Preparation and Optical Nonlinearity of Quantized InAs Nanocrystals

Hiroyuki Uchida, Takahiro Matsunaga, and Hiroshi Yoneyama*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565, Japan

Takao Sakata and Hirotaro Mori

Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Yamada-oka 2-1, Suita, Osaka 565, Japan

Takatomo Sasaki

Department of Electrical Engineering, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565, Japan

Received December 16, 1992. Revised Manuscript Received March 8, 1993

Indium arsenide nanocrystals ranging from 1 to 8 nm in diameter were prepared in triglyme and characterized by transmission electron microscopy, electron diffraction, absorption and fluorescence spectroscopy, and composition analysis by fluorescent X-ray spectroscopy. Large third-order nonlinearity was observed in the degenerative four-wave mixing experiments.

Introduction

Recently, great interest has been devoted to the photochemical and photophysical properties of quantized semiconductor nanocrystals.[1-3] Much attention has focused on the optical nonlinearity of semiconductor nanocrystals, i.e., resonant third-order nonlinear optical processes for II–VI (CdS_xSe_{1-x}) or I–VII (CuCl) semiconductor-doped glasses or polymers.[4-7] Since III–V semiconductor nanocrystals must exhibit large size-quantization effects due to very small effective masses of electrons and holes, they must show remarkable optical nonlinearity as expected from results obtained on GaAs quantum wells.[8]

InAs (E_g = 0.35 eV) is one of the narrow, direct-gap, III–V semiconductors[9] and its optical bandgap is potentially tunable from the near infrared to the visible range, depending on the degree of size quantization. However, only two reports are available for the preparation of InAs nanocrystals for optical applications. Wang and Herron have reported the application of metalorganic chemical vapor deposition (MOCVD), i.e., reaction of $In(C_2H_5)_3$ with AsH_3, in porous glass supports[10], although the optical bandgap of InAs-doped glass seemed to be still narrow as judged from its black color. The other report concerns a magnetron rf sputtering of InAs, GaAs, and SiO_2 targets, which resulted in $In_xGa_{1-x}As$ nanocrystals embedded in a SiO_2 glass substrate.[11] Recently, organometallic synthetic methods have been developed to prepare quantized GaAs nanocrystals which can be well characterized.[12-16]

In the present paper, we report a new synthesis of colloidal InAs nanocrystals by an organometallic reaction, and its crystal structure and chemical composition are evaluated. Furthermore, it is demonstrated that the quantized InAs nanocrystals prepared in this study show a large third-order optical nonlinearity.

Experimental Section

Indium(III) acetylacetonate, $In(acac)_3$, was prepared from the reaction of $In(OH)_3$ with acetylacetone, followed by repeated recrystallizations and vacuum drying. The $In(acac)_3$ prepared in this way contained the stoichiometric amount of In, as determined by atomic absorption spectroscopy. Tris(trimethylsilyl)arsine, $As(SiMe_3)_3$, was prepared according to the literature[17] and purified by a vacuum distillation. These reagents were stored in a drybox. Triethylene glycol dimethyl ether (triglyme) was purchased from Aldrich and distilled over CaH_2

---

(1) Brus, L. *IEEE J. Quantum Electron* **1986**, *QE-22*, 1909. Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555. Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471. Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183. Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.

(2) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113. Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(3) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.

(4) Jain, R. K.; Lind, R. C. *J. Opt. Soc. Am.* **1983**, *73*, 647.

(5) Yao, S. S.; Karagoleff, C.; Gabel, A.; Fortrnberry, R.; Seaton, C. T.; Stegeman, G. L. *Appl. Phys. Lett.* **1985**, *46*, 801. Roussignol, P.; Ricard, D.; Rustagi, K. C.; Flytzais, C. *Opt. Commun.* **1985**, *55*, 143. Nuss, M. C.; Zinth, W.; Kaiser, W. *Appl. Phys. Lett.* **1986**, *49*, 1717. Olbright, G. R.; Peyghambarian, N. *Appl. Phys. Lett.* **1986**, *48*, 1184. Wang, Y.; Mahler, W. *Opt. Commun.*, **1987**, *61*, 233. Hanamura, E. *Phys. Rev. B* **1988**, *37*, 1273. Wang, Y. *Acc. Chem. Res.* **1991**, *24*, 133.

(6) Yumoto, J.; Fukushima, S.; Kubodera, K. *Opt. Lett.* **1987**, *12*, 832.

(7) Nakamura, A.; Tokizaki, T.; Akiyama, H.; Kataoka, T. *J. Lumin.* **1992**, *53*, 105.

(8) Chemla, D. S.; Miller, D. A. B. *J. Opt. Soc. Am. B* **1985**, 2, 1156. Schmitt-Rink, S.; Miller, D. A. B.; Chemla, D. S. *Phys. Rev. B* **1987**, *35*, 8113.

(9) Madeling, O., Ed. *Landolt-Börnstein*; Springer: Berlin, 1983; New Series, Vol. 17a.

(10) Wang, Y.; Herron, N. *Res. Chem. Intermed.* **1991**, *15*, 17.

(11) Tsunetomo, K.; Yamamoto, M.; Osaka, Y. *Jpn. J. Appl. Phys.* **1991**, *30*, L521.

(12) Byrne, E. K.; Parkanyi, L.; Theopold, K. H. *Science* **1988**, *241*, 332.

(13) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4. Wells, R. L.; Hallock, R. B.; McPhail, A. T.; Pitt, C. G.; Johansen, J. D. *Chem. Mater.* **1991**, *3*, 381.

(14) Olshavsky, M. A.; Goldstein, A. N.; Alivasatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

(15) Uchida, H.; Curtis, C. J.; Nozik, A. J. *J. Phys. Chem.* **1991**, *95*, 5382.

(16) Uchida, H.; Curtis, C. J.; Kamat, P. V.; Jones, K. M.; Nozik, A. J. *J. Phys. Chem.* **1992**, *96*, 1156.

(17) Becker, G.; Gutekunst, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1980**, *462*, 113.

0897-4756/93/2805-0716$04.00/0

under reduced pressure, ca. 10 Torr. All compounds were manipulated in a standard vacuum line or under a high-purity nitrogen (>99.999%) atmosphere dried with molecular sieves. A mixture containing 0.5 mmol of $In(acac)_3$ and 0.5 mmol of $As(SiMe_3)_3$ in 25 cm^3 of triglyme was heated at reflux (216 °C) for 70 h. As a blank sample, triglyme containing the same concentration of $In(acac)_3$ was heated under the same conditions.

The InAs colloids were filtered under nitrogen atmosphere using Amicon type YM1 filter with molecular weight cutoffs (MWCO) of 1000 (average pore size $d = 1.2$ nm) and Advantec type T020A filter ($d = 0.2$ μm). The dark brown powders separated on the 0.2-μm filter were dried in vacuum and characterized by X-ray diffraction, XRD (Shimadzu XD-3A) with the use of Cu Kα ($\lambda = 0.1542$ nm) radiation. The absorption and fluorescence spectra of the filtrates were measured with a photodiode-array spectrophotometer (Hewlett-Packard, 8452A) and a fluorescence spectrometer (Hitachi, F-3010). A high-resolution transmission electron microscope, TEM (Hitachi H-9000, 300 kV), was employed to observe InAs nanocrystals deposited onto carbon-evaporated copper grid. The lattice spacings of InAs nanocrystals in the TEM pictures and the electron diffraction pattern were measured by reference to $d(200)$ of an Au single crystal observed under the same conditions.

The concentration of In and As in the colloids was determined by a fluorescent X-ray spectrometer (Rigaku, 3270A): 0.1 cm^3 of the colloid or the standard solution (atomic absorption analysis grade) was dropped on a filter paper (Rigaku, 3379C1), dried in vacuum, and then determined using calibration curves prepared with the use of the intensity of In Kα or As Kα. The composition of the dark brown powders was determined similarly after dissolving them in concentrated nitric acid.

The third-order optical nonlinearity of InAs colloids was examined by using the configuration of the degenerative four-wave mixing (DFWM) with two forward incident beams[18-20] at room temperature. To obtain the colloid with a higher concentration of InAs nanocrystals, the 0.2-μm filtrate of the original InAs colloid was concentrated to one-half of its volume by a vacuum evacuation. The 0.2-μm filtrate of the original InAs colloid, the concentrated one, and the blank sample containing $In(acac)_3$ in triglyme were used for the DFWM in a glass cell with the optical pass length of 2 mm. A commerical colored glass filter (HOYA, Y-52, thickness = 1.05 mm) was also used as a reference sample. The sample was excited with two laser beams intersecting at an angle of 1.5° from a Q-switched Nd:YAG laser (Spectra Physics, GCR-11) generating 532-nm pulses with a width of 7–11 ns. The signal beam diffracted by the laser-induced grating was introduced to a monochromator (McPherson, 2035) equipped with a photomultiplier (Hamamatsu Photonics, R955) and was recorded by a digitizing oscilloscope (Hewlett-Packard, 54510A).

Results and Discussion

Characterization of InAs Nanocrystals. Brown turbid slurries were obtained by the reaction of $In(acac)_3$ with $As(SiMe_3)_3$ in triglyme at the reflux temperature. Transparent brown colloids were obtained from the slurries by filtering them through a 0.2-μm filter. The colloids stored under nitrogen in the dark were very stable and did not aggregate for at least 6 months.

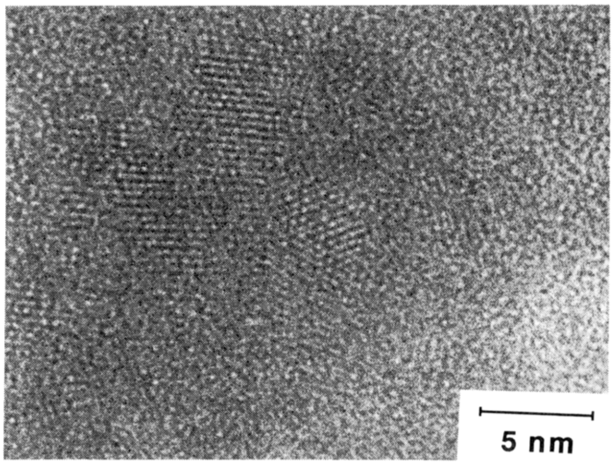

Figure 1. Transmission electron micrograph of InAs nanocrystals.

Table I. Lattice Spacing, *d*, of InAs Nanocrystals Determined by Electron Diffraction

d/nm (JCPDS data)[21]	*hkl*	*d*/nm (obsd)[a]	error/%[b]
0.3498	111	0.3441	−1.7
0.3030	200	0.2964	−2.2
0.2142	220	0.2141	−0.1
0.1826	211	0.1835	+0.5

[a] Lattice spacing determined by reference to $d(200)$ of Au single crystal measured under the same conditions. [b] Experimental error for d, compared with JCPDS data.

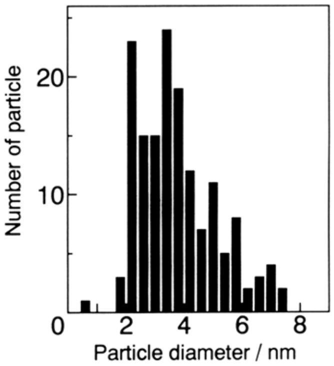

Figure 2. Size distribution of InAs nanocrystals determined from TEM picture. Total number of particles counted was 154.

Figure 1 shows a typical TEM photograph of the InAs particles obtained by filtration with a 0.2-μm filter. Clear lattice planes are seen in Figure 1. By reference to the lattice spacing of the (200) plane of the Au single crystal in the TEM picture obtained under the same conditions, the lattice spacing of the particles was determined to be 0.346 ± 0.003 nm, which is assigned to $d(111) = 0.3498$ nm of InAs[21]. The electron diffraction of the particles gave clear zinc blende type patterns of (111), (220), and (311) and weak (200) of InAs, as summarized in Table I. Figure 2 shows the size distribution of the InAs particles, which was obtained for 154 particles with clear lattice fringes on several TEM photographs. The particle size ranges from 1 to 8 nm, and the average diameter is 3.76 nm with a standard deviation of 1.35 nm.

Dark brown powders produced in the original slurries were collected on the 0.2-μm filter. After drying under vacuum, 0.193 g of a dark brown powder was obtained. As shown in Figure 3, the X-ray diffractogram of the dark brown powder shows very broad peaks which can be assigned to zinc blende type InAs. The particle size estimated by Scherrer's equation is about 4 nm, being consistent with that observed by TEM for nanocrystals in the colloids. This result suggests that the dark brown powders contain either InAs nanocrystals which were not dispersed in the colloids or poorly crystalline InAs bulk powders.

Figure 4 shows the absorption spectra of the 0.2-μm and 1.2-nm filtrates of the InAs colloids. For the 0.2-μm filtate,

---

(18) Yajima, T.; Taira, Y. *J. Phys. Soc. Jpn.* **1979**, *47*, 1620.
(19) Horan, P.; Blau, W. *J. Chem. Phys.* **1990**, *92*, 4139.
(20) Kobayashi, T. *Oyo Butsuri* **1990**, *59*, 785.
(21) JCPDS International Centre for Diffraction Data, No. 15-869.

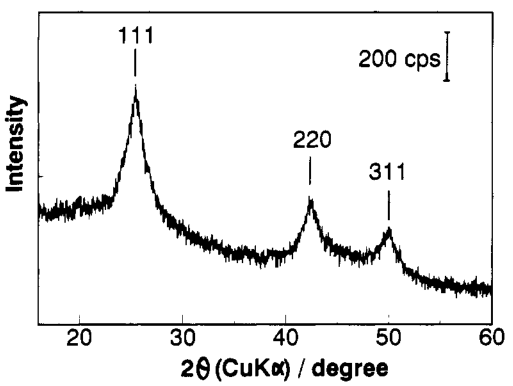

Figure 3. X-ray diffractogram of the dark brown powders which were obtained by filtlation of the original slurries with 0.2-μm filter. Peak assignments are based on zinc blende type $InAs$[21].

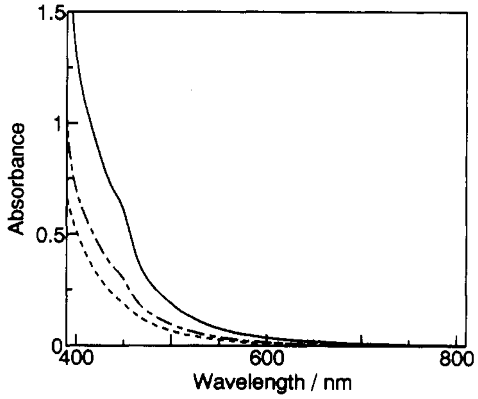

Figure 4. Absorption spectra of the InAs colloid filtered through 0.2-μm (—) and 1.2-nm (- • -) pore size filters. A spectrum of $In(acac)_3$ triglyme blank solution filtered through a 0.2 μm filter (---) is also shown. Optical path length = 2 mm.

the absorption onset is about 730 nm (1.7 eV), being blue-shifted greatly from that of the bulk material (3543 nm). Since the InAs colloid which was concentrated to one-half of the original volume exhibited almost the same absorption onset, the absorption onset at about 730 nm seems to be a characteristic of the InAs nanocrystals. Using a simple effective mass approximation for the relation between the bandgap and the particle size[1], the diameter of the InAs particle is estimated to be 6.6 nm. This is consistent with the TEM results (Figure 2), since the optical absorption threshold of the colloids must be determined by the largest particles in the colloids.[2] The spectrum for the 1.2-nm filtrate is quite different from that of the 0.2-μm filtrate and is rather similar to that of an $In(acac)_3$ triglyme blank solution containing no InAs particles. The weak absorption from ca. 600 nm for the blank solution is probably due to an In–(acac)–triglyme complex, since triglyme is a good complexing agent for many metal ions.[22]

Fluorescence spectra are shown in Figure 5 for the InAs filtrates and the blank $In(acac)_3$ solution. Although the emission observed for the InAs colloid prepared by filtration with use of a 0.2-μm filter is stronger than that for the blank solution, the spectral shapes of them are similar; the emission onsets near 700 nm and peaks at about 550 nm. Therefore, the emission properties of the InAs nanocrystals may be masked by molecular species (In–acac–triglyme complex) in the present system, being different from the case of GaAs colloids prepared in triglyme.[16]

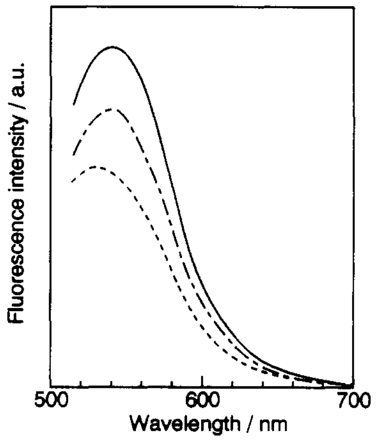

Figure 5. Fluorescence spectra of 0.2-μm (—) and 1.2-nm (- • -) filtrates of InAs colloids and of the $In(acac)_3$ blank solution (---). Excitation was at 500 nm.

Table II. Content of In and As Contained in 0.2-μm and 1.2-nm Filtrates of the InAs Colloid and in the Dark Brown Powders Determined by Fluorescent X-ray Analysis

no.	sample	In/mmol[a]	As/mmol[a]
		Solutions	
1	loaded[b]	0.500	0.500
2	0.2-μm filtrate	0.187	0.033
3	1.2-nm filtrate	0.123	0.019
4	Δ(2–3)[c]	0.064	0.014
		Dark Brown Powders	
		0.360 (21.4 wt %)	0.304 (11.8 wt %)

[a] In 25 cm^3 of each solution or in 0.193 g of the dark brown powders. [b] Original amount of the starting material. [c] Difference between the run nos. 2 and 3, corresponding to the composition of InAs nanocrystals greater than 1.2-nm particles.

Table II shows analytical results for the content of In and As in the InAs colloids. The content of In is much higher than that of As for both 0.2-μm and 1.2-nm filtrates. The composition of the InAs particles in the colloids was estimated by subtracting the amount of In and As obtained for the 1.2-nm filtrate from that for the 0.2-μm filtrate, since, as mentioned above, almost all of the InAs particles were removed by the 1.2-nm pore-size filter. The composition of the InAs nanocrystals obtained in this way contained excess In, whose source may be the In–acac–triglyme complex which may serve as a stabilizing agent to prevent the aggregation of the InAs nanocrystals. The amount of InAs produced in this synthesis is estimated to be 0.014 mmol (0.55 mM), with the assumption that the amount of As determined for the residue on the 1.2 nm filters is that from the InAs nanocrystals. This means that 2.8% of $As(SiMe_3)_3$ in the original solution was used in the chemical synthesis of InAs. A large portion of the loaded materials was found to be included in the brown powders as shown in Table II. Judging from the content of In and As, the dark brown powders contain an appreciable amount of organic moieties besides InAs crystals confirmed by the XRD.

Optical Nonlinearity of InAs Nanocrystals. When a nonlinear optical material is excited with two forward laser beams in the directions denoted by k_1 and k_2 wave vectors, the diffracted signals due to the third-order nonlinearity must be observed in the directions of $2k_2-k_1$

---

(22) den Heijer, M.; Driessen, W. L. *Inorg. Chim. Acta* **1980**, *39*, 43. Van Gils, N.; Zuur, A. P.; Driessen, W. L. *Inorg. Chim. Acta* **1982**, *58*, 187. Wang, W. J.; Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Coord. Chem.* **1990**, *22*, 43.

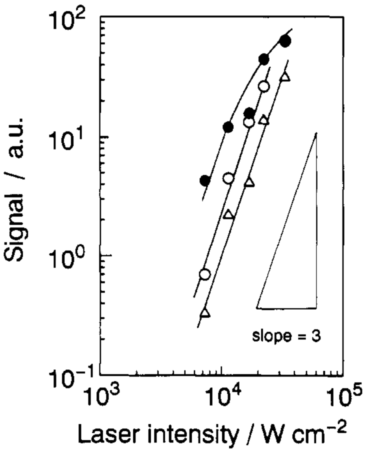

Figure 6. Beam powder dependence of diffracted DFWM signal: (•) Y52 glass filter; (○) concentrated InAs colloid; (△) original InAs colloid. Theoretical cubic slope (eq 1) is also shown in the figure.

Table III. Linear and Nonlinear Optical Properties of InAs Colloids and Y52 Glass Filter at 532 nm

sample	T/%[a]	α/cm^{-1} [b]	$\chi^{(3)}$/esu[c]	vol fraction[d]
InAs colloid (concentrated)	59.4	2.61	3.0×10^{-10}	4×10^{-5}
InAs colloid (original)	78.4	1.22	1.6×10^{-10}	2×10^{-5}
Y-52 filter	85.2	1.52	1.3×10^{-9}	$2–5 \times 10^{-3}$

[a] Transmittance. [b] Absorption coefficient. [c] The third-order nonlinearity evaluated at 7.3 kW cm^{-2}. [d] Volume fraction of semiconductor particles included in the sample.

and $2k_1{-}k_2$ on the opposite side of the sample.[18] The intensity of the diffracted signal beam I_s is related both to the incident beam intensity I_0 and to the absolute value of the third-order susceptibility $|\chi^{(3)}|$ as follows:[7,19]

$$I_s = 2^8\pi^4\omega^2(1-T)^2T|\chi^{(3)}|^2I_0^3/n^4c^4\alpha^2 \tag{1}$$

where α is the absorption coefficient, T the transmittance, n the refractive index, c the light velocity, and ω the angular frequency of the laser beam. As given by eq 1, the intensity of the diffracted signal I_s should depend cubically on that of the incident beam I_0.

We performed the DFWM experiments using the original and the concentrated InAs colloids, the 1.2-nm filtrate, the blank sample, and a commercial CdS_x-Se_{1-x}-doped glass (HOYA, Y-52) as a reference sample whose $|\chi^{(3)}|$ at 532 nm is reported to be 1.3×10^{-9} esu.[6] Distinct diffracted signals were observed for the InAs colloids, and their intensities indeed increased cubically with increasing the laser power as shown in Figure 6. On the other hand, no signals were detected for the 1.2-nm filtrate and the blank sample, indicating that the InAs nanocrystals are responsible for the optical nonlinearity. The signal intensity is higher for the concentrated InAs colloid than that for the original colloid. The value of $|\chi^{(3)}|$ for the concentrated InAs colloids was determined to be 3×10^{-10} esu by applying a reference method[20,23] to eq 1 as shown in Table III, where results on the Y-52 filter also are included.

In the DFWM experiments, we must take thermally induced refractive index changes into account.[19,24] The thermally induced third-order susceptibility $|\chi^{(3)}{}_{\text{thermal}}|$ is given as follows:[19,24]

$$|\chi^{(3)}{}_{\text{thermal}}| = \frac{dn}{dT}\,\frac{4n^2c\epsilon_0\alpha\tau\Phi}{3\rho C_p} \tag{2}$$

where dn/dT is the rate of change of the refractive index n of the solvent with temperature, α is the absorption coefficient, τ is the laser pulse width, Φ is the fraction of absorbed radiation converted to heat, and ρ and C_p are the density and specific heat. The accurate Φ was not known for the InAs colloid, although the sample used in this experiment exhibited an emission by the excitation at 532 nm ($\Phi < 1$). Using the specific values reported for triglyme[25] and $dn/dT = 10^{-4}$ K^{-1},[26] we can estimate $|\chi^{(3)}{}_{\text{thermal}}|$ to be $<1 \times 10^{-10}$ esu for the concentrated InAs colloid. To evaluate the thermal effect, control DFWM experiments were carried out using pararosaniline, that shows purely thermal grating.[27] The compound was dissolved in triglyme in such a way as to give the same α as that of the concentrated InAs colloid. Then, 1×10^{-10} esu was obtained for $|\chi^{(3)}{}_{\text{thermal}}|$. However, in the case of pararosaniline solution, the full width at half-maximum (fwhm) of the diffracted signal was broader (12.5 ns) than that of the laser beam (11.3 ns) due to a delay by the thermal effects. No such broadenings were detected for the InAs colloids and Y-52. Even if the correction of the thermal effect is made by subtracting $|\chi^{(3)}{}_{\text{thermal}}|$ from the obtained $|\chi^{(3)}|$ value for the concentrated InAs colloid, $|\chi^{(3)}|$ was little changed. Accordingly, we can conclude that the intrinsic $|\chi^{(3)}|$ for the InAs nanocrystals is very high. Since the colloid solution contained only a small volume fraction of InAs ($\sim 10^{-5}$), compared to the caes of the Y-52 colored glass where $(2–5) \times 10^{-3}$ volume fraction of CdS_xSe_{1-x} is contained, $|\chi^{(3)}|$ for the InAs nanocrystals will be in the order of 10^{-8} esu if the volume fraction of the semiconductor particles is adjusted to the same value as that of Y-52. Furthermore, the InAs particles that can respond to the monochromatic light of 532 nm must be limited to those having the diameter larger than 5.4 nm if the bandgap vs the particle size relation derived by Brus[1] is applied. Large particles occupy only 12% of the prepared InAs nanocrystals as judged from the particle size distribution given in Figure 2. Since $|\chi^{(3)}|$ depends on the wavelength and volume fraction, much higher $|\chi^{(3)}|$ may be obtained at shorter wavelength if the InAs nanocrystals are doped in a solid matrix at high concentration.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research No. 03453089 from the Ministry of Education, Science and Culture, Japan. We are grateful to Dr. Y. Asahara of HOYA Materials Research Laboratory for kindly providing a Y-52 filter.

---

(23) Sarid, D.; Rhee, B. K.; McGinnis, B. P.; Sandroff, C. J. *Appl. Phys. Lett.* **1986**, *49*, 1196.

(24) Caro, R. G.; Gower, M. C. *IEEE J. Quan. Electron.* **1982**, *QE-18*, 1376.

(25) Trejo, L. M.; Costas, M.; Patterson, D. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3001; Wallace, W. J.; Shephard, C. S.; Underwood, C. *J. Chem. Eng. Data* **1968**, *13*, 11.

(26) dn/dT for triglyme has not been reported. dn/dT of many organic solvent is in the order of 10^{-4} K^{-1}: *Beilstein Handbuch der Organishen Chemie*, 4th ed.; Springer: Berlin, 1920.

(27) Hoffmann, H. J. *J. Opt. Soc. Am. B* **1986**, *3*, 253.