

Man-made synthesis of ultrafine photoluminescent nanodiamonds containing less than three silicon-vacancy colour centres

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ABSTRACT

Silicon-vacancy (SiV) centred diamond exhibits near infrared emission at 738 nm with narrower zero-phonon line and shorter lifetime comparative with nitrogen-vacancy (NV) centre, considered as a promising room-temperature single-photon source. However, unlike NV centred nanodiamonds easily obtained by detonation, man-made synthesis of ultrafine SiV nanodiamonds is a key challenge. Here, we provide a controllably method for synthesizing nanodiamonds with one or few SiV emitters by reducing their size to the near minimum via oxygen plasma treatments. The size of nanodiamond is uniformly reduced from 11 to 1.7 nm under different treatment durations. It is found that nanodiamonds of a size between 2.1 and 4 nm contain fewer than three emitters. Size dependence of microstructure and photoluminescence suggests that SiV centres exist in the outer shell of nanodiamonds with diameter larger than ~2 nm. This material has significant applications in nanophotonics platform, quantum communications and quantum photonics.

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1. Introduction

Fluorescent centres in diamond have significant applications in fields such as quantum communications, quantum photonics, and biological imaging. Fluorescent diamond is generally considered as a photostable solid-state single photons source at room temperature, supplying prominent candidates for generating and manipulating quantum states of light. In addition, the stability of the diamond defects constitutes the main advantage over other systems [1]. Furthermore, nanodiamonds are biocompatible, optically stable, anticorrosion and easy to surface functionalize, making them ideally suited for biological applications, catalyst and catalyst carrier [2–4].

Out of more than 500 colour centres, fewer than ten centres in diamond have thus far been identified as bright, stable single-photon emitters [1]. Of these centres, nitrogen-vacancy (NV) centres have been thoroughly studied [5–11]. Electrically neutral (NV⁰) and negatively charged (NV⁻) centres exhibit one zero-phonon line

(ZPL) at 575 nm and 637 nm with a characteristic broad phonon sideband that extends from 580 to 650 nm and to 800 nm, respectively. The wide emission band and long lifetime of NV centres, up to 25 ns, renders them unsuitable for single-photon-source [12–14]. In contrast, the silicon-vacancy (SiV) centre has a ZPL centred at 738 nm (1.681 eV), with a very narrow band (~5 nm) and short luminescence lifetime (~1.2 ns) [1,15,16]. These characteristics facilitate the excellent performance of SiV centred diamond, which have recently attracted increasing attentions.

It is possible to obtain one SiV centre in one diamond grain small enough in size to support a single-photon source. The calculation based on the first-principles density functional theory showed that isolated diamond nanoparticles as small as 1.6 nm, were capable of housing stable photoluminescent SiV centres. It was also found that molecular-sized (~1.6 nm) fluorescent SiV nanodiamonds containing approximately 3 emitters existed in meteorites [17]. However, unlike NV centred nanodiamonds easily obtained by detonation [8,9], the man-made synthesis of SiV centred ultrafine nanodiamonds is so far an outstanding challenge. This dramatically limits the related research and applications.

Here, we provide a controllably method for preparing ultrafine nanodiamonds with one or few SiV emitters by reducing the

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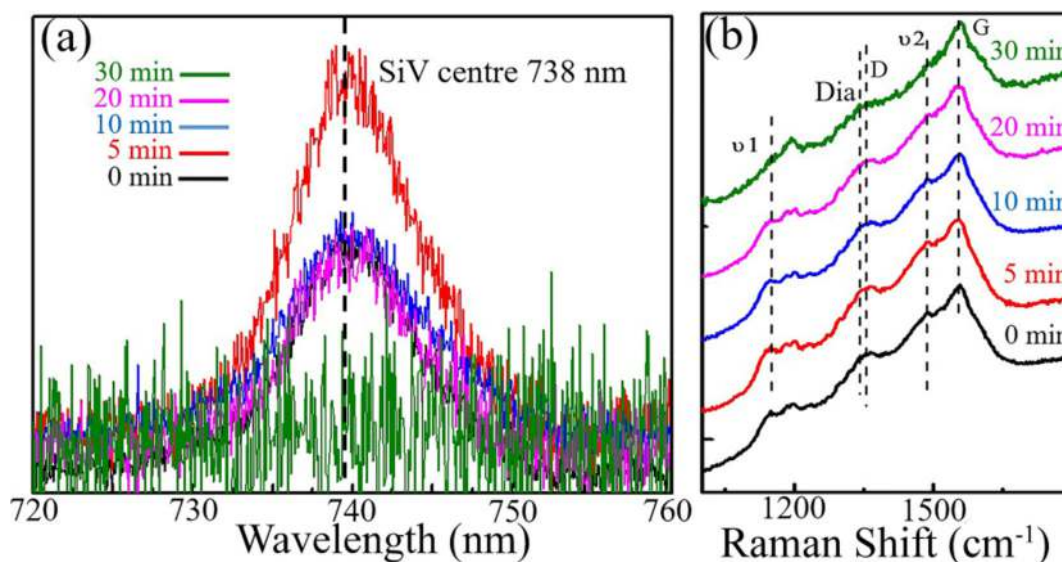


Fig. 1. (a) Photoluminescence (PL) and (b) Raman spectra of the nanocrystalline diamond films treated with oxygen plasma for 0–30 min.

diamond grain size in nanocrystalline diamond films to the near minimum via oxygen plasma treatments. Then, the photon statistics of SiV fluorescence in these man-made nanodiamond grains were investigated. The results show that the size of diamond grains uniformly decreases from 11 to 1.7 nm via different treatment durations. The finest diamond grains that can emit SiV PL are in the size range of 2.1–4 nm, and these grains were separated from the film and immobilized on a fused silica slide. Hanbury Brown-Twiss (HBT) measurements show that fewer than three emitters are present within the fluorescent spot, indicating that sub-4-nm nanodiamond grains with few SiV emitters are prepared. This method is of significant importance for the applications of SiV photoluminescent diamonds as nanophotonics platform, quantum communications and quantum photonics.

2. Results and discussion

Fig. 1 (a) shows photoluminescent spectra in the range of 720–760 nm of the nanocrystalline diamond films treated with oxygen plasma for different durations, denoted O-*n*, where *n* is the treatment duration. The untreated nanocrystalline diamond film (black line, nearly the same with the blue line and magenta line) shows a SiV peak meaning that the diamond grains contain SiV centres, because silicon atoms diffuse from the silicon substrate into the growing diamond crystals [18,19]. After a 5-min oxygen plasma treatment, the intensity of the luminescent SiV peak is enhanced, as shown in Fig. 1 (a), and the red peak is obviously higher than the others. As the treatment duration increases from 10 to 20 min, the luminescent SiV peak weakens. After 30 min treatment, the peak disappears.

Fig. 1 (b) shows the Raman spectra in the range of 1000–1800 cm⁻¹ of the nanocrystalline diamond films treated with oxygen plasma for different durations. Each Raman spectrum in Fig. 1 (b) shows the typical characteristics of nanocrystalline diamond films with a grain size smaller than 10 nm, and five obvious peaks were labelled by vertical dashed lines. The peaks at approximately 1140 (ν_1) and 1480 (ν_2) cm⁻¹ are related to *trans*-polyacetylene (TPA) and can be assigned to the C–H bending and/or C–C stretching modes and the C=C stretching mode of the TPA chains, respectively [20,21]. The peak at 1332 cm⁻¹, known as the diamond peak, is very weak, indicating small size of diamond

grains. In addition, sp² graphitic phases are visible at 1340 (D band) and 1560 cm⁻¹ (G band) [21,22].

The Raman spectra of the O-0, O-5, O-10 and O-20 samples show very few differences, indicating that their phase composition continuously evolves. After 30 min of oxygen plasma etching, the diamond peak is nearly undetectable, indicating a further decrease in the content or grain size of the diamond. This leads to the disappearance of the SiV PL in the O-30 sample. As oxygen plasma can oxidize the film, different treatment durations will alter the film compositions and structures, thereby affecting the SiV PL. To analyse the effects of oxygen plasma treatment on the composition of the film, we collected the X-ray photoelectron spectroscopy (XPS) wide scan spectra and the C 1s core-energy level spectra of the O-0, O-5, O-20 and O-30 samples, as shown in Fig. 2.

Fig. 2 (a) shows that the O 1s peak of the O-5 sample is much stronger than that of the O-0 sample and slightly stronger than those of the other samples. This indicates that more oxygen-related bonds are present on the surface of the nanocrystalline diamond films after treatment and that the O-5 sample has the highest content of oxygen-related bonds. We further analysed the C 1s core-energy level spectra, which were deconvoluted into five components at 283.5, 284.8, 285.2, 286.3 and 287.0 eV, attributed to C–Si, sp² carbon (C=C), sp³ bulk carbon (C–C), C–O and C=O bonds, respectively [23–25]. The oxygen plasma-treated samples exhibit a C–Si bond peak, which may originate from the exposed silicon substrate owing to the oxygen plasma treatment. In addition, we enlarged the spectral range from 286.0 to 288.5 eV, related to C=O bonds, as shown in Fig. 2(c). The C=O bond peak is much stronger for the O-5 sample than for the O-0, O-20 and O-30 samples. This result is consistent with the changes in the SiV PL of the samples, suggesting that C=O bonds tend to increase the intensity of the SiV PL. This finding agrees with those of our previous work [26], in which C=O bonds produced a much larger positive electron affinity, trapping the excited-state electrons and allowing them to scatter back to the ground state, resulting in SiV PL [27,28].

Comparing the XPS results of the O-20 and O-30 samples, we find that their surface composition is nearly the same. However, the O-20 sample exhibits SiV PL, while the O-30 sample does not, indicating that in this case, the surface termination is not the decisive factor for the disappearance of SiV PL in the O-30 sample. To further understand the correlation between oxygen plasma

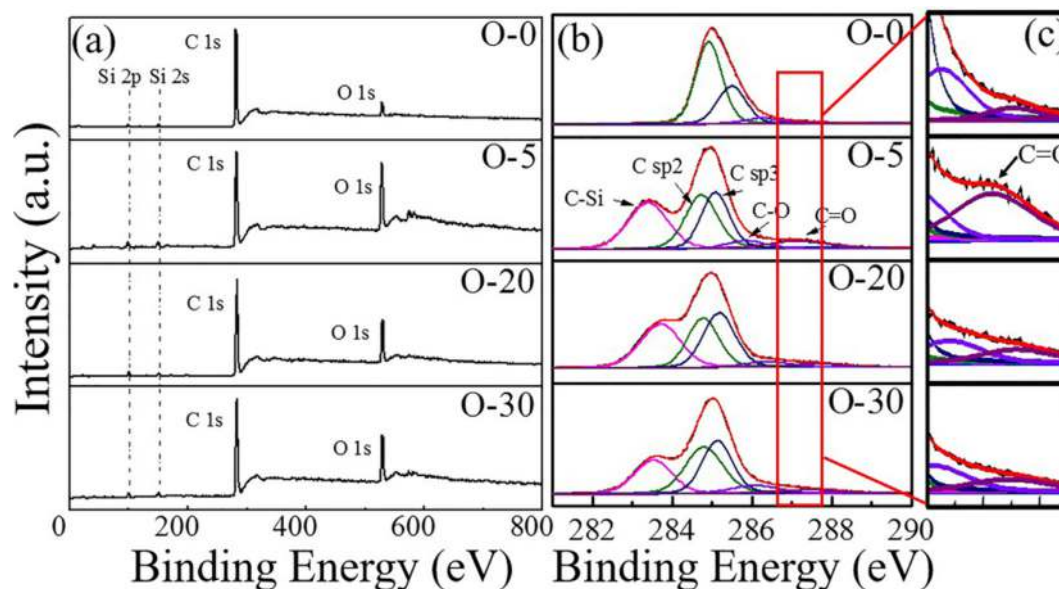


Fig. 2. (a) X-ray photoelectron spectroscopy (XPS) wide scan spectra and (b) C 1s core-energy level spectra and their deconvolution of the O-0, O-5, O-20 and O-30 samples. (c) is the enlarged images of the red square in (b).

etching and SiV PL, we analysed the microstructural evolution of the samples under different conditions using high-resolution transmission electron microscopy (HRTEM). Fig. 3 shows low-magnification HRTEM images of the samples O-5, O-10, O-20 and O-30, which illustrate that nanocrystalline diamond grains are uniformly distributed in the film. And the particle size distribution of the samples O-5, O-10, O-20 and O-30 were shown on the right

of Fig. 3. The grain size is approximately 7–11 nm, 3.5–6.2 nm, 2.1–4 nm and 1.7–2.3 nm for the O-5, O-10, O-20 and O-30 samples, respectively, indicating that the diamond grain size decreases with increasing oxygen plasma treatment duration. This relation leads to a dramatic decrease in the diamond content in the O-30 sample, which is in good agreement with the disappearance of the diamond peak in its Raman spectrum. More importantly,

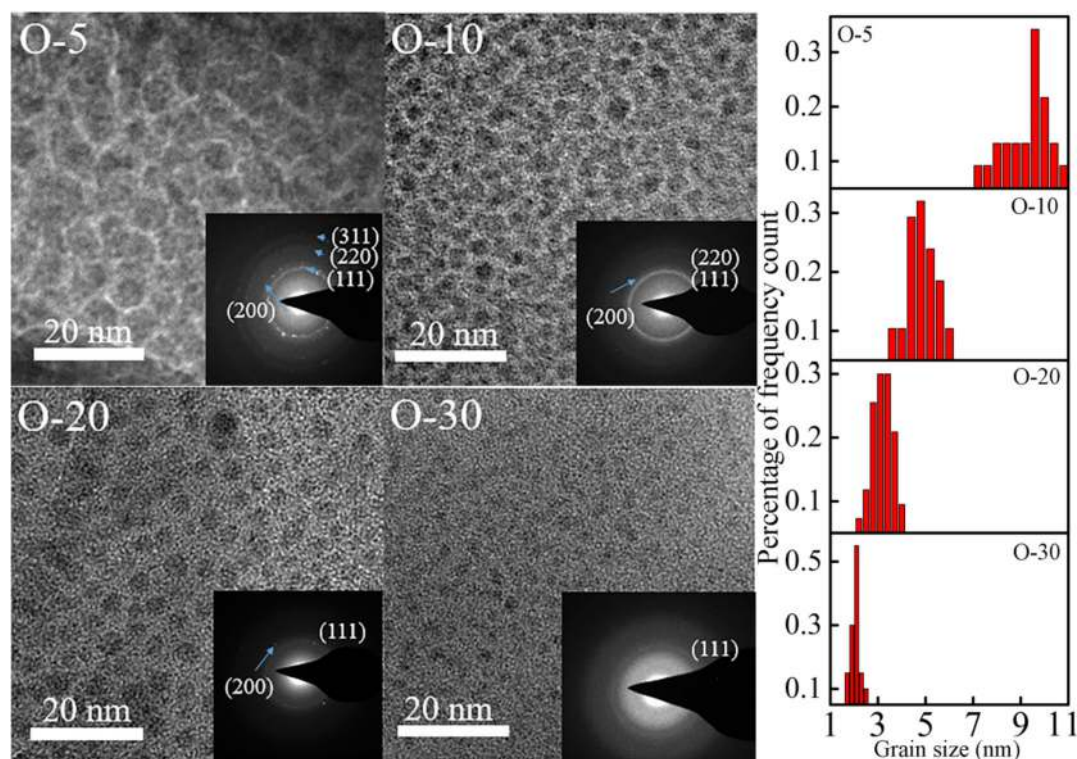


Fig. 3. (Left image) Bright-field transmission electron microscopy (TEM) images of the O-5, O-10, O-20 and O-30 samples. The insets show the corresponding selected area electron diffraction (SAED) patterns. The diamond diffraction rings of the (111), (200), (220) and (311) planes are labelled in the SAED patterns. (Right) Particle size distribution of the samples O-5, O-10, O-20 and O-30.

comparing the results of the grain size and PL spectra, the finest grains that can emit SiV PL are 2.1–4 nm in size. These are currently the smallest man-made nanodiamonds that can emit SiV PL.

The insets of Fig. 3 show the evolution of the selected area electron diffraction (SAED) patterns of the samples. The SAED pattern of the O-5 sample contains sharp diffraction rings corresponding to the (111), (220), and (311) lattice planes of the diamond structure, confirming that the main content of the film is diamond. There is also a ring corresponding to the (200) plane of n-diamond (n-D), a metastable form of diamond with space group Fm3m symmetry and a cell parameter of 0.356 nm [29–31]. After oxygen plasma treatment for 10 min, the SAED pattern contains diffraction rings corresponding to the (111), (220), and (200) planes, while the (311) plane diffraction ring disappears. With a treatment duration of 20 min, SAED pattern exhibits (111) plane, and the (220) and (311) diffraction rings both disappear. It is also difficult to observe the (200) diffraction ring. After 30 min of oxygen plasma treatment, there is only a (111) diffraction ring, and the (200) ring also disappears. A larger Miller index corresponds to a larger unit cell. Thus, the disappearance of the (311) and (220) diffraction rings can be attributed to a decrease in the diamond grain size. However, as the

(200) diffraction ring is very close to the (111) diffraction ring, its disappearance can be ascribed to the decrease in grain size or the diminishment of the n-D phase after 30 min of oxygen plasma treatment. Above results discover the crystal plane evolution of nanocrystalline diamond grains with oxygen plasma treatment duration.

Furthermore, Fig. 4 shows the magnified HRTEM images of the granular structure. The insets, (1), (2) and (3), show the Fourier transform (FT) diffractograms of the selected areas outlined by red squares, indicating the composition evolution of the films. The phase of the areas outlined by red squares is labelled in the bottom left of the FT images (cubic diamond (c-D), n-diamond (n-D), graphite (G) and amorphous carbon (a-C)). And FT image (0) corresponds to entire structure image. In the O-5 sample, areas (1) and (2) are c-D, ~10 nm in size, with a (111) diffraction spot shown in the corresponding FT image, and area (3), the grain boundary zone of the O-5 sample, is a-C with a prominent diffused ring exists in the centre of the FT image. In FT image (0) of the O-5 sample, (200) diffraction spot can be observed indicating the presence of n-D. In the O-10 sample, c-D and n-D structures, ~5 nm in size, can also be found in areas (1) and (2), respectively. The grain boundary zone of

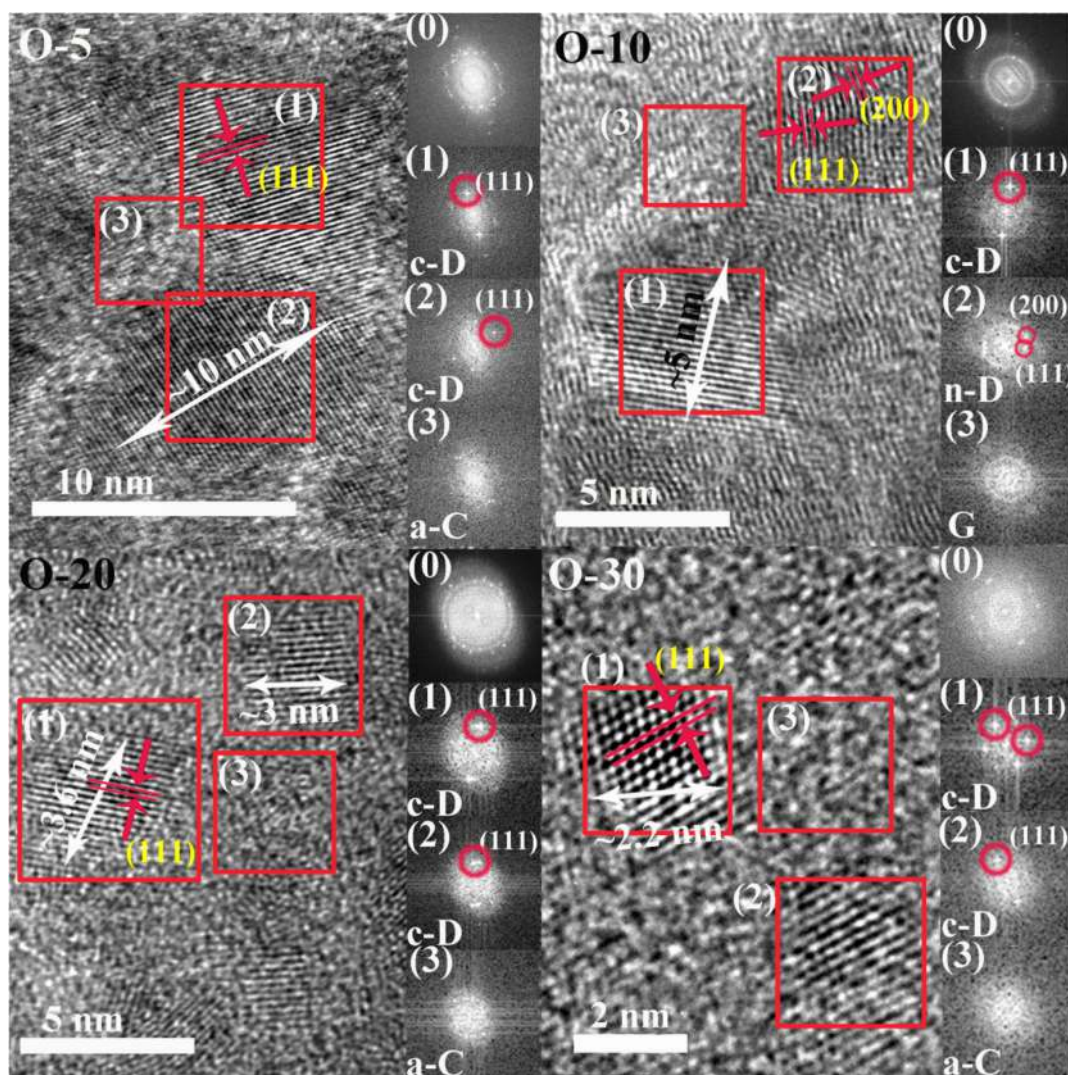


Fig. 4. High-resolution transmission electron microscopy (HRTEM) images of the O-5, O-10, O-20 and O-30 samples. The insets on the right side show the Fourier transform (FT) images corresponding to the areas outlined by red squares. In addition, the phase of the areas outlined by red squares is labelled in the bottom left of the FT images (cubic diamond (c-D), n-diamond (n-D), graphite (G) and amorphous carbon (a-C)). Inset FT image (0) corresponds to entire structure image. (A colour version of this figure can be viewed online.)

the O-10 sample contained graphite (G) with a donut-shaped diffusion ring. In the O-20 sample, both c-D and n-D structures, ~ 3 nm in size, are found. It is not easy to find the area in which c-D is close to n-D. Thus, here, to clearly show the diamond grain, only c-D is shown in the image. The (200) diffraction spot still can be observed in FT image (0) of O-20 sample. However, for the O-30 sample, it is easy to find the c-D structure, ~ 2.2 nm in size, but the n-D structure disappears. This reveals that metastable diamond diminishes. Nevertheless, a prominent diffused ring exists both in the centre of the SAED image of the O-30 sample and the FT image (3) of O-30 sample, indicating the presence of some sp^2 phase or a-C. These suggest that n-D (metastable diamond) is mainly transformed into a-C, which gives contribution to the disappearance of SiV PL.

To evaluate the photon statistics of SiV fluorescence in the diamond grains, we separated the particles from the O-20 sample using ultrasonic vibration. Then, confocal fluorescence scans were performed on the particles, as shown in Fig. 5. Fig. 5 (a) demonstrates that the saturation intensity ranges from 1.6×10^4 to 3.8×10^4 counts per second per pixel, with lower counts on the edge of the particle. Thus, we measured an autocorrelation function $g^{(2)}$ on the edge of the particle labelled by the red cross in Fig. 5 (a). Fitting the background-corrected autocorrelation function and assuming emission from multiple identical emitters, we obtained $g^{(2)}(0) = 0.64$, indicating the presence of three emitters within a

fluorescent spot, as shown in Fig. 5 (b) [32]. The corresponding PL spectrum in Fig. 5 (d) displays a luminescent peak at 738 nm with a full width at half maximum (FWHM) of approximately 6.4 nm, confirming that the emitters are SiV centres. This indicates that SiV fluorescence from three emitters has been found on the edge of the particle.

Furthermore, we used HRTEM to observe the microstructure of the particle, as shown in Fig. 5 (c). The isolated nanocrystalline diamond grains with a size of approximately 2.5 nm are distributed at the edge of the particle, and their shape is displayed in the inset of Fig. 5 (c). As the fluorescent spots of the confocal fluorescence scans are on the micron scale, there are tens of sub-4-nm diamond grains in the fluorescent spot. This indicates that fewer than three emitters are present in one nanocrystalline diamond grain. All these data confirm that we have prepared sub-4-nm diamond grains that can emit SiV PL with less than three emitters. Assuming that the emitting centres have the same probability existing in each grain, it would be of high probability for the emitters distribute in different grains, i.e., one diamond grain only contains one SiV centre. It suggests that we can obtain nanodiamond grains capable of emitting single photon by reducing the grain size to the minimum. These results have great significance for nanodiamond-based applications involving single-photon sources, nanophotonics platform and quantum communications.

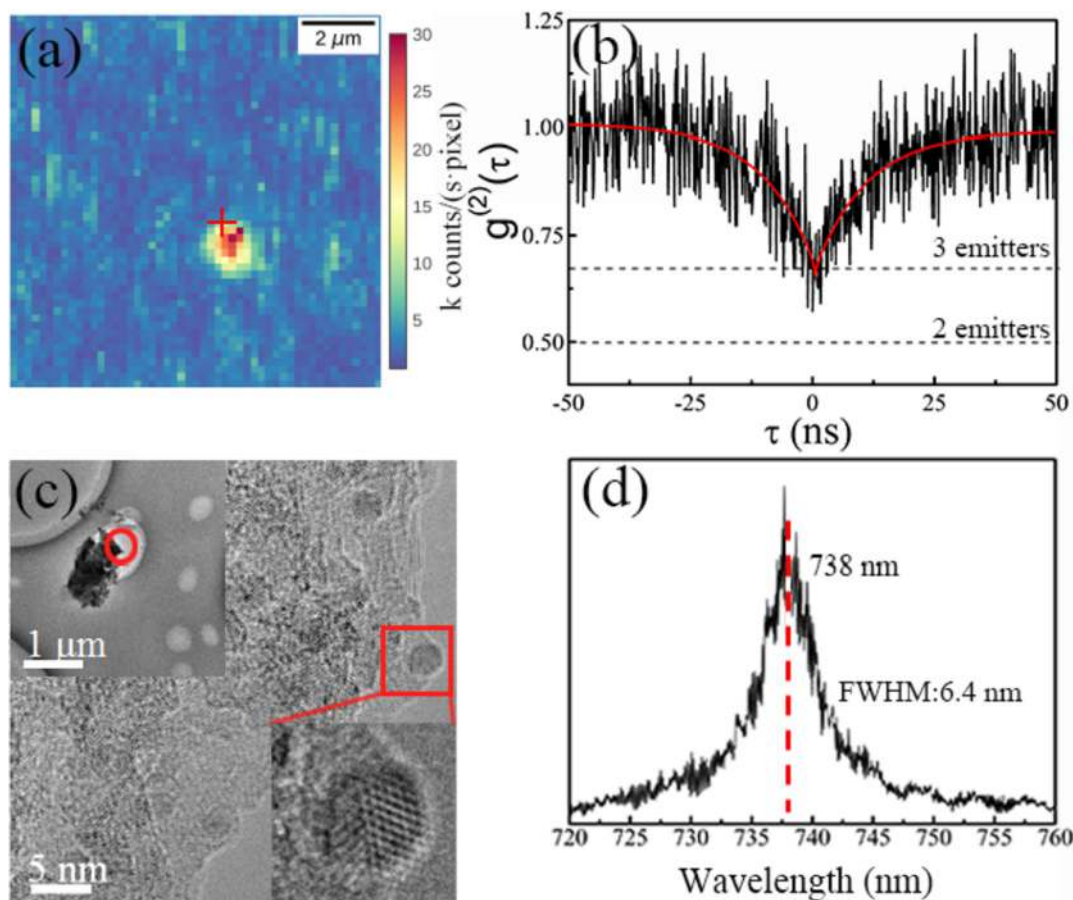


Fig. 5. Detailed analysis of a diamond grain with a sub-4-nm size, containing less than three silicon-vacancy (SiV) emitters. (a) Confocal fluorescence image obtained using a fluorescent bandpass filter around SiV fluorescence, in which the excitation laser wavelength was 532 nm. Pixel size was $200 \times 200 \text{ nm}^2$. (b) Autocorrelation function showing the background-corrected raw data (black line) and its fitted line (red). (c) High-resolution transmission electron microscopy (HRTEM) image of a particle obtained from the O-20 sample showing a few isolated diamond grains on the edge of the particle. Left inset: TEM image of the particle showing the full view. The red circle denotes the area at which the HRTEM image was obtained. Right inset: enlarged image of the red square in the HRTEM image. (d) Background-subtracted SiV photoluminescence (PL) spectra of the particle in (a) measured at room temperature with 532-nm laser excitation. (A colour version of this figure can be viewed online.)

3. Conclusions

In summary, we reduced the size of diamond grains by treating nanocrystalline diamond films with oxygen plasma. Ultrafine diamond grains in size of 2.1–4 nm (sub-4-nm) that can emit SiV PL with less than three emitters were produced after 20 min of oxygen plasma etching. This approach so far provides the smallest man-made photoluminescent nanodiamonds with less than three SiV emitters, which have significant potential for applications involving single-photon sources, nanophotonics platform and quantum communications. Our results open a way to controllably adjust the size and properties of nanomaterials.

4. Experimental section

4.1. Preparation of diamond film

The nanocrystalline diamond films were deposited on mirror-polished Si wafers in a MPECVD system. A mixture of CH₄ and Ar, at a flow rate of 4 and 196 sccm, respectively, was used as the reactant gas for the microwave discharge. The plasma was induced with a microwave power of 1200 W and a pressure of 150 Torr. All samples were grown for 60 min, and no external heater was used to heat the substrate. The substrate was heated by plasma bombardment to a temperature of 470 °C, which was monitored by a thermocouple embedded in the stainless-steel substrate holder.

4.2. Plasma bombardment

A mixture of O₂ and N₂, at flow rates of 20 and 80 sccm, respectively, was used as the reactant gas for the oxygen plasma. The plasma was induced with a microwave power of 900 W and a pressure of 0.5 Torr. Nanocrystalline diamond films were subjected to oxygen plasma bombardment for 5, 10, 20 and 30 min [33].

4.3. HBT measurement

Diamond particles were prepared for confocal imaging via common ultrasonication in alcohol. Ultrasonication was performed on the diamond film with the substrate for 4 h. Alcohol containing the diamond particles was dropped onto a fused silica slide and rapidly dried. HBT measurements were performed on the nanodiamond grain using a home-made confocal setup. The resolution of our confocal microscope is 200 nm.

4.4. Other measurements

The luminescent properties of the samples were characterized by PL spectroscopy at a wavelength of $\lambda = 532$ nm. The films were also analysed by visible Raman spectroscopy (EnSpectr R532) at a wavelength of $\lambda = 532$ nm. The SiV luminescence was filtered out by a bandpass filter. The atomic concentrations of the present elements and their chemical bonds were characterized using XPS (Axis Ultra DLD spectrometer). The detailed microstructures were examined using TEM (Tecnai G2 F30 S-Twin produced by Philips-FEI).

Author contributions

Chengke Chen and Xiaojun Hu designed the experiments. Chengke Chen and Yingshuang Mei performed the experiments and data analysis. Xiaojun Hu, Xiao Li, Meiyang Jiang and Shaohua Lu commented on the data analysis and wrote the manuscript. Jingming Cui set up and performed the fluorescence measurements. All authors discussed the results and commented on the

manuscript and have given approval to the final version of the manuscript.

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