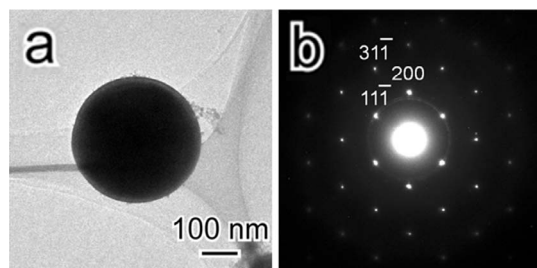
Figure 5 | TEM image and diffraction pattern of a microsphere of another material. (a) TEM image of a CeO_2 microsphere. (b) Electron diffraction pattern of the CeO_2 sphere shown in (a), taken along the [011] zone axis.

city and desirable sizes using laser ablation, the pulse intensity of the laser should be higher than 0.2 J/cm². When the pulse intensity was below this value, the fabricated ZnO particles were smaller than 1 μm in diameter. When the pulse intensity was higher, the amount of melted ZnO was sufficient for the formation of micron-sized particles. Microspheres were formed from the melted ZnO via rapid cooling in superfluid helium. If the cooling was not performed quickly, the ZnO particles had a tendency to grow into microrods[8] owing to the wurtzite structure of bulk ZnO. We could fabricate at least tens of micron-sized and hundreds of submicron-sized ZnO spheres in superfluid helium. Note that the threshold pulse intensity required is similar in value to the upper limit of the intensity required during the pulsed heating method, which provides aggregated submicron-sized spheres of semiconductors and metals[4]. On the other hand, the present method allows for the fabrication of larger, isolated microspheres of much higher sphericity. The threshold of the intensity of the laser for the fabrication of the microspheres of the other materials is of the same order of magnitude.

So far, compared to a vacuum, air, or water, superfluid helium is a much better medium for creating single-crystalline microspheres of high sphericity. If we can extract for the cooling process the requisite conditions that enable single-crystalline growth, superfluid helium may be replaced by another medium such as liquid nitrogen, which would be a very important development for real applications. In addition, our findings show the possibility of the fabrication of anisotropic materials in any shape if we can control their environment. In the process of laser ablation in superfluid helium, the shapes of the fabricated particles are determined by the surface tension and pressure of the liquid helium: by applying additional pressure or other perturbations, we could control the shape regardless of the original crystal structures.

Methods

Fabrication of microspheres. The targets of starting materials include ZnO with a diameter of 10 mm and a thickness of 3 mm, CdSe with a cross section of 10 × 10 mm and a thickness of 1 mm, ZnSe with a cross section of 10 × 10 mm and a thickness of 1 mm, and CeO_2 with a diameter of 10 mm and a thickness of 5 mm. A target was placed on a sample holder in a cryostat (CryoVac) filled with superfluid helium (Supplementary Fig. S1). A glass plate, a Si substrate, and a TEM grid substrate were then positioned under the target (Supplementary Fig. S2). The surface of the target was irradiated with the second harmonic (SH) of a pulsed Nd:YAG laser (Spectra Physics GCR-130) placed outside the cryostat. The wavelength of the laser radiation was 532 nm, the pulse duration was 10 ns, and the repetition rate was 10 Hz. The laser beam was focused such that it formed a spot measuring 200 μm in

diameter on the surface of the target. Using this setup, we ablated the surface of the target in superfluid helium with the laser for approximately 30 min. After the ablation, the glass plate and the substrates were removed from the cryostat, and the fabricated spheres were used for SEM, TEM, or micro-PL measurements.

TEM observations. The microstructures of the fabricated particles were characterised using high-resolution transmission electron microscopy (HRTEM; FEI Tecnai 20G2), which was performed at an accelerating voltage of 200 kV.

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Author contributions

S.O., K.I., S.I. and M.A. designed and performed the experiments. T.I. and H.I. performed the theoretical calculations. All authors contributed to the discussion of the results and to the writing of the paper.

Additional information

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