

# Experimental estimation of the maximum size of a dressed photon

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**Abstract:** This article describes experimental estimation of the maximum size of a dressed photon (DP) by a photochemical vapor deposition method that has been used for forming a metallic zinc nanoparticle (Zn-NP) on a sapphire substrate. Because of the localized feature of the DP and of a unique non-resonant DP–molecule interaction, this method succeeded in excluding the contribution of the propagating light in the Zn-NP formation. The size of the deposited Zn-NP increased with increasing deposition time. Finally, the size saturated to a value that was independent of the radius of curvature of the fiber probe tip and the wavelength of the light used for irradiating the end of the fiber probe. From these results, it was concluded that the experimentally estimated maximum size was 50–70 nm.

## 1. Introduction

A dressed photon (DP) is a quasi-particle representing the coupled state of a photon and an electron–hole pair in a nanometer-sized material (nanoparticle: NP) [1]. It has been confirmed that the size  $a_{DP}$  of a DP is

equivalent to the size  $a_{NP}$  of the NP on which the created DP is localized [2].

This size is much smaller than the wavelength  $\lambda$  of conventional propagating light.

Because of the unique localization feature mentioned above and

because  $a_{DP} < \lambda$ , a variety of application technologies developed so far [3] have realized an ultrahigh spatial resolution beyond the diffraction limit of conventional optical technologies. To realize further developments in these technologies, it is essential to estimate the minimum and maximum sizes of the DP ( $a_{DP,Min}$  and  $a_{DP,Max}$ , respectively). A reasonable estimate is to assume that the minimum size  $a_{DP,Min}$  is equivalent to the size of an atom  $a_{atom}$ . This is because a fundamental interaction takes place between a photon and an electron in an atom for creating the DP\*.

On the other hand, the maximum size  $a_{DP,Max}$  has never been estimated. The advent of a novel theory is expected to make this estimation possible. To this end, this article describes experimental estimations of the maximum size  $a_{DP,Max}$  by using the localized features of the DP mentioned above and also a unique feature, called non-resonant DP–molecule interaction.

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Experiments on DPs have been carried out by using ultraviolet light, visible light, or infrared light as a light source for creating the DP. Some infrared wavelengths can excite molecular vibrations, which can be treated by a theoretical model known as the dressed-photon–phonon model [4]. Microwaves have also been used to realize a spatial resolution as high as  $\lambda / 4000$ , where the wavelength  $\lambda$  was 12 cm [5]. Here, it should be noted that microwaves do not interact with the electron in the atom even though it can excite a molecular rotation. Thus, the experiments using microwaves are not compatible with the present study described here.

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## 2. Methods for experimental estimation

Photochemical vapor deposition (PCVD) based on DP–molecule interaction was adopted as the most appropriate method to experimentally estimate the maximum size  $a_{DP,Max}$ . This is because the size, conformation, and position of the DP were transcribed to those of an NP formed on a substrate as a result

of deposition. As shown in Figs. 1(a) and (b), this method involved molecular dissociation by the DP and subsequent deposition of the dissociated atoms on the substrate [6,7].

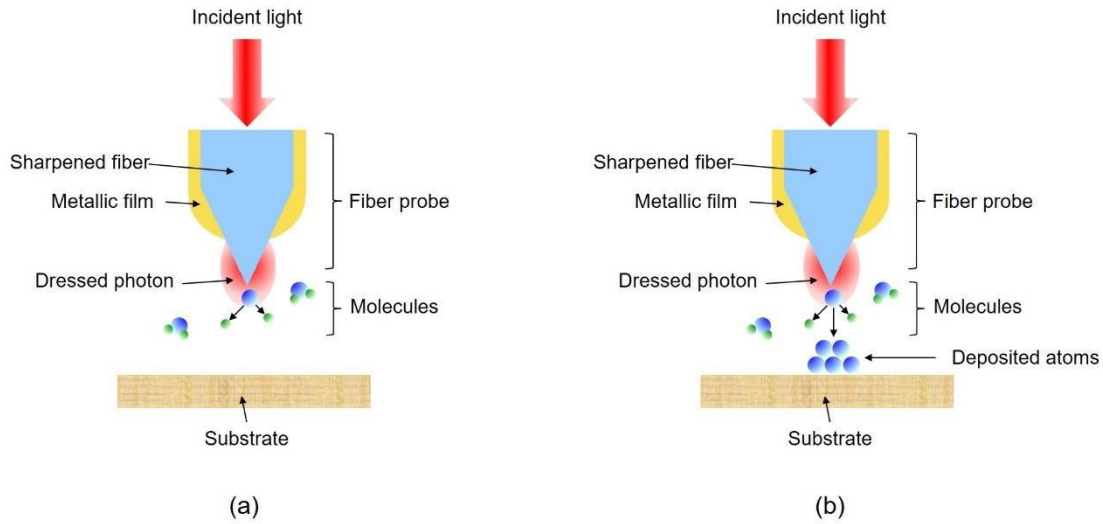


Fig. 1 Photochemical vapor deposition based on DP–molecule interaction.

(a) Dissociation of molecules. (b) Deposition of the dissociated atoms.

First,  $\text{Zn}(\text{C}_2\text{H}_5)_2$  (DEZn for short) was adopted as a specimen molecule. Gaseous DEZn molecules were filled into the vacuum chamber. A fiber probe and a substrate were also installed in the chamber. A DP was created on the tip of the fiber probe by irradiating the end of the fiber probe with propagating light. The DEZn molecules were dissociated when these freely flying molecules jumped into the field of the DP. The dissociated Zn atom subsequently landed on the substrate. After a very short migration on the substrate, the atom was adsorbed on the substrate. By repeating these processes, the number of adsorbed Zn atoms increased, resulting in the deposition of Zn atoms and the formation of a nanometer-sized metallic zinc nanoparticle (Zn-NP) on the substrate. Since the DEZn molecules were dissociated in the field of the DP, the size, conformation, and position of the formed Zn-NP were equivalent to those of the DP.

In the case of dissociating the DEZn molecules by conventional propagating light instead of by a DP, the wavelength of this light had to be shorter than 270 nm (photon energy 4.59 eV) for exciting an electron in the

DEZn molecule. To estimate  $a_{DP,Max}$ , the DEZn molecules must be dissociated only by the DP on the tip of the fiber probe (Fig. 1(a)), for which the contribution of the propagating light used for creating the DP must be excluded. To achieve this, three ingenious tricks were employed:

(1) The first was a photochemical trick: The wavelength of the propagating light for creating the DP was set longer than 270 nm. As a result, it was expected that the DEZn molecules would not be dissociated even if irradiated with propagating light, which scattered out from the tip of the fiber probe. Instead, it was expected that the DP on the tip would dissociate the DEZn molecules due to the non-resonant DP–molecule interaction. It has been confirmed that this novel dissociation originated from the multi-step excitation of the electron via molecular vibration energy levels, triggered by the DP [6,7].

(2) The second was an instrumentational trick: A primitive bare fiber probe was employed on which no metallic films were formed. As shown in Fig. 2(a), a conventionally used fiber probe was fabricated by sharpening a fiber with an advanced selective chemical etching method [8], resulting in high-precision control of the nanometer-sized tip diameter, cone angle, and throughput of the DP creation. This high precision was essential to control the size, conformation, and position of the created DP on the tip for estimating  $a_{DP,Max}$ . The tapered part of the sharpened fiber was subsequently coated with

an opaque metallic film in order to prevent the scattered propagating light from leaking out from the fiber probe. In contrast, the fiber probe used here was fabricated by a very primitive method. That is, the fiber was heated and mechanically pulled to sharpen it. As a result, high-precision control of the size, cone angle, and throughput were not expected. In addition, the probe was not coated with a metallic film (Fig. 2(b)), allowing the scattered propagating light to leak from the taper and tip of the fiber probe. Even when using such an unreliable fiber probe, the contribution of the propagating light was expected to be excluded because of its long wavelength, as discussed in (1) above.

(3) The third was again a photochemical trick: For further insurance, the DEZn molecules were replaced by zinc-bis(acetylacetonate) ( $Zn(acac)_2$  for short) molecules [9,10].  $Zn(acac)_2$  is known to be an optically inactive molecule,

and thus, it has never been dissociated by propagating light. However, it was expected here that it could be dissociated by the DP via excitation of a molecular vibration for depositing the dissociated Zn atoms on the substrate. This is also the application of a non-resonant DP–molecule interaction.

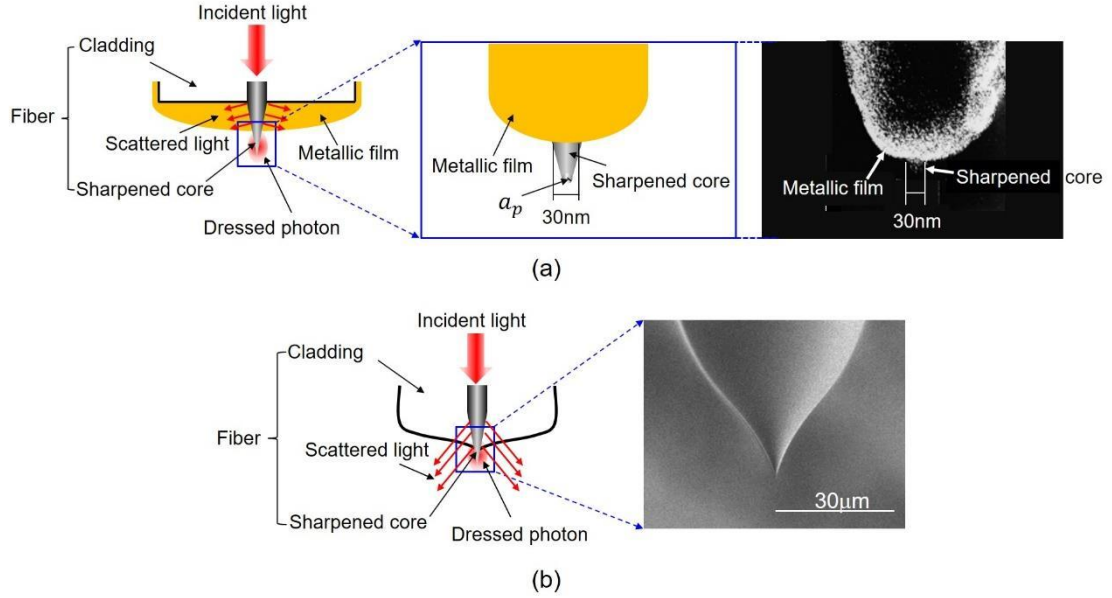


Fig. 2 Structures and scanning electron microscopic images of fiber probes. (a) A high-precision fiber probe, which has been popularly used for high-spatial-resolution microscopy and spectroscopy.  $a_p$  is the radius of curvature of the tip. (b) A primitive fiber probe, which was used for the present experiments.

### 3. Estimated results and discussion

Figures 3(a)-(c) show images of a three-dimensional Zn-NP formed on a sapphire substrate by dissociating DEZn molecules; these images were acquired by using an atomic force microscope (AFM) [7]. The wavelengths  $\lambda$  of the propagating light for creating the DP were 325, 488, and 684 nm, respectively. In the case of Fig. 3(a), this wavelength was close to the value of 270 nm given in Section 2. Thus, the contribution from the conventional propagating light might not have been sufficiently excluded. Tails represented by white broken curves in this figure were attributed to this contribution.

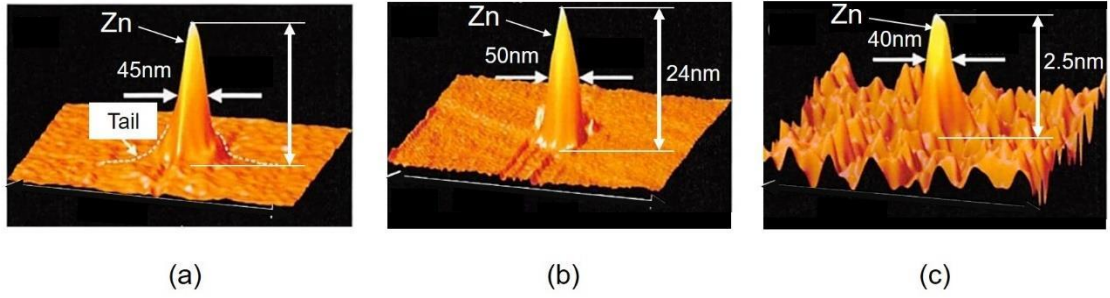


Fig. 3 AFM images of three-dimensional Zn-NPs formed on a sapphire substrate. The DEZn molecules were dissociated by the DP. The wavelengths of the propagating light for creating the DP were (a) 325 nm, (b) 488 nm, and (c) 684 nm.

In contrast to Fig. 3(a), the wavelengths of the propagating light in Figs. 3(b) and (c) were sufficiently longer than 270 nm, which means that the contribution from the propagating light was sufficiently excluded due to tricks (1) and (2) described in Section 2. That is, the DEZn molecules were dissociated only by the non-resonant DP–molecule interaction, resulting in AFM tail-free images of the Zn-NPs. The full width at the half-maximum (FWHM) of the AFM images were 45, 50, and 40 nm\*, respectively, in Figs. 3 (a)-(c), which were independent of the wavelength  $\lambda$  of the propagating light. Thus, it was confirmed that these values corresponded to the size of the DP used for the present PCVD.

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It should be noted that these values contained a systematic error originating from the spatial resolution of the AFM, which corresponded to the tip size of several nanometers of the AFM probe. Thus, the corrected values of the FWHM, obtained by subtracting this error, were slightly smaller than 45, 50, and 40 nm.

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Figure 4 shows images of the three-dimensional Zn-NPs formed on a sapphire substrate, where DEZn molecules were replaced by Zn(acac)<sub>2</sub> molecules based on tricks (2) and (3) in Section 2 [9,10]. The wavelength  $\lambda$  of the propagating light for creating the DP was 457 nm. In the case of Fig. 4(a), low-power (65  $\mu$ W) propagating light entered the fiber in order to form a small Zn-NP on the substrate by maintaining the deposition rate sufficiently low. Because high-precision control of the deposition time was ensured by this low deposition rate, an FWHM for the Zn-NP as narrow as 5–

10 nm was realized, which was the smallest value realized by the present PCVD method. The height was as low as 0.3 nm, which corresponded to the thickness of two layers of Zn atoms, demonstrating the high precision of deposition.

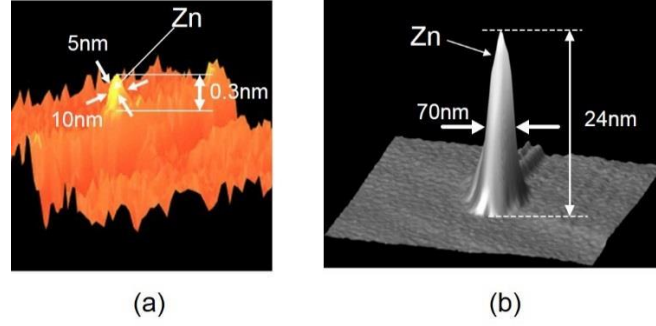


Fig. 4 AFM images of three-dimensional Zn-NPs formed on a sapphire substrate. The  $\text{Zn}(\text{acac})_2$  molecules were dissociated by the DP. The wavelength of the propagating light for creating the DP was 457 nm. (a) The power of the propagating light incident on the fiber probe was  $65 \mu\text{W}$ . The irradiation time was 30 s. (b) The power of the propagating light incident on the fiber probe was 1 mW. The irradiation time was 15 s.

By increasing the incident propagating light power (1 mW), a larger Zn-NP was formed, from which the maximum size  $a_{DP,Max}$  of the DP was accurately estimated. Figure 4(b) shows the result. The value of the FWHM was 70 nm, which was close to the values in Fig. 3.

Figure 5 shows the dependence of the rate  $R$  of depositing Zn atoms on the FWHM of the formed Zn-NP. Here, the value of the FWHM increased with increasing deposition time [11]. The  $\text{DEZn}$  molecules were dissociated by irradiating the end of the fiber probe with 325 nm-wavelength propagating light. This figure shows that the rate  $R$  took the maximum when the FWHM was equal to the tip diameter  $2a_p$  ( $a_p=4.4$  nm: tip radius of the fiber probe tip). This was due to the size-dependent resonance of the DP energy transfer between the tip of the fiber probe and the formed Zn-DP [12]. Further increases in the deposition time decreased  $R$  while the size of the Zn-NP increased. Finally, the size and conformation of the Zn-NP became stable, independently of the value of  $a_p$ . As a result, the value of the FWHM

saturated. Figures 3 and 4(b) show the profiles acquired after this stabilization.

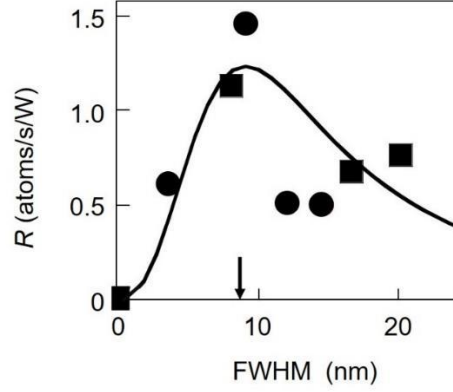


Fig. 5 Dependence of the deposition rate  $R$  on the FWHM of the Zn-NP.

The wavelength of the propagating light for creating the DP was 325 nm. Closed circles and squares represent the measured values when the powers of the light incident on the fiber probe were  $5 \mu\text{W}$  and  $10 \mu\text{W}$ , respectively. The downward arrow represents the value of  $2a_p$ .

The FWHM values in Figs. 3 and 4(b) were 50–70 nm, including systematic errors due to the spatial resolution of the AFM. They were independent of  $a_p$  and the wavelength  $\lambda$  of the light used for irradiating the end of the fiber probe. A larger FWHM was not realized even by increasing the deposition time. From these unique results, it was concluded that the experimentally estimated maximum size  $a_{DP,Max}$  of the DP was 50–70 nm.

#### 4. Summary

In order to stimulate the advent of a novel theory for describing the maximum size  $a_{DP,Max}$  of a DP, this article described experimental estimation of  $a_{DP,Max}$  by PCVD for dissociating DEZn molecules and  $\text{Zn}(\text{acac})_2$  molecules in order to form a Zn-NP on a sapphire substrate.

The experimental methods and results are summarized as follows:

(1) The present PCVD method excluded the contribution of the propagating



light even though this light leaked out from the fiber probe. This exclusion was ensured by using a non-resonant DP–molecule interaction.

(2) The size of the Zn-NP increased with increasing deposition time, and finally, the size and conformation of the Zn-NP became stable. As a result, the value of the FWHM saturated.

(3) The saturated value of the FWHM was independent of the tip radius  $a_p$  of the fiber probe and the wavelength  $\lambda$  of the propagating light used for creating the DP.

From the results above, it was concluded that the experimentally estimated maximum size  $a_{DP,Max}$  of the DP was 50–70 nm.

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