Comprehensive synthesis of monohydroxy-cucurbit[n]urils (n = 5, 6, 7, 8): High purity and high conversions
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Biexciton Binding of Dirac fermions Confined in Colloidal Graphene Quantum Dots

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ABSTRACT: We present transient absorption measurements and microscopic theory of biexciton binding in triangular colloidal graphene quantum dots consisting of 168 sp²-hybridized C atoms. We observe optical transitions from the lowest orbitally dark singlet exciton states to states below the energy of an unbound dark+bright singlet-exciton pair. Through microscopic calculations of the low-energy exciton and biexciton states via tight-binding, Hartree–Fock, and configuration interaction methods, the spectra reveal a biexciton consisting primarily of a dark-bright singlet-pair bound by ~0.14 eV.

KEYWORDS: Graphene quantum dot, Dirac fermions, biexciton binding, transient absorption, Hartree–Fock, configuration interaction

A central topic in nanoscience is the interactions between quasiparticles. In strongly confined nanoscale systems, these interactions are enhanced and lead to quantitatively and even qualitatively different phenomena than those observed in their bulk counterparts. These include enhanced biexciton binding, rapid nonradiative Auger recombination, and potentially efficient carrier multiplication. At the heart of such phenomena are the enforced proximity of carriers and the large extent of the carrier wave functions in momentum space, which reduces constraints associated with conservation of crystal momentum. In the context of biexcitons, graphene quantum dots are especially interesting, since screening is much weaker in a two-dimensional lattice of light atoms than in a three-dimensional crystal of heavy atoms such as Cd and Se that feature so prominently in semiconductor quantum dot systems. Only recently, though, have graphene quantum dots been synthesized by bottom-up techniques in sizes large enough that the lowest confinement-induced electron and hole states can be understood in terms of confining Dirac fermions. This offers opportunities for new insights into interactions between Dirac fermions and applications in nanotechnology.

In graphene, understanding interactions of Dirac fermions and the nature of the possible ground states remains challenging. Unlike in metals where the ratio of the Coulomb energy to the kinetic energy is proportional to the average distance between electrons, r_e in graphene this ratio is independent of density and proportional to (r_eκ)⁻¹ where r_e is the Fermi velocity and κ is the dielectric constant. Several theoretical predictions include insulating ground states and excitonic instabilities. However, many experimental properties can be explained based on a noninteracting model of Dirac fermions; electron–electron (e–e) interactions appear to lead only to renormalization of the Fermi velocity while e–e interactions of Dirac fermions consistent with weak e–e interactions in a semimetallic state. In contrast, there are few experimental reports of excitonic signatures in graphene, particularly with regard to those that can be described in terms of binding of electrons and holes within the region of the graphene spectrum dominated by the linear dispersion of the Dirac cones.

Here we present a theory and experimental observations of the interaction of excitons composed of Dirac fermions confined in triangular colloidal graphene quantum dots (GQDs). In these dots valley degeneracy translates into degeneracy of conduction and valence band edges and existence of orbitally bright and dark exciton states. We observe interband transitions from the lowest orbitally dark singlet exciton states to a bound two-electron–two-hole state (biexciton) that can be described in terms of a dark exciton and bright exciton bound by ~0.14 eV. While this binding is 1 order of magnitude less than the gap, it is strong compared to biexciton binding in semiconductor quantum dots and carbon nanotubes. The importance of strong Coulombic interactions in multiple exciton generation in solar cells.
Quasi-electrons and quasi-holes in finite size graphene, graphene quantum dots (GQDs), can be understood in terms of confined Dirac fermions. In particular, scaling of the optical gap with the size of the quantum dot from nanometer to submicron agrees very well with that of confined Dirac Fermion electrons and holes. The inset in Figure 1 shows the states at the top of the valence and bottom of the conduction band in colloidal graphene quantum dots with the atomic structure shown as arrows. The GQDs labeled C168 have double-armchair edges and exactly 168 carbon atoms in the sp$^2$-hybridized core. Confinement opens a gap of $\Delta m = \pm 1$, labeled with arrows. $\Delta m = +1$ corresponds to $\sigma^+$ photon polarization (red arrow), and $\Delta m = -1$ corresponds to $\sigma^-$ photon polarization (blue arrow). The transitions relevant to transient-absorption measurements at long delays, when only the ground and the nominally dark singlet exciton states $X_{1,2}$ are populated, are indicated by solid arrows. Black arrows represent orbitally forbidden transitions that become allowed due to electron-phonon coupling. Filled circles represent conduction-band electrons, and open circles represent (valence-band) holes.

Figure 1. Extrapolated singlet exciton ($X$) and bie exciton (XX) states, relative to the ground state (GS), of confined Dirac fermions derived from the two-fold orbitally degenerate HOMO and LUMO states illustrated in the inset. Bie exciton states are colored according to the single-exciton states that make the dominant contributions to the corresponding bie exciton. Partially transparent horizontal lines indicate the bie exciton states in the case of zero bie exciton binding energy. As an example, the binding energy for bie exciton state $X_{1,2}$ is shown by $\Delta_{XX}$. Dipole-allowed interband electronic transitions, corresponding to $\Delta m = \pm 1$, labeled with arrows. $\Delta m = +1$ corresponds to $\sigma^+$ photon polarization (red arrow), and $\Delta m = -1$ corresponds to $\sigma^-$ photon polarization (blue arrow). The transitions relevant to transient-absorption measurements at long delays, when only the ground and the nominally dark singlet exciton states $X _ {1,2}$ are populated, are indicated by solid arrows. Black arrows represent orbitally forbidden transitions that become allowed due to electron-phonon coupling. Filled circles represent conduction-band electrons, and open circles represent (valence-band) holes.

Figure 2. (a) Experimental (blue) and theoretical (black) absorption cross section of C168. Inset shows the molecular structure of C168, with the GQD core in blue and ligands in black. (b) Calculated singlet exciton ($X$) and bie exciton states (XX). Gray lines show higher-energy single-exciton states obtained by either dipole-allowed excitation from the ground state or by one of the carriers excited from $X_{1,2}$. The XX states are the bie exciton states accessible by absorption of a photon from $X_{1,2}$.

The exciton states give rise to the calculated and measured absorption spectra shown in Figure 2a. Although $X_{1,2}$ (or collectively LX) are orbitally dark, their coupling to phonons allows for borrowing of oscillator strength from higher-energy bright excitons thereby producing the absorption shoulder at 1.7 eV. The pronounced peak at 2.1 eV is associated with $X_{1,2}$. Figure 2b shows excited singlet exciton states obtained by either dipole-allowed excitation from the ground state or by excitation of one of the carriers from the states $X_{1,2}$. The XX states studied here experimentally are the bie excitons accessible by optical absorption from $X_{1,2}$.

Measurement of bie exciton emission in C168 is extremely challenging on account of the low photoluminescence quantum yield of C168 single excitons ($\sim$0.002) and rapid rate (3 ps$^{-1}$) of bie exciton Auger recombination. Moreover, rapid carrier cooling allows for measurement of photoluminescence only from the lowest-energy single- and bie exciton states. Therefore, we study bie excitons by transient absorption (TA) measurements in which the single-to-bie exciton transition does not require a long-lived bie exciton for its observation and in which one can access higher-energy bie excitons. TA measurements on C168 were performed as described previously. C168 was prepared following the synthesis of Yan and Li. Prior characterization has established the high structural and size uniformity of the synthetic product. C168 was dissolved in anhydrous toluene, and loaded in a nitrogen atmosphere in a 1 mm path length fused-silica cuvette sealed with Teflon valves. GQD solutions were prepared to optical densities of $\sim$0.2 at 3.1 eV. C168 in toluene was excited at 3.1 eV and probed with $\sim$130 fs temporal resolution using a broadband continuum (for...
photon energies $\hbar \omega_{\text{probe}} \geq 1.1$ eV) or the output of a $\beta$-BaB$_2$O$_4$-based optical parametric amplifier (for $0.5$ eV $\leq \hbar \omega_{\text{probe}} < 1.05$ eV). Spectra above $1.1$ eV were measured with a charge-coupled-device (CCD) spectrometer and below $1.1$ eV with a monochromator and InGaAs photodiode. In each case, the spectral resolution was $2$ nm. To account for the solvent response, identical measurements were performed on a cuvette filled with toluene alone, the response of which was subtracted from the data for C168 in solution.

Excitation of C168 at $3.1$ eV with a pump fluence of $0.8$ mJ cm$^{-2}$ per pulse yields the TA spectrum of Figure 3. The effective absorption cross section of the GQDs at $3.1$ eV is $\sigma_0 \sim 6 \times 10^{-15}$ cm$^2$ so that the optical response is saturated\cite{13} and essentially all the GQDs are initially excited with at least two excitons. Resolution-limited carrier cooling is followed by essentially all the GQDs are initially excited with at least two excitons.

Figure 3. Transient absorption spectrum showing $-\Delta \alpha L$ as a function of probe photon energy and delay for C168 excited at $3.1$ eV at a fluence of $0.8$ mJ cm$^{-2}$ per pulse ($1.6 \times 10^{10}$ photons cm$^{-1}$ per pulse). The color scale corresponds to the data at $t = 5.0$ ps. The data at $t > 8$ ps are multiplied by $3$ to match scales. The black curves indicate the contours for $\Delta \alpha L = 0$.

The Hamiltonian for the many-body Hamiltonian of the GQD describes population of $X$ excitons. The spectral shape is unchanged for times of at least $10^5$ cm$^{-1}$, which are characteristic of biexciton binding;\cite{12} transitions from $X$ excitons. The CI Hamiltonian matrix is built in the space of multipair excitations of Dirac fermions out of the HF ground state $|0\rangle$:

$$
\hat{H} = \sum_{i,j=1}^{N} \sum_{\sigma} \varepsilon_i^+ \varepsilon_i^{-\sigma} + \frac{1}{2} \sum_{i,j,k,l} \sum_{\sigma,\sigma'} \langle ij | V_{ijkl} | kl \rangle \varepsilon_i^+ \varepsilon_j^{-\sigma} \varepsilon_k^+ \varepsilon_l^{-\sigma'}
$$

The first term is the one-electron tight-binding Hamiltonian, and the second term, $\langle ij | V_{ijkl} | kl \rangle$, describes the screened electron-electron interactions, $V(r-R) = 2/(k(r-R))$.\footnote{13} Screening by sigma electrons and the surrounding fluid is included through the dielectric constant $\kappa$. We next perform Hartree–Fock calculations, which rotate the $\varepsilon_i^+$ site operators into HF operators $b_i^+\sigma$, where $j$ labels the HF states. The ground and excited states of the GQD are expanded in multipair excitations of biexcitons present in the low-energy shoulder, one at $1.68$ eV and another of half the amplitude at $2.22$ eV, corresponding to excitations derived from other than a band-edge electron-hole pair. The spectral widths of the $X \rightarrow X + X$ and $0 \rightarrow X$ transitions are set as equal because the main source of additional line broadening for transitions to biexciton states is...
expected to be Auger recombination, which leads to a biexciton lifetime of $\tau_{XX} \approx 0.3$ ps.\textsuperscript{31} This corresponds to broadening 1 order of magnitude less than the optical gap but stronger than in semiconductor quantum dots\textsuperscript{32,33} and carbon nanotubes.\textsuperscript{2} The observation of such large biexciton binding in a structure only about 2 nm across may be surprising. In colloidal CdSe quantum dots, biexciton binding increases with decreasing dot radius until a radius $\lesssim 1.8$ nm (substantially larger than the size of C168) at which point the trend reverses\textsuperscript{40} on account of the balance between confinement and Coulomb interactions. In a system with parabolic band structure, the confinement energy scales with nanocrystal size $L$ as $L^{-2}$, whereas the Coulomb interaction scales as $L^{-4}$. At sufficiently small size, confinement dominates the Coulomb interaction to a degree that the latter cannot produce sufficient deformation of the wave function of the four-particle relative motion to produce continuing growth in the biexciton binding.\textsuperscript{32} However, in the size regime where the low-energy electronic structure of GQDs can be described in terms of confined Dirac fermions, that is, for a linearly dispersive band structure, the confinement energy only scales as $L^{-2}$ so that Coulomb interactions grow in step with confinement. Our conclusions are drawn for Coulomb interactions screened by surrounding fluid; future work will investigate the effect of size and microscopic screening on exciton–exciton interactions.

Determination of the binding of biexciton states characteristic of the degenerate HOMO and LUMO levels of graphene quantum dots has several implications for the photophysics of GQDs. For example, efficient multiple-exciton generation (MEG) is dependent on strong Coulomb interactions and relaxed momentum-conservation constraints that allow gen-
eration of multiple carriers to occur before excess carrier energy is lost. These are reflected respectively in the biexciton binding energy observed here and the fast Auger recombination reported previously. Extended graphene has been found to display high rates of MEG at low excitation fluences. While that may be useful in photodetectors, it is of limited utility for photo voltaic solar cells, where one desires a band gap of \( \gtrsim 1.0 \text{ eV} \), as can be generated in GQDs. The possibility of efficient MEG in graphene nanostructures has been seen in computations, while semiconducting single-walled carbon nanotubes have already been found to display surprisingly efficient impact ionization. The rapid extraction of carriers from GQDs, as reported for GQDs anchored to TiO\(_2\), would be an essential step in overcoming rapid Auger recombination and making use of any excess carriers generated by MEG.

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**Notes**

The authors declare no competing financial interest.

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