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Ultrafast exciton dynamics in colloidal aluminum phosphide nanocrystals

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ABSTRACT

The primary exciton dynamics of colloidal indirect bandgap AlP nanocrystals are characterized with ultrafast transient absorption spectroscopy. A 400-nm excitation results in a high yield formation of an emissive exciton with a ~1-ns lifetime and a 50-nm bandwidth red-shifted emission. Multi-wavelength target analysis is used to decompose the measured signals into sequential and parallel models, which interpret the measured data as an emissive exciton with a 1.2-ns decay time and a dark exciton which is attributed to surface trapping. Reconstructed nonlinear absorption spectra resolve a broad optical gain persisting for >1 ns. The 15% emission yield demonstrates that colloidal AlP nanocrystals are useful as a potential broadband, high efficiency optoelectronics material.

1. Introduction

Type III–V semiconductors are a class of important materials often used for optoelectronic applications with electroluminescent properties [1] including light emitting diodes (LED) [2], lasers [3], electronics [4], light therapy [5], and ultrafast light amplification [6]. Unfortunately, many of the visible emitting II–VI semiconductor nanocrystal systems are not ideal for industrial applications since they often contain highly toxic heavy metals (e.g., cadmium and mercury), which limit their use due to growing environmental and health concerns (e.g., the European Union's RoHS initiative). Hence, much attention has been directed towards the development of less toxic III-V semiconductor nanocrystals (NCs) [7–9], mainly indium phosphide and arsenide; unfortunately they have proven difficult to synthesize in good quality although recent advancements are promising [10–12]. Of these III–V materials, aluminum phosphide is the most elementally abundant with the lowest cost and environmental impact [13].

For use in optical or optoelectronic applications, materials must exhibit long exciton lifetimes, high emission quantum yields, high photo-stability, and in the case of lasing, appreciable gain. In this regard, nanocrystal systems have proven to be particularly well suited [14,15]. AlP has previously been studied in alloys with other III–V semiconductors to make high efficiency LEDs [16], and can be assembled into NCs [17] and nanotubes [18]. This demonstrates the broad potential of AlP for optoelectronic applications and suggests that unalloyed AlP systems may have similar material properties. Presented here is the first characterization of primary photodynamics of colloidal AlP NCs with femtosecond transient absorption spectroscopy.

2. Experimental

AlP NCs were synthesized via the reaction of trimethyl aluminum with trimethylsilylphosphine; the complete synthesis protocol and static characterization are detailed elsewhere [19]. Dispersed transient absorption measurements were performed with the setup described in detail elsewhere [20] and the relevant details are briefly described below. 300 microliters of the AlP sample was diluted into 1 ml of hexane and placed into a 2 mm flow cell that was moved with motorized actuators. The 400-nm excitation pulses were generated by second harmonic generation with 800-nm fundamental light from a commercial Ti:Sapphire laser (Spectra-Physics Spitfire Pro). Broadband probe pulses were generated via supercontinuum generation by focusing 800 nm fundamental pulses into a slowly translating 2-mm CaF_2 disk. Pump–probe delay times were controlled with a computer-controlled translation stage (Newport IMS600LM). The transmitted probe light was spectrally dispersed and imaged onto a homebuilt 256-pixel Si diode detector system and digitized on a shot-by-shot basis. An optical chopper (Thorlabs MC100) was used to modulate the pump pulses at 500 Hz. The transient data was acquired under excitation fluences of ~470 and ~75 $\mu J/cm^2$/pulse with a 350-μm spot size for the pump and 60 μm for the probe pulses, respectively. Within this intensity range, the transient spectra and timescales are power independent, but with differing amplitudes.

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3. Results and discussion

The ground-state absorption spectrum of AlP NCs exhibit three peaks centered at approximately 210, 310, and 380 nm (Figure 1A). A 410-nm (3 eV) band-edge exciton energy is estimated based on the onset of absorption. The photoluminescence (PL) spectrum peaks at 415 nm and extends beyond 500 nm (Figure 1A, inset). Transmission electron microscopy images (TEM) resolve ~8-nm diameter AlP NCs (Figure 1B). The 400-nm initiated transient spectra of these suspended AlP NCs exhibit four features within the visible wavelength range (Figure 2): [1] a negative ground state bleach from 375 to 400 nm, [2] a negative stimulated emission (SE) from 410 to 550 nm, and [3,4] two positive induced absorption (IA) bands at $\lambda < 375$ and $\lambda > 550$ nm. The higher energy induced absorption [3] is centered at 350 nm with a ~30-nm width (Figure 2). The low-energy induced absorption [4] is a broad absorption feature initially observed at $\lambda > 550$ nm, that blue shifts at later times.

The bleach shows no resolvable decay in the first 100 ps after excitation with approximately 90% of the initially formed population decaying with a ~800-ps half-life (Figure 3B). Though there is little dynamic Stokes' shifting of the SE, there is a slight red-shifting that is noticeable only on the low energy side of the SE band. The decay kinetics of this IA are nearly identical to the SE kinetics (Figure 4A and C). Approximately 10% of the initially formed excitons persist beyond the 8-ns timescale of the measurement (Figure 3D).

The transient signals were analyzed within a multi-compartment global analysis formalism [21,22], which fits the data to an underlying 'target' model with time-dependent populations (i.e. concentration profiles) with time-independent spectra. This is accomplished by fitting the data with numerical solutions of linear first-order differential equations describing a postulated model Eq. (1):

$$\frac{d_i n}{dt} = A_i I(t) + \sum_{i,j} K_{ij} n_i \qquad (1)$$

In Eq. (1), n_i represents the ith microscopic population of interest, A_i is the initial occupancy of ith excited-state, $I(t)$ is the pump pulse temporal envelope, and K_{ij} are the rate constants describing the *exponential* flow from one population into another. If the underlying target model accurately describes the dynamics, the extracted spectra from the analysis are termed Species Associated Difference Spectra (SADS) and represent the true difference spectra of the constituent populations. If the model inaccurately describes the dynamics, the resulting spectra from the global fitting are Evolution Associated Difference Spectra (EADS) and are linear combinations of the underlying SADS [21–24].

The global analysis was initially conducted within a three-population sequential reaction scheme (Scheme 1A) that fits and decomposes the data, without introducing a bias with 'target' model. The sequential modeling yields good kinetic fits (not shown), with the EADS and concentration profiles in Figure 4A and B. Three components are required to fit the data with characteristic timescales of 18 ps, 600 ps, and 3.1 ns. The 18-ps process shows predominately spectral relaxation with no population loss as the SE

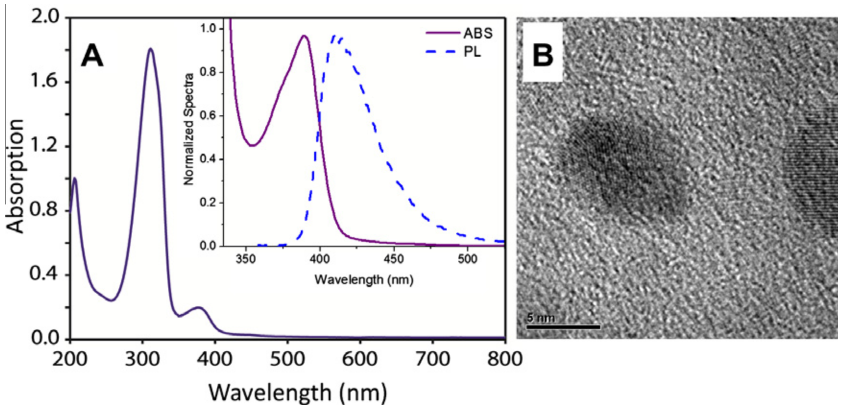

Figure 1. A Ground-state absorption of colloidal AlP nanocrystals in hexane. Inset: low energy absorption band (solid purple curve) with overlapping photoluminescence spectrum (dashed blue curve). (2) TEM image of AlP nanocrystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

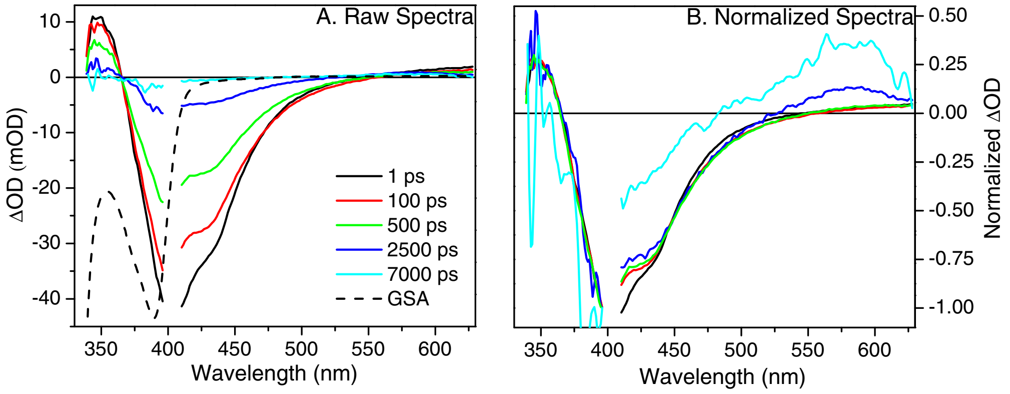

Figure 2. Transient spectra after 400-nm excitation are displayed as raw spectra (Panel A) and normalized spectra (Panel B). The inverted ground state absorption spectrum is overlaid in Panel A for reference.