Origin of Photoluminescence from Colloidal Gallium Phosphide Nanocrystals Synthesized via a Hot-injection Method

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Experimental Section

Materials

Gallium (III) chloride (GaCl$_3$, Aldrich, ≥99.999% trace metals basis), Palmitic acid (P.A, TCI, 95%), 1-Octadecene (ODE, Sigma Aldrich, 90%), Tris-(trimethylsilyl)- phosphine 10 wt % hexane solution ((TMS)$_3$-P, Stream, 98%), Polystyrene (PS, Sigma Aldrich), 3-mercaptopropionic acid (MPA: Aldrich)

Synthesis of gallium phosphide (GaP) Nanocrystals

0.36 mmol of P.A and 8 ml of ODE were mixed into a 50 ml 3-neck flask. The mixed solution was degassed by stirring under vacuum at 110 °C for 2 hours. After that, mixed solution was kept the temperature under N$_2$ atmosphere. The gallium and phosphine complex precursor was prepared by 0.06 mmol of (TMS)$_3$-P and 0.06 mmol of GaCl$_3$ in 2 ml of ODE in a glovebox. Then, the solution of palmitate form was heated to 300 °C under nitrogen. At this temperature,

the gallium and phosphine complex precursor was rapidly injected after removing mantle and maintained to 200°C for 30 min. The color of reaction solution was changed slowly from colorless to yellow color. 3-neck flask cooled down to room temperature. Finally, the nanocrystals were precipitated with 15ml of IPA and 20ml of ethanol and centrifuged at 3500rpm for 5min. repeated two or three times.

Device fabrication

  To deposit the GaP/PS hybrid layer on the on a clean fluorine-doped tin oxide (FTO, Pilkington, TEC15) glass by the spin-coating method. 100 μL of the GaP QDs in a hexane–PS (10/1 vol/vol) in dichlorobenzen hybrid solution was spin-coated on a 3-mercaptopropionic acid pre-treated FTO substrate at 2500 rpm for 20 second. We repeated spin-coating 3 times for the MPA and GaP QDs. And then, a 60 nm-thick, 2 mm-spacing of Au counter electrode was then deposited using thermal evaporation.

Characterization

A transmission electron microscopy (TEM) image of the synthesized GaP QDs was taken using a Tecnai G2 F30 S-Twin field emission-TEM (FEI) with an accelerating voltage of 300 kV Absorption spectra were measured by a Scinco PDA S-3100 UV/Vis spectrophotometer. Emission spectra were obtained using a Jasco FP-6500 fluorescence spectrometer. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima III diffractometer equipped with a rotating anode and a Cu Kα radiation source (λ = 0.15418 nm). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was measured using the OPTIMA 5300DV, PerkinElmer (U.S.). Photoluminescence excitation (PLE) data were obtained using Shimadzu RF-5301PC spectrofluorophotometer. PL life time of GaP QDs was taken using HL920 by Edinburgh Instruments.

Theoretical calculation of band gap energy

The energy of direct and indirect energy is calculated by using effective mass approximation,

$$E_{direct}(r) = E_{bulk,\ direct} + \frac{\hbar^2\pi^2}{2m^*_{e,\Gamma}r^2} + \frac{\hbar^2\pi^2}{2m^*_h r^2} - \frac{1.786e^2}{\varepsilon_r r}$$

$$E_{indirect}(r) = E_{bulk,\ indirect} + \frac{\hbar^2\pi^2}{2m^*_{e,X}r^2} + \frac{\hbar^2\pi^2}{2m^*_h r^2} - \frac{1.786e^2}{\varepsilon_r r}$$

where $m^*_{e,\Gamma}$, $m^*_{e,X}$ are the effective masses of electron at the Γ and X points. The reported values of $m^*_{e,\Gamma}$, and $m^*_{e,X}$ are in the range of 0.09~0.17m_0 and 0.19~0.275m_0, but we picked one of the recommended value, equal to 0.13m_0 and 0.253m_0, respectively. The effective mass of hole, m^*_h is 0.76m_0. ε_r is the relative permittivity of GaP (11.1).(Ref 31)

Device characterization

The photocurrent response of GaP QDs/PS film along with wavelength was measured by illuminating the monochromatic light (monochromater = Newport Cornerstone 260; light source = Newport 300W Xenon lamp 66920, multimerter = Keithley 2001) to the device under 1 V of applied bias voltage.

Table S1. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of GaP NCs

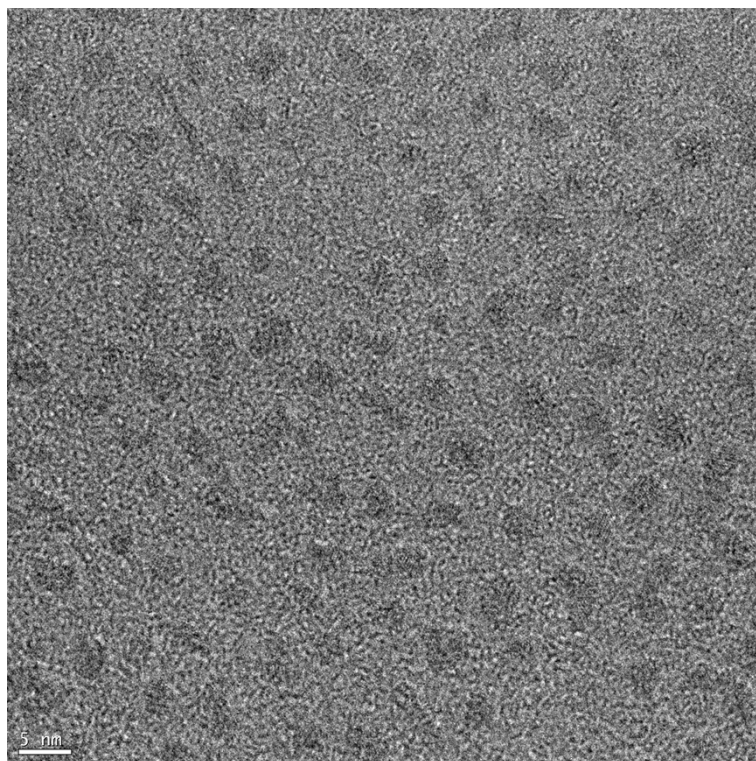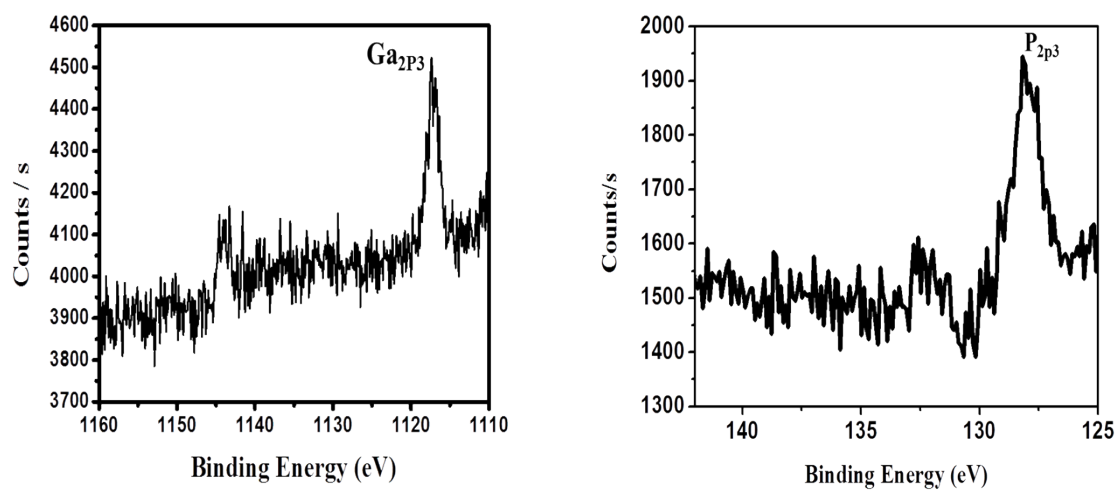|	P	Ga	
(ppm)	59	161	
/MW(mM)	1.904838	2.309237	
product %	45.2%	54.8%	100.0%

Figure S1. HR-TEM image of GaP NCs.

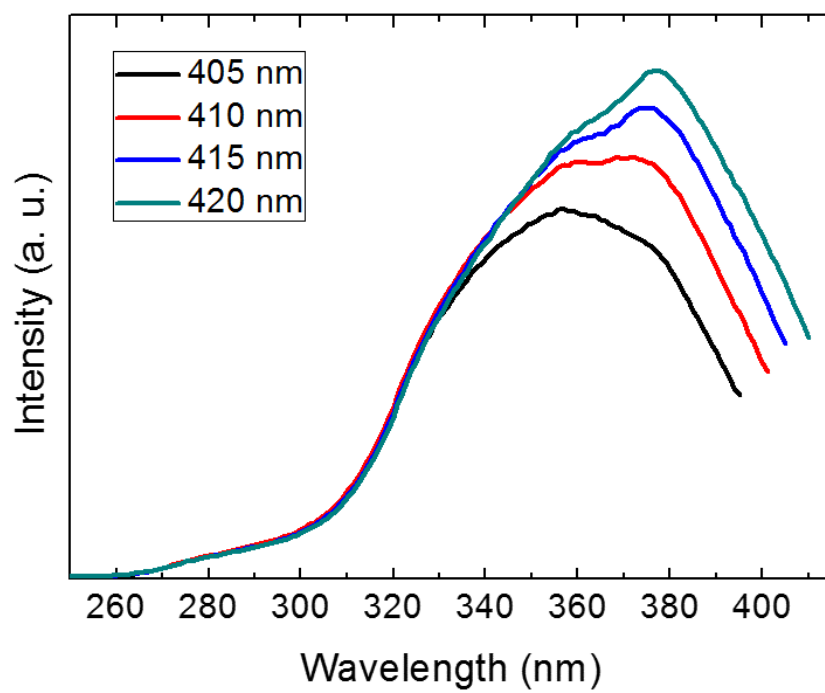Figure S2. High resolution X-ray photoelectron spectroscopy (XPS) spectrum of GaP NCs.

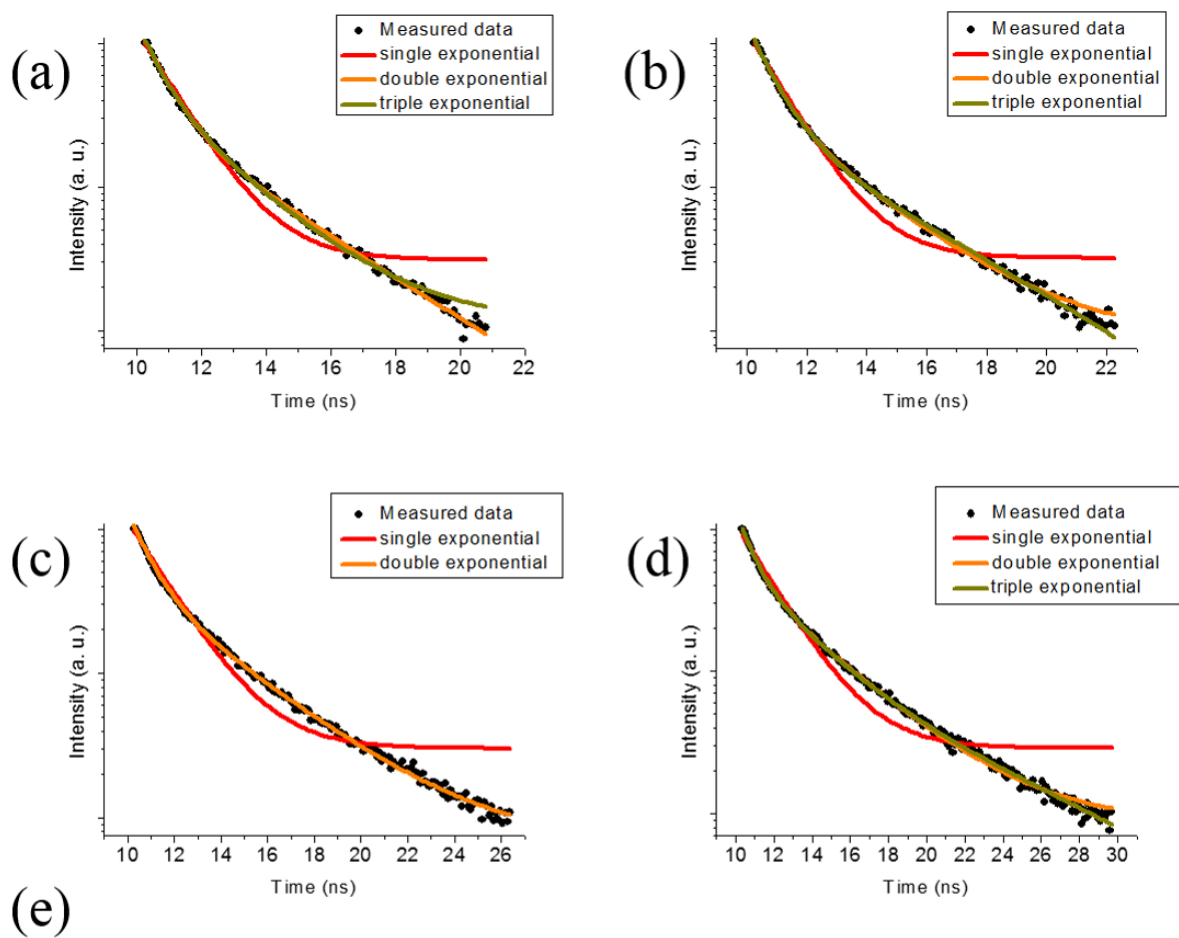Figure S3. Photoluminescence excitation (PLE) spectrum of GaP NCs at 405, 410, 415, and 420 nm.

	1st	2nd	3rd	$\tau_{average}$ (ns)
400 nm	0.99161	**0.99860**	0.99834	1.40
450 nm	0.99043	0.99796	**0.99810**	1.51
500 nm	0.98865	**0.99873**	N/A	1.86
550 nm	0.98584	0.99955	**0.99956**	2.39

Figure S4. The single- and multi-exponential fits of PL decay of GaP NCs at (a) 400, (b) 450, (c) 500, and (d) 550 nm. (e) Adjusted R^2 of various order of exponentials and average lifetime.