# Preparation, characterization and nonlinear optical properties of colloidal gallium arsenide nanocrystals

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**Abstract:** GaAs nanocrystals were prepared via a simple mechanical ball milling technique. The prepared GaAs nanocrystals have high purity and could form colloidal ethanol suspension without any surfactant additives. The colloidal GaAs nanocrystal suspension displayed excellent two-photon absorption property over the visible and near-infrared region from 490 nm to 1064 nm, which enables it to become a promising broadband optical limiting material.

Key words: gallium arsenide; nanocrystals; nonlinear optics; ball milling technique

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# 1. Introduction

Semiconductor nanocrystals have novel properties, which are markedly different from those of bulk solids [1-4] and have many technological potential applications in electroluminescence, solar energy conversion, non-linear optical devices, etc. [5-10]. Experimental studies on semiconductor nanocrystals have largely been restricted to the II-VI and III-V group semiconductor nanocrystals [1-4, 11]. Compared to the II-VI group semiconductors, the III-V group ones have a greater degree of covalent bonding, less ionic lattice, and a larger exciton diameter. For this reason, quantum size effects on the optical spectra can be predicted to be more pronounced in the III-V group nanomaterials than that in the II-VIs [1-4, 12], and then III-Vs nanocrystals are expected to exhibit strong nonlinear optical properties while the synthesis of III-Vs nanocrystals is more difficult for unstable reactants and impurity [11]. Recently, one of the most important direct band gap semiconductors in III-Vs, GaAs (the exciton diameter of bulk GaAs is 19 nm) nanocrystallites have been

synthesized by the reaction of GaCl<sub>3</sub> with As(SiMe<sub>3</sub>)<sub>3</sub> in different organic solutions [12-15], or by the reaction of Ga(acac)<sub>3</sub> with As(SiMe<sub>3</sub>)<sub>3</sub> in triglyme [16]. In 1991, GaAs nanocrystalline was synthesized by room temperature grinding of elemental powders [17]. The reaction of GaCl<sub>3</sub> with As(SiMe<sub>3</sub>)<sub>3</sub> in trioctylphosphine was also used to prepare core/shell nanocrystals of InAs/GaAs [18]. Kher and Wells have reported a metathetical reaction to GaAs nanocrystals between (Na/K)<sub>3</sub>As and GaCl<sub>3</sub> [19]. Then, they obtained colloidal nanocrystals of methanol-capped GaAs by multiple extracting with methanol [20]. Single precursor of AsCl<sub>3</sub>Ga<sub>2</sub>[21] or [H<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> [22] was also used to prepare GaAs nanocrystals. More recently, GaAs nanoclusters were deposited on different substrates by pulsed laser deposition [23]. Although there was great interest in the studies related to GaAs nanocrystals, most of the mentioned reports were restricted to the synthesis and radical characterization. More efforts should be devoted to simplifying the preparation and dispersion process of GaAs nanocrystals and to exploring their exotic optical

properties.

Mechanical grinding method via ball milling technique is the general method to prepare nanocrystals [24-25]. This preparation process is very simple and no by-products are introduced. Moreover, the high purity of bulk materials can ensure the same purity of the prepared nanocrystals. In this paper, the GaAs nanocrystals were prepared by mechanical grinding method via ball milling technique. The nanocrystals could well be dispersed in ethanol to form colloidal suspension without any surfactant additives, which may well lead to deep theoretical and experimental studies of the III-V group nanocrystals. The prepared colloidal GaAs nanocrystals suspension performed excellent two-photon absorption property over the visible and near infrared region from 490 nm to 1064 nm, which enables it to become a promising broadband optical limiting material.

### 2. Experimental

High purity of bulk GaAs (charge carrier concen-tration  $< 3 \times 10^{16}$  cm<sup>-3</sup>) was manually grinded and sealed in an agate container along with agate balls. The container was evacuated (10<sup>-5</sup> torr) and after that, the high purity argon was filled in. The rotation speed was 500 r/min and rotation time was 36 h. After cooling down, blank powder was collected.

X-ray Diffraction (XRD) data were collected on a Rigaku Dmax/2000 using Cu  $K_{\alpha}$  radiation. Transmission Electron Microcopy (TEM) was recorded on a JEM-200CX microscope at a voltage of 160 kV. Absorption spectra were recorded with an Agilent 8453 UV-Vis photodiode array spectrophotometer and the prepared brown colloidal GaAs suspension in a 10 mm-thick quartz cell was employed using ethanol as blank. XPS analysis was performed with an Axis Ultra spectrometer (Kratos, UK) Using Mono Al  $K_{\alpha}$  (1486.71 eV) radiation at a power of 225 W (15 mA, 15 kV). To compensate for surface charges effects, binding energies were calibrated using C1s hydrocarbon peak at 284.8 eV.

# 3. Results and discussion

Fig. 1 shows the XRD patterns of bulk GaAs

powders used in the experiment and GaAs nanocrystals prepared by mechanical grinding process. In the XRD pattern of the bulk GaAs, the strongest peak was (220), which indicates that the powders are preferentially along [001] axis. In one of the prepared blank GaAs nanopowders, the (220) peak became the second strongest peak and all the peaks matched well with the literature data of random zinc-blende GaAs powders (JCPDS card: 32-389). Compared to the pattern of bulk GaAs powders in Fig. 1, one of the prepared blank GaAs powders apparently shows line broadening due to the size effect of the nanoparticles. The XRD line broadening can be used as a measurement of average particle size. The average particle size was calculated to be 7.7 nm from the Debye-Scherrer formula [12,26].

$$d = \frac{0.9\lambda}{\sqrt{\beta_{\rm M}^2 - \beta_{\rm S}^2}\cos\theta} \tag{1}$$

where  $\lambda$  (0.15406 nm) is the electron wavelength and *d* is the crystallite diameter.  $\beta_{\rm M}$  ( $\Delta$ (2 $\theta$ ) = 1.09°) and  $\beta_{\rm S}$  ( $\Delta$ (2 $\theta$ ) = 0.13°) are the half-width of GaAs nanocrystals and the stretch of instrument, respectively.



Fig. 1. XRD patterns of bulk GaAs powders (B-GaAs, corresponding to the right ordinate) and GaAs nanocrystals (NC-GaAs, corresponding to the left ordinate) prepared by mechanical grinding process.

XPS was also used to characterize the prepared GaAs nanocrystals and the survey scan is given in Fig. 2. The peaks for Ga, As, C, and O elements are detected. Fig. 3 indicates the signals of Ga 3d and As 3d. The Ga 3d spectrum shows a peak at 19.486 eV originating from GaAs while the other peak 20.647 eV originates from gallium-oxygen species. Similarly the As 3d spectrum indicates a peak at 41.395 eV due to GaAs while the peak at 44.527 eV is due to arsenic-oxygen species. As reported in Ref. [19], the surface oxidation of III-V materials due to atmospheric exposure is known to occur.



Fig. 2. XPS survey scan of GaAs nanocrystals.



Fig. 3. XPS spectra of Ga 3d (a) and As 3d (b).

It was found that the GaAs nanocrystals could well be dispersed in ethanol without any surfactant additives. 0.16 g GaAs nanocrystals were dispersed in 150 mL ethanol by ultrasonic irradiation for 6 h at a power level of 200 W. The resulting dispersion was then centrifuged at 3500 r/mim for 6 min. The upper suspension was then centrifuged for 3 min. A brown colloidal suspension was carefully collected. The concentration of GaAs nanocrystals is  $2.3 \times 10^{-2}$  mg/mL. Fig. 4 shows the UV-Vis absorption spectrum of the colloidal GaAs suspension. The onset in Fig. 4 exhibits blue-shifted characterization compared to bulk GaAs (the band gap of bulk GaAs is 1.43 eV), which proved that the GaAs nanocrystals have pronounced quantum confinement. The relationship between the particle size and band gap could be expressed as [12-13]:

$$E = E_{\rm g} + \frac{\hbar^2 \pi^2}{2R^2} (\frac{1}{m_{\rm e}} + \frac{1}{m_{\rm h}}) - \frac{1.8e^2}{4\pi \epsilon \epsilon_0 R}$$
(2)

where  $E_g$  is the bulk band gap, R is the particle radius,  $m_e$  (0.07) and  $m_h$  (0.68) are the effective masses of the electron and hole, and  $\varepsilon$  is the high-frequency dielectric constant (10.9). As we know, the onset in the absorbance of bulk GaAs is steep and the band gap is 1.43 eV, while the onset in Fig. 2(c) is slow and the range is about 400-800 nm corresponding to band gap 3.10-1.55 eV. The difference in the absorbance can be explained thus: the GaAs nanocrystals have different sizes as shown in TEM results. From Eq. (2), the nanocrystals with different sizes have different band gaps and the size range of the GaAs nanocrystals is 3.9-16.4 nm. Considering the surface oxidization of the prepared GaAs nanocrystals, the calculated result is only a reference value.



Fig. 4. UV-Vis spectrum of the colloidal suspension of GaAs nanocrystals in ethanol.

In the TEM measurement, the particles from the colloidal GaAs suspension were deposited onto an amorphous film on a Cu grid and were imaged by a transmission electron microscope. TEM analysis shows most of the GaAs nanocrystals to be 30-150 nm, as shown in Fig. 5(a) while the nanocrystal size calculated from the XRD pattern is much smaller than that in TEM. This can be explained that the particle size obtained in XRD pattern is average size of

single particle and the particles observed in TEM are aggregations, which can be proved from that there are some smaller particles (about 5-20 nm) in Fig. 5(a). Fig. 5(b) is the corresponding selective area electron diffraction (SLED) of Fig. 5(a). The diffractive circles match well with zinc-blended GaAs and can be indexed to (111), (220), and (311). This result is identical with the above XRD result. The XRD was also used to measure the particles in the colloidal GaAs suspension. In the experiment, the solvent in the colloidal GaAs suspension was removed in vacuum and then the obtained solid on the Cu sheet was used for the measurement. The XRD pattern is shown in Fig. 6. In the pattern, besides GaAs and back Cu sheet, As<sub>2</sub>O<sub>3</sub> is found, while As<sub>2</sub>O<sub>3</sub> is not found in Fig. 1. It reveals that the GaAs nanocrystals were partly oxidized when treated by ultrasonic irradiation in ethanol. The oxidation of GaAs may be attributed to water in ethanol, as the ethanol used in our experiment was not dried and ethanol is very hygroscopic.



Fig. 5. TEM (a) and selective area electron diffraction (SLED) (b) of GaAs nanocrystals.

We also attempted to disperse the GaAs nanocrystals into some other solvents. Equal quality of GaAs nanocrystals (10 mg) was dispersed into different solvents, such as water, methanol, ethanol, chloroform, and *n*-hexane with the same volume (20 mL). The five mixtures were then treated with ultrasonic irradiation for 1 h. After settling down for 48 h, only ethanol solution was suspension though some precipitation settled down at the bottom. The other four organic solutions were clear, colorless liquid and almost all of the GaAs nanocrystals settled at the bottom. It indicates that of the five kinds of solvents, GaAs nanocrystals can only be dispersed

into ethanol. Previous UV photoemission spectroscopy study showed that methanol could chemisorb molecularly at a lower coverage with its oxygen end to the GaAs surface [27]. Kher and Wells have also reported a metathetical route to GaAs nanocrystals and obtained methanol capped GaAs colloidal suspension [19-20]. Their studies indicated that methanol was not merely absorbed or a free solvent on the GaAs quantum dots, but strongly bound to the GaAs surface [20]. It is strange that our GaAs nanocrystals could not form methanol colloidal suspension, but could form ethanol colloidal suspension. We thought that this is possible as prepared GaAs nanocrystals were bigger than that in Ref. [20], and the chain length of alcohol molecules should play a role in stabilizing the colloids with different sizes.



Fig. 6. XRD pattern of the solid obtained from the colloidal GaAs suspension.

As a direct band gap semiconductor, bulk GaAs exhibit TPA in the near-infrared wavelength region [28-30]. According to the theory of TPA, the intensity-dependent transmittance can be expressed as:

$$\frac{1}{T} = e^{\alpha l} + \frac{e^{\alpha l} - 1}{\alpha} \beta I_i$$
(3)

where  $I_i$  is the input intensity, l is the thickness of the sample,  $\alpha$  is the linear absorption coefficient and  $\beta$  is the TPA coefficient. The intensity-dependent transmittance of the prepared colloidal GaAs nanocrystals suspension was measured using the fundamental output of a Q-switched YAG laser (Continuum Corporation, USA, 5.6 ns pulse duration). The experimental setup was similar to that used in our previous work [31]. With a concentration of  $2.3 \times 10^{-2}$  mg/mL, the sample was transparent at a wavelength of 1064 nm. As shown in Fig. 7(a), the transmittance



Fig. 7. Intensity-dependent transmittance of the colloidal suspension consisting of GaAs nanocrystals and ethanol: (a) with the linear transmittance of 98% at wavelength 1064 nm; (b) with the linear transmittance of 68% at wavelength 550 nm.

of the sample decreases significantly with the increase in the input laser intensity. The solid curve is a fitting curve using Eq. (3) with the value of  $\beta = 5.6$ cm/GW, which is only 4 times smaller than that for bulk GaAs ( $\beta$ ~20 cm/GW [28-30]). Considering the small content of GaAs nanocrystals in the solution, it reveals that the TPA coefficient for a single molecule of GaAs in nanocrystal form is several orders higher than that for the molecule in bulk form. In addition, due to the blue-shifted nature of absorption, the linear transmittance of GaAs nanocrystals in visual field is high. Using an optical parameter oscillator (Continuum Corporation, USA, 3 ns pulse duration) as the laser source, the nonlinear optical property was also measured in visual field. Taking the wavelength of 550 nm as an example, the experimental result is shown in Fig. 7(b), the solid curve is a theoretical curve obtained by use of Eq. (3) with the best fitting value of  $\beta = 21.4$  cm/GW. For other wavelengths, the results are shown in Table 1. The

Table 1. The linear transmittance and the TPA coefficients ( $\beta$ ) of the colloidal GaAs nanocrystals suspension at different wavelengths

Linear transmit- tance / %	Wavelength / nm	$\beta$ /(cm·GW <sup>-1</sup> )
59	490	30.9
63	520	37.0
72	580	24.9
76	610	21.1
79	640	21.5
82	670	23.6

experimental results can also be well fitted by Eq. (3). It can be concluded that the observed nonlinear optical properties of colloidal GaAs over the visible region of 490 nm to 670 nm are attributed to TPA, which implies that it will be a promising broadband optical limiting material.

# 4. Conclusion

GaAs nanocrystals with high purity were prepared by the ball milling technique. The prepared GaAs nanocrystals could form colloidal ethanol suspension, which exhibits blue-shifted characteristics in the absorption curve as the evidence of pronounced quantum confinement. The prepared colloidal suspension displayed excellent TPA properties over the visible and near-infrared broadband optical range.

#### References

- Brus L.E., A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites, *J. Chem. Phys.*, 1983, **79** (11): 5566.
- [2] Lippens P.E. and Lannoo M., Calculation of the band gap for small CdS and ZnS crystallites, *Phys. Rev. B*, 1989, **39**: 10935.
- [3] Manciu F.S., Sahoo Y., Macrae D.J., Furis M., Mccombe B.D., and Prasad P.N., Optical phonon spectra of GaP nanoparticles prepared by nanochemistry, *Appl. Phys. Lett.*, 2003, 82: 4059.
- [4] Krishna M.V.R. and Friesner R.A., Quantum confinement effects in semiconductor clusters, *J Chem. Phys.*, 1991, 95 (11): 8309.

- [5] Colvin V.L., Schlamp M.C., and Alivisatos A.P. Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature*, 1994, **370**: 354.
- [6] Coe S., Woo W., Bawendi M., and Bulovic V., Electroluminescence from single monolayers of nanocrystals in molecular organic devices, *Nature*, 2002, **420**: 800.
- [7] Gao M., Richter B., and Kirstein S., White-Light Electroluminescence from Self-Assembled Q-CdSe/PPV Multilayer Structures, Adv. Mater., 1997, 9 (10): 802.
- [8] Uchida H., Matsunaga T., Yoneyama H., Sakata T., Mori H., and Sasaki T. Preparation and optical nonlinearity of quantized InAs nanocrystals, *Chem. Mater.*, 1993, 5: 716.
- [9] Tiginyanu I.M., Kravetsky I.V., Monecke J., Cordts W., Marowsky G., and Hartnagel H.L., Semiconductor sieves as nonlinear optical materials, *Appl. Phys. Lett.*, 2000, **77** (15): 2415.
- [10] Kundu M., Khosravi A.A., Kulkarni S.K., and Singh P., Synthesis and study of organically capped ultra small clusters of cadmium sulphide, *J. Mater. Sci.* 1997, **32**: 245.
- [11] Green M., Solution routes to III-V semiconductor quantum dots, *Curr. Opin. Solid State Mater. Sci.*, 2002, 6: 355.
- [12] Olshavsky M.A., Goldstein A.N., and Alivisatos A.P., Organometallic synthesis of GaAs crystallites exhibiting quantum confinement, J. Am. Chem. Soc., 1990, 112: 9438.
- [13] Butler L., Redmond G., and Fitzmaurice D., Preparation and spectroscopic characterization of highly confined nanocrystallites of GaAs in decane, *J. Phys. Chem.*, 1993, **97**: 10750.
- [14] Wells R.L., Pitt C.G., Mcphail A.T., Purdy A.P., Shafieezad S., and Hallock R.B., Use of tris(trimethylsilyl)arsine to prepare gallium arsenide and indum arsenide, *Chem. Mater.*, 1989, 1: 4.
- [15] Uchida H., Curtis C.J., and Nozik A.J., GaAs nanocrystals prepared in quinoline, J. Phys. Chem., 1991, 95: 5382.
- [16] Uchida H., Curtis C.J., Kamat P.V., Jones K.M., and Nozik A.J., Optical properties of GaAs nanocrystals, *J. Phys. Chem.*, 1992, 96: 1156.
- [17] Paolo M. and Giovanni F., Synthesis of nanocrystalline gallium and aluminum arsenides by room temperature grinding of elemental powders, *Mat. Res.*

Bull. 1991, 26: 1283.

- [18] Cao Y. and Banin U., Growth and properties of semiconductor core/shell nanocrystals with InAs cores, J. Am. Chem. Soc., 2000, 122: 9692.
- [19] Kher S.S. and Wells R.L., A straightforward, new method for the synthesis of nanocrystalline GaAs and GaP, *Chem. Mater.*, 1994, 6: 2056.
- [20] Kher S.S. and Wells R.L., Synthesis and characterization of colloidal nanocrystals of capped gallium arsenide, *Nanostruct. Mater.*, 1996, 7 (6): 591.
- [21] Wells R.L., Hallock R.B., Mcphail A.T., Pitt C.G., and Johanse J.D., Preparation of a novel gallium arsenide single-source precursor having the empirical formula AsCl<sub>3</sub>Ga<sub>2</sub>, *Chem. Mater.*, 1991, **3**, 381.
- [22] Janik J.F., Wells R.L., Young V.G., Jr, Rheingold A.L., and Guzei I.A., New pnictinogallaes [H<sub>2</sub>GaE(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (E = P, As)-formation, structural characterization, and thermal decomposition to afford nanocrystalline GaP and GaAs, J. Am. Chem. Soc., 1998, **120**: 532.
- [23] Dinh L.N., Hayes S.E., Wynne A.E., Wall M.A., Saw C.K., Stuart B.C., and Balooch M., Properties of GaAs nanoclusters deposited by a femtosecond laser, *J. Mater. Sci.*, 2002, **37**: 3953.
- [24] Goya G.F., Nanocrystalline CuFe<sub>2</sub>O<sub>4</sub> obtained by mechanical grinding, J. Mater. Sci. lett. 1997, 16: 563.
- [25] Bobet J. and Chevalier B., Reactive mechanical grinding applied to a (Ti + Ni) mixture and to a TiNi compound, *Intermetallics*, 2002, 10: 597.
- [26] Zhang L.D. and Mu J.M., Nanomaterials and Nanostructure, Science Publication, Beijing, 2001.
- [27] Büchel M. and Lüth H., Adsorption of water and methanol on GaAs(110) surfaces studied by ultraviolet photoemission, *Surf. Sci.*, 1979, 87: 285.
- [28] Boggess T.F. Jr, Smirl A.L., Moss S.C., Boyd I. W., and Stryland E.W.V., Optical limiting in GaAs, *IEEE J. Quantum Elect.*, 1985, QE-21(5): 488.
- [29] Tutt L.W. and Boggess T.F., A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors, and other materials, *Prog. Quant. Electron.*, 1993, 17: 299.
- [30] Bosacchi B. and Bessey J.S., Two-photon absorption of neodymium laser radiation in gallium arsenide, J. Appl. Phys., 1978, 49 (8): 4609.
- [31] Li C., Liu C.L., Li F.S., and Gong Q.H., Optical limiting performance of two soluble multi-walled carbon nanotubes, *Chem. Phys. Lett.*, 2003, 380: 201.