Quantum confined Rydberg excitons in Cu$_2$O nanoparticles

Konstantinos Orfanakis, Sai Kiran Rajendran, and Hamid Ohadi

SUPA, School of Physics and Astronomy, University of St Andrews, St Andrews, KY16 9SS, United Kingdom

Sylwia Zieleńska-Raczyńska, Gerard Czajkowski, Karol Karpiński, and David Ziemkiewicz

UTP University of Science and Technology, Bydgoszcz, Poland

(Dated: April 27, 2021)

The quantum confinement of Rydberg excitons is an important step towards exploiting their large nonlinearities for quantum applications. We observe Rydberg excitons in natural nanoparticles of Cu$_2$O. We resolve up to the principal quantum number $n = 12$ in a bulk Cu$_2$O crystal and up to $n = 6$ in nanoparticles extracted from the same crystal. The exciton transitions in nanoparticles are broadened and their oscillator strengths decrease as $\propto n^{-4}$ compared to those in the bulk (decreasing as $\propto n^{-3}$). We explain our results by including the effect of quantum confinement of exciton states in the nanoparticles. Our results provide an understanding of the physics of Cu$_2$O Rydberg excitons in confined dimensions.

I. INTRODUCTION

Solid-state quantum systems provide unprecedented capabilities for the realization of novel devices owing to their robustness, miniaturization capability and scalability. The operation of such devices requires developing means to efficiently produce, control and detect strongly interacting particles. Excitons, elementary excitations in semiconductors consisting of a Coulomb-bound pair of an electron and a hole, are considered major candidates towards this direction. An exciton represents a solid-state analog of the hydrogen atom and hence excited states can be observed as a hydrogen-like discrete series at energies $R_n/\mu^2$ below the bandgap, with $R_n$ the Rydberg energy and $\mu$ the principal quantum number. Excitons in cuprous oxide (Cu$_2$O) were observed as early as 1952, and their various physical properties have been studied since then. However only energy levels up to $n = 8$ in Cu$_2$O were observed for many decades until the Rydberg spectrum was extended to $n = 12$ in 1996.

Among semiconductors, Cu$_2$O has the advantage of a large Rydberg energy which allows access to much higher excited states. In a recent high-resolution laser absorption study, it was shown that Cu$_2$O hosts Rydberg excitons up to $n = 25$. This demonstration opened the portal to the field of giant Rydberg excitons in solid-state, in close analogy with their highly excited counterparts in atomic Physics. Owing to their giant microscopic dimensions (up to $\sim 1\mu$m) leading to the onset of exciton blockade, Rydberg excitons in Cu$_2$O exhibit enhanced optical nonlinearities at much smaller densities compared with other traditional semiconductors. These nonlinearities can be harnessed by quantum confinement of the excitons in semiconductor low-dimensional structures such as quantum wells and quantum dots. Studying these excitons in confined dimensions is a crucial step towards harnessing these nonlinearities for applications. nanoparticles are naturally a suitable system for quantum confinement and an interesting platform for realising quantum technologies with Rydberg excitons, potentially underpinning future devices such as single-photon sources and single-photon switches.

In this work, we report the observation of Rydberg excitons in nanoparticles of Cu$_2$O. We resolve the yellow $p$-exciton states in natural nanoparticles up to $n = 6$, while we observe up to $n = 12$ in the bulk crystal that the particles were extracted from. We show that the reduction of the crystal structure from bulk to nanoparticles leads to broadened linewidths and an apparent reduction of the oscillator strength of the excitonic peaks compared to that in the bulk. We describe both effects by the quantum confinement of the Rydberg states and the size distribution of our nanoparticles. Our results are the first demonstration of the effect of quantum confinement in linewidth and oscillator strength of Rydberg excitons.

II. EXPERIMENTAL METHODS

Cu$_2$O nanoparticles were extracted from the residual powder from polishing a natural crystal mined in Tsumeb, Namibia. After forming a suspension of Cu$_2$O nanoparticles
Figure 2. Transmission spectrum for a natural crystal of Cu$_2$O at 4 K, where excitons up to $n = 12$ are resolved (red line) and for natural nanoparticles (blue line).}

powder in water, a droplet of this suspension is deposited onto a CaF$_2$ substrate. Scanning electron microscopy (SEM) reveals that Cu$_2$O particles tend to aggregate and form a thin layer due to Van der Waals forces as the particles redistribute during water evaporation [Fig. 1(a)]. The particles are of various sizes and shapes with an average and median diameter size of $\sim 1.1$ and $\sim 0.7$ nm [Fig. 1(b)]. We refer to these particles as natural nanoparticles (NNPs). Nanoparticles are compared to a thin slab of natural bulk crystal that is cut and mechanically polished down to a thickness of $\sim 60$ µm.

We perform broadband transmission spectroscopy (see Supplementary Information 1 for setup). The excitation source is a green-yellow light-emitting diode (LED) with a center wavelength of 554 nm (Thorlabs MINTF4). The resulting signal is collected, dispersed and analyzed in a spectrometer (Andor Shamrock 750) coupled to a CCD camera. For transmission spectroscopy, an objective lens (20× Mitutoyo Plan Apo, NA = 0.42) focuses the excitation light to a spot on our sample ($\sim 100$ µm diameter) and a second objective lens (same NA as excitation) collimates the transmitted light before it enters the spectrometer. The sample is maintained at 4 K using a liquid-helium flow cryostat. We use CaF$_2$ substrates because of their excellent thermal conductivity at cryogenic temperatures and transparency in the visible spectrum.

III. EXPERIMENTAL RESULTS

The transmission spectrum of the bulk crystal reveals a series of absorption lines corresponding to the excited states of Rydberg excitons in Cu$_2$O [red line in Fig. 2(b)]. These states are labelled by their principal quantum number, $n$. We can reliably identify Rydberg states up to $n = 12$ overlaid on a continuous phonon background. By fitting the exciton resonance energies to the Rydberg formula, we extract the bandgap energy $E_g = 2.173$ eV and the Rydberg energy $R_y = 97.1$ meV, which agree with those reported in the literature.

The reduced number of exciton lines observed in our experiment compared to previous works is primarily attributed to the small diameter and broadband spectrum of our excitation source. The asymmetric lineshape stems from the Fano interference between the discrete excitonic states and the absorption background originating from phonon-assisted absorption of the 1s exciton. By fitting the exciton resonance energies to the Rydberg formula, we extract the bandgap energy $E_g = 2.173$ eV and the Rydberg energy $R_y = 97.1$ meV, which agree with those reported in the literature.

The transmission spectra of the nanoparticles covering a large area ($\sim 100$ µm diameter) on the substrate show clear exciton peaks [blue line in Fig. 2(b)]. Exciton resonances are evident as discrete asymmetric dips on top of the phonon background. Noticeable differences between the spectra of clusters and that of the thinned bulk crystal is that, in the former, is the sharp decrease in the peak absorption of the excitons as $n$ increase, such that we can only resolve resonances up to $n = 6$.

Repeating the measurements on synthetic nanoparticles (SNPs) of comparable sizes can show if the reduced number of observed excitonic resonances in NNPs could be due to the polishing procedure. The transmission spectrum for SNPs, exhibits the same number of resonances as the one for NNPs (see Supplementary Information 2). Therefore, we rule out polishing as the reason for the observation of the reduced number of transitions. We note that resonances with the same $n$ are
slightly blueshifted in the bulk crystal compared to those in nanoparticles due to a small temperature variation in each experiment (see Supplementary Fig. 3).

The comparison of oscillator strength (peak area) of the excitons in bulk and NPs shows (see Fig. 3a) that the relative peak area of excitons in nanoparticles of Cu2O decreases as $\propto n^{-4}$ compared to that in the bulk (decreasing as $\propto n^{-3}$, which is the theoretical dependence). Individual peaks were fitted with an asymmetric Lorentzian \cite{11} to extract their linewidth. The linewidth of NPs is approximately double the linewidth of the bulk thin crystal for the first three observed resonances. The broadening is more pronounced for thin crystal for the first three observed resonances. The Lorentzian absorption spectra of bulk Cu2O NPs in the full energy range and in the vicinity of $n = 5$ state.

Figure 4. Experimental (a),(c) and theoretical (b),(d) absorption spectra of bulk Cu2O NPs in the full energy range and in the vicinity of $n = 5$ state.

From the point of view of the classification of low-dimensional semiconductor structures, the considered nano-crystals are quantum dots (QDs). The SEM images (Fig. 1) suggest that the best model shape is a spherical quantum dot, with a median diameter of $\sim 700$ nm. Assuming that the interaction between dots is small enough, we may consider interband transitions in an isolated QD, and then average the results over a size distribution of QDs. As it has been shown previously\cite{33}, the optical properties of QDs can be studied with the real density matrix approach (RDMA). In this method, the optical response (absorption, reflection, transmission) is obtained by solving a set of equations for the excitonic amplitude $Y(r_e, r_h, t)$ and electric field vector $E(R, t)$ of the wave propagating in the nanostructure. The quantities $r_e, r_h$ are the coordinates of the electron and the hole, and $R$ is the center-of-mass coordinate of the electron-hole pair. The basic equations of RDMA have the form\cite{31}

$$-i(\hbar \partial_t + \Gamma)Y(r_e, r_h, t) + H_{eh}Y(r_e, r_h) = ME,$$ \hspace{1cm} (1)

where $\Gamma$ is a phenomenological damping coefficient, $M(r)$ is a smeared-out transition dipole density, $E_g$ is the fundamental gap, and $r = r_e - r_h$ is the relative electron-hole distance. The operator $H_{eh}$ stands for the two-band effective mass Hamiltonian, which includes the electron and hole kinetic energy, the electron-hole interaction potential and the confinement potentials. In consequence, the Hamiltonian $H_{eh}$ is given by

$$H_{eh} = E_g + \frac{p_e^2}{2m_e} + \frac{p_h^2}{2m_h} + V_{eh}(r_e, r_h) + V_h(r_h) + V_e(r_e),$$ \hspace{1cm} (2)

where the second and the third terms on the r.h.s. are the electron and the hole kinetic energy operators with appropriate effective masses, the fourth term is the electron-hole attraction, and the two last terms are the surface confinement potentials for the electron and hole. The total polarization of the medium is related to the coherent amplitude by

$$P(R) = 2Re \int d^3r M(r)Y(R, r).$$ \hspace{1cm} (3)

This, in turn, is used in Maxwell’s field equation

$$c^2 \nabla^2 E(R) - \epsilon_0 \dot{E} = \frac{1}{\epsilon_0} \ddot{P}(R),$$ \hspace{1cm} (4)

where $\epsilon_0=7.5$ is the QD material dielectric constant. Equations (1)-(4) form a system of coupled integro-differential equations in 6-dimensional configuration space $(r_e, r_h)$ The optical properties of spherical QDs can be described by means of the exciton center-of-mass (COM) quantization method\cite{33}. One assumes that the COM is confined within a sphere of radius $R_{\text{max}}$, which will give the confinement states. Those states will overlap with the 3-dimensional exciton states. The effective QD susceptibility in this limit is given by the formula

IV. THEORETICAL DESCRIPTION

From the point of view of the classification of low-dimensional semiconductor structures, the considered nano-crystals are quantum dots (QDs). The SEM images (Fig. 1) suggest that the best model shape is a spherical quantum dot, with a median diameter of $\sim 700$ nm. Assuming that the interaction between dots is small enough, we may consider interband transitions in an isolated QD,
(see supplementary information)

$$
\chi_{QD} = e_b \sum_{n=2}^{n_{\text{max}}} \sum_{N=1}^{N_{\text{max}}} \left( \mathcal{F}_{n1} \mathcal{F}_{N} \frac{2L_T^{(2)}}{R_{y}} \right)^2,
$$

where

$$
\mathcal{F}_{n1} = \frac{1}{6\pi} \left| j_2(x_{\frac{3}{2}, N}) \right|^2 \left[ \frac{\kappa_{Tn}}{\kappa_{y}} \right] \left[ \int_0^1 u \phi^2 \sum_{s=1}^{\infty} \left( 1 - \frac{x_{\frac{3}{2}, N}^2}{x_{\frac{3}{2}, s}^2} \right) \right]^2,
$$

and

$$
R = \frac{R_{\text{max}}}{a^*},
$$

$$
f_{n1} = \frac{32(n^2 - 1)}{3a^5} \left[ \frac{1}{2r_0} \right] \left[ \frac{1}{2r_0} \right] \left[ \frac{1}{2r_0} \right] \left[ \frac{1}{2r_0} \right]
$$

where $j_N(x)$ are the spherical Bessel functions ($N = 1, 2, \ldots$), $x_{N,s}$ are roots of the equation $j_N(x) = 0$, $s = 1, 2, \ldots$, $a^* = 1.1 \text{ nm}$ is the Rydberg radius and $E_{Tn}$ and $E_{y}$ are energies of excitonic levels.

Figure 4 shows a comparison of experimental and calculated absorption spectra. The bulk crystal spectrum is also calculated from Eq. (5) by taking a very large NP radius $R > 10 \mu \text{m}$. Due to the relatively large size of considered NPs and the corresponding confinement energy shifts on the order of $\sim 0.1 \text{ meV}$, the direct observation of them can be challenging. To get a clearer picture of the results, the absorption coefficient obtained for bulk and nanoparticle systems has been normalized and the NP spectrum was shifted to obtain an exact match of $n = 2$ lines, removing the influence of different experimental conditions such as temperature mentioned before. In such a case, we observe a difference of $\Delta E \sim 25 \text{ meV}$ between bulk and NP lines for $n = 5$ state (vertical lines on Fig. 4 (c) and (d)), both in the experimental spectra and calculation results. This amounts to the difference between confinement energy of $n = 5$ and $n = 2$ state, the latter one being negligible. This result is a close match to the theoretical predictions of Konzelmann et al.\textsuperscript{41}. Our calculations show an excellent match between the measured oscillator strength and the theoretical estimates when the size distribution of the nanoparticles in considered [blue line in Fig. 3(a)]. The calculation for single NP size $(R = 350 \text{ nm})$ fails to fully explain the oscillator strength reduction [orange line in Fig. 3(a)], further confirming that quantum dot size distribution is crucial to the understanding of the observed effects. Moreover, upper confinement states $(N > 1)$ contribute to $\sim 25\%$ of the peak area for $n = 5$, with a smaller effect for $n < 5$. The calculated linewidths match the experimental data for $n = 3, 4, 5$, while slightly underestimating the linewidth of $n = 2$ state [blue line in Fig. 3(b)]. Again, we find that it is crucial to take into account the size distribution of the NPs, further evidencing the effect of NP size.

V. DISCUSSION

Previous studies\textsuperscript{11} have shown that the power-dependent optical bleaching (reduction of peak area) only becomes visible for $n = 12$ for a pump intensity of $\sim 1 \text{ mW/mm}^2$. Moreover, the intensity required to see optical bleaching scales as $n^{10}$. Therefore, to notice any nonlinearities at $n = 6$ one needs laser power on the order of $1 \text{ W/mm}^2$. The intensity of the illuminating light in our experiment ($\sim 1 \text{ mW/mm}^2$) is sufficiently low that the nonlinear effects observed in bulk can be neglected for the observed excitonic states. We note that in nanoparticles, the blockade diameter can become comparable to particle size for low $n$ (see Supplementary Fig. S4). The intensities in our experiment, however, are 3 orders of magnitude weaker than that required to reach the blockade effect.

The reduction in oscillator strength due to damage to crystal structure can be ruled out since we observe this reduction in natural as well as synthetic NPs (see Supplementary Information 2). Strain on Cu$_2$O crystals can cause a change in the absorption strength due to change from isotropic to anisotropic $n p$ states\textsuperscript{34}. The substrates can exert stress on Cu$_2$O crystals and affect the exciton transitions especially if the crystal is glued onto the cold finger or strongly sandwiched between two substrates. However, the nanoparticles here are held in place only by the van der Waals forces.

Electron-hole plasma generated due to the incident broadband light can affect the excitons. The collision of excitons with electron-hole plasma results in the reduction of exciton lifetime, broadening of the transitions as well as reducing the exciton oscillator strength. However, this effect was observed\textsuperscript{35} to be significant only for $n$ levels higher than $n = 10$.

The quantum confinement, however, is the dominant effect here. Theoretically, for $n = 5$ excitons in Cu$_2$O three dimensional confinement to 700 nm diameter, the lowest confinement state $(N = 1)$ would exhibit a blueshift...
of $\sim 20 \mu eV^{23}$, which is an order of magnitude smaller than the linewidth of the $n = 5$ transition. However, the states $N = 2, 3, 4...$ provide a non-trivial contribution to the total area of the observed excitonic line, which is a measure of oscillator strength. This is shown on the Fig. 5, where $N = 1, 2, 3$ states are marked by red, blue and green lines respectively. Since the energy shift of those states is proportional to $N$, it can reach values of over $200 \mu eV$ for $N > 2$. Moreover, for the given dot radius $R$, the energy shift is approximately proportional to $R^{-2}$ and a relatively large energy shift on the order of $0.5 \mu eV$ can be expected at the lower end of the obtained NP sizes. This is clearly seen in Fig. 5, where strongly blueshifted peaks corresponding to small NPs are visible. All these factors contribute to the shape of the total line (black curve) and result in an apparent reduction of the oscillator strength; every observed excitonic line is an overlap of the primary confinement state ($N = 1$) and multiple blueshifted higher states which are too close to each other to discern them on the spectrum. The contribution of these states is twofold. 1- They make the transitions more symmetric. Since they have higher energy than the $N = 1$ state, their effect is more pronounced on the right-hand side of the absorption peak; this is visible in Fig. 4(c) and (d) where the asymmetric lineshape of the bulk crystal is transformed into Gaussian shape. The effect is also visible for lower $n$ states [Fig. 4(a) and (b)], but it is much less pronounced due to smaller energy shifts. 2- They significantly increase the background absorption. Since the oscillator strength of confinement states quickly decreases with $N$, their contribution affects mostly the base of the absorption line. The widened bases overlap, forming a strong absorptive background. This greatly reduces the area of the peak visible above that background resulting in an apparent reduction of the oscillator strengths.

In conclusion, we successfully observed Rydberg excitons in nanoparticles of Cu$_2$O. Through optical spectroscopy, we showed that reducing the size of the system leads to a subsequent reduction in the oscillator strength and an apparent linewidth broadening. We explained our observations through the quantum confinement of the excitons in the nanoparticles. Our work paves the way for exploiting Cu$_2$O Rydberg excitons in the nanoscale for their large nonlinearities.

ACKNOWLEDGEMENTS

We acknowledge EPSRC Grant No. EP/S014403/1 and The Royal Society RGS[R2]192174. K.O. acknowledges EPSRC for PhD studentship support through grant no. EP/L015110/1. We thank Michael Huang, Matthew Jones, Stephen Lynch, Stefan Scheel and Mikhail M. Glazov for fruitful discussions.

---

* ho35@st-andrews.ac.uk

1 R. W. Keyes, IBM Journal of Research and Development 32, 84 (1988).

2 D. D. Awschalom, L. C. Basset, A. S. Dzurak, E. L. Hu, and J. R. Petta, Science 339, 1174 (2013).

3 M. H. Devoret and R. J. Schoelkopf, Science 339, 1169 (2013)

4 J. C. Loredo, N. A. Zakaria, N. Somaschi, C. Anton, L. de Santis, V. Giesz, T. Grange, M. A. Broome, O. Gazzano, G. Coppola, I. Sagnes, A. Lemaître, A. Auffeves, P. Senellart, M. P. Almeida, and A. G. White, Optica 3, 433 (2016).

5 K. F. Mak and J. Shan, Nature Photonics 10, 216 (2016).

6 M. F. Gonzalez-Zalba, arXiv:1801.06722 [cond-mat] (2018).

7 M. Fox, Optical properties of solids, 2nd ed., Oxford master series in condensed matter physics No. 3 (Oxford Univ. Press, Oxford, 2011) eCLC: 772954632.

8 M. Hayashi and K. Katsuki, Journal of the Physical Society of Japan 7, 599 (1952).

9 B. K. Meyer, A. Polity, D. Reppin, M. Becker, P. Hering, B. Kramm, P. J. Klar, T. Sander, C. Reindl, C. Heiliger, M. Heinemann, C. Mülller, and C. Ronning, Oxide Semiconductors, edited by B. G. Svensson, S. J. Pearton, and C. Jagadish, Semiconductors and Semimetals, Vol. 88 (Elsevier, 2013) pp. 201 – 226.

10 H. Matsumoto, K. Saito, M. Hasno, S. Kono, and N. Nagasawa, Solid. Stat. Comm. 97, 5 (1996).

11 T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz, and M. Bayer, Nature 514, 343 (2014).

12 J. Thewes, J. Heckötter, T. Kazimierczuk, M. Aßmann, D. Fröhlich, M. Bayer, M. Semina, and M. Glazov, Physical Review Letters 115, 207402 (2015).

13 P. Grünwald, M. Aßmann, J. Heckötter, D. Fröhlich, M. Bayer, H. Stolz, and S. Scheel, Physical Review Letters 117, 133003 (2016).

14 J. Heckötter, M. Freitag, D. Fröhlich, M. Aßmann, M. Bayer, M. A. Semina, and M. M. Glazov, Physical Review B 96, 125142 (2017).

15 J. Heckötter, M. Freitag, D. Fröhlich, M. Aßmann, M. Bayer, M. A. Semina, and M. M. Glazov, Physical Review B 95, 035210 (2017).

16 M. Takahata and N. Naka, Physical Review B 98, 195205 (2018).

17 S. O. Krüger and S. Scheel, Physical Review B 97, 205208 (2018).

18 S. A. Lynch, C. Hodges, W. W. Langbein, L. Gallagher, J. Rogers, C. S. Adams, M. P. A. Jones, and R. P. Singh, in 2018 20th International Conference on Transparent Optical Networks (ICTON) (IEEE, Bucharest, 2018) pp. 1–4.

19 J. Mund, C. Uihlein, D. Fröhlich, D. R. Yakovlev, and M. Bayer, Physical Review B 99, 195204 (2019).

20 S. Zielinska-Raczyńska, G. Czajkowski, K. Karpiński, and D. Ziemińkiewicz, Physical Review B 99, 245206 (2019).

21 M. P. A. Jones, L. G. Marcassa, and J. P. Shaffer, Journal of Physics B: Atomic, Molecular and Optical Physics 50, 060202 (2017).

---
22 V. Walther, R. Johne, and T. Pohl, Nature Communications 9, 1309 (2018).
23 A. Konzelmann, B. Frank, and H. Giessen, Journal of Physics B: Atomic, Molecular and Optical Physics 53, 024001 (2020).
24 A. M. Smith and S. Nie, Accounts of Chemical Research 43, 190 (2010).
25 M. Khazalí, K. Heshami, and C. Simon, Journal of Physics B: Atomic, Molecular and Optical Physics 50, 215301 (2017).
26 S. Baur, D. Tiarks, G. Rempe, and S. Dürr, Physical Review Letters 112, 073901 (2014).
27 P. W. Baumeister, Physical Review 121, 359 (1961).
28 A. Jolk and C. F. Klingshirn, physica status solidi (b) 206, 841 (1998).
29 Y. Toyozawa, Journal of Physics and Chemistry of Solids 25, 59 (1964).
30 V. T. Agekyan, B. S. Monozon, and I. P. Shiryapov, physica status solidi (b) 66, 359 (1974).
31 A. Ekimov, A. Onushchenko, A. Plyukhin, and A. L. Efros, Journal of Experimental and Theoretical Physics 61, 891 (1985).
32 A. Ekimov, A. Onushchenko, M. Raikh, and A. L. Efros, J. Exp. Theor. Phys. 63, 1054 (1986).
33 D. Ziemkiewicz, K. Karpiński, S. Zielińska-Raczyńska, and G. Czajkowski, Physical Review B 101, 205202 (2020).
34 V. T. Agekyan, physica status solidi (a) 43, 11 (1977).
35 J. Heckötter, M. Freitag, D. Fröhlich, M. Aßmann, M. Bayer, P. Grünwald, F. Schöne, D. Semkat, H. Stolz, and S. Scheel, Physical Review Letters 121, 097401 (2018).
Supplementary information: Quantum confined Rydberg excitons in Cu$_2$O nanoparticles

Konstantinos Orfanakis, Sai Kiran Rajendran, Hamid Ohadi$^1$

SUPA, School of Physics and Astronomy, University of St Andrews, St Andrews, KY16 9SS, United Kingdom,

Sylwia Zielińska-Raczyńska, Gerard Czajkowski, Karol Karpiński, David Ziemkiewicz

UTP University of Science and Technology, Bydgoszcz, Poland

1 Setup

Figure S1: Experimental setup for transmission spectroscopy. Broadband light is focused and collected using two objective lenses (NA = 0.42, and $f = 20$ mm).

2 Synthetic nanoparticles

We compare the commercial synthetic nanoparticles (Nanografi) with an average size distribution of 0.6 $\mu$m with our natural nanoparticles. We refer

$^1$ho35@st-andrews.ac.uk
Figure S2: Transmission spectrum for NNPs (green) and SNPs (orange).

Comparison of the two spectra shows a similar number of transitions, and broadening of the transitions (Fig. S2).

3 Temperature dependence

The temperature evolution of the excitation transmission line for both SNPs and bulk crystal of Cu2O is shown in Fig. S3. The temperature range spans from 4 to 200 K, the highest temperature where the exciton line can be resolved in our system. The increase of temperature results in a progressive red-shift in the exciton transition energy, a behaviour characteristic of semiconductors. The variation of the bang-gap of semiconductor can be described in terms of a hyperbolic cotangent relation [1]:

\[
E_g(T) = E_g(0) - S \langle \hbar \omega \rangle \left[ \coth(\frac{\hbar \omega}{2k_B T}) - 1 \right],
\]

where \( E_g(0) \) is the band gap energy at 0 K, \( S \) is a dimensionless constant describing the strength of the electron-phonon coupling, \( k_B \) is the Boltzmann constant, and \( \langle \hbar \omega \rangle \) is an average phonon energy. This equation can be used to describe the redshift of the \( n = 2 \) line with parameters summarized in Table 1.
Table 1: Fitting parameters of temperature dependence of the exciton transitions in NPs and bulk using Eq. S1.

|                | NPs    | Bulk crystal |
|----------------|--------|--------------|
| $E_g(0)$ (eV)  | 2.1475 | 2.1478       |
| S              | 1.60   | 1.66         |
| $\langle \hbar \omega \rangle$ (meV) | 9.8    | 10.5         |

Figure S3: Variation of the exciton line with temperature for SNPs and bulk crystal of Cu$_2$O, shown as orange dots and blue diamonds, respectively. The corresponding fitted curve using Eq. S1 is shown as a line in each case.
Figure S4: Exciton (red) and Blockade (blue) diameter as a function of principal quantum number $n$. The solid line is used as a guide to the eye.

4 Blockade volume

Estimation of the dipole blockade volume, hence blockade radius, was done using the following equation [2]:

$$V_{\text{blockade}} = 3 \cdot 10^{-7} \mu m^3 n^7. \quad (S2)$$

For $n = 6$, the first transition we cannot resolve in nanoparticles, the blockade diameter is $\sim 540$ nm, i.e. approximately equal to the average diameter of our SNPs (Fig. S4). For comparison, the average exciton diameter for $n = 6$, is approximately 120 nm calculated from

$$d_n = a_b(3n^2 - l(l + 1)), \quad (S3)$$

where $a_b = 1.11$ nm is the Bohr radius for P-excitons [2].
5 Calculation of Cu$_2$O quantum dot susceptibility

The Hamiltonian (2) for larger nanocrystals, when the relative electron-hole motion can be separated from the center-of-mass motion, has the form [3]

\[ H_{eh} = E_g + H_r + H_R, \]
\[ H_r = -\frac{\hbar^2}{2\mu} \nabla^2 r + V(r), \]
\[ H_R = -\frac{\hbar^2}{2M} \nabla^2 R + V_{\text{conf}}(R). \]

Here $V(r)$ is the screened Coulomb potential, and $V_{\text{conf}}(R)$ describes the confinement of the exciton center-of-mass (COM) motion within a sphere of radius $R_0$. With the above Hamiltonian, we are looking for a solution of the constitutive equation (1) in terms of eigenfunctions of the Hamiltonians $H_r$, and $H_R$. The first mentioned operator is the Hamiltonian of a hydrogen-like atom, with the eigenfunctions

\[ \psi_{n\ell m}(r) = N_{nt} R_{nt}(r) Y_{\ell m}(\theta, \phi), \quad (S4) \]

where $Y_{\ell m}(\theta, \phi)$ are spherical harmonics, and the detailed form of the eigenfunctions is well-known [4]. For the second Hamiltonian, we will use the no-escape boundary conditions for the COM motion, so that the eigenfunctions will have the form

\[ \Psi_{NLM}(R) = A_{NL} j_L(k_{LN} R) Y_{LM}(\Theta, \Phi), \quad (S5) \]

where $j_L(kR)$ are the spherical Bessel functions, $k$ results from the equation

\[ k_{LN} R_0 = x_{L,N}, \quad (S6) \]

where $x_{L,N}$ are the zeros of $j_L$, and $A_{NL}$ are the normalization factors

\[ A_{NL} = \sqrt{\frac{2}{R_0^3}} [j_{L+1}(k_{LN} R_0)]^{-1}. \]

Assuming the harmonic time dependence of the quantities $\mathcal{Y}, \mathbf{E}$, we obtain the constitutive equation in the form

\[ (H_{eh} - \hbar \omega - i\Gamma) \mathcal{Y}(r, R) = M(r) \mathbf{E}(R). \quad (S7) \]
Inserting the expansion
\[ \mathcal{Y}(\mathbf{R}, \mathbf{r}) = \sum_{n\ell m NLM} c_{n\ell m NLM} \psi_{n\ell m}(\mathbf{r}) \Psi_{NLM}(\mathbf{R}) \] (S8)
into Eq. (S7) we obtain the values of the expansion coefficients \( c \). With the exciton amplitude, we can determine the mean effective QD susceptibility from the relation (3), where we have inserted the dipole density \( \mathbf{M}(\mathbf{r}) \) defined in Ref. [3], and assumed the long wave approximation. The final result is presented in Eq. (5).

References

[1] K. P. O’Donnell and X. Chen, Appl. Phys. Lett. 58, 2924 (1991).
[2] T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz, and M. Bayer, Nature 514, 343 (2014).
[3] Sylwia Zielińska-Raczyńska, Gerard Czajkowski, and David Ziemkiewicz, Phys. Rev. B 93, 075206 (2016).
[4] L.D. Landau, E.M. Lifshitz, Quantum Mechanics, Non Relativistic Theory 3rd ed. (Pergamon Press, Oxford, 1962).