Laser-induced wavelength-controlled self-assembly of colloidal quasi-resonant quantum dots

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Abstract: Self-assembly of colloidal semiconductor quantum dots controlled solely by laser-induced interaction is demonstrated for the first time. Pairs of CdTe nanoparticles are formed under irradiation with nanosecond pulses at wavelengths 555 or 560 nm. Formation of pairs is justified by corresponding changes of absorption spectra. Conditions of experiment are in excellent agreement with those predicted by the theory of laser-induced dipole-dipole interaction of QDs. The fraction of QDs assembled into pairs is up to 47%.

OCIS codes: (220.4241) Nanostructure fabrication; (250.5403) Plasmonics; (350.4855) Optical tweezers or optical manipulation.

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1. Introduction

Irradiation of ensembles of micro- and nanoparticles with optical radiation leads to various effects allowing the control of their motion. One of these effects is optical binding, being the effect based on optically induced interaction between particles [1], in contrast to optical trapping [2,3] which is based on forces raised from interaction of individual particles with light. In optical binding effect, electric field of a light wave polarizes particles, and ac polarizations of particles interact each other. For interparticle distances much smaller than the wavelength this can be treated as the local field effect, i.e. external ac electric field acting onto individual particle becomes modified by the account of the field produced by neighboring particles. Optically induced interaction of particles becomes noticeable at certain level of light intensity when the potential energy associated with this interaction is comparable with kinetic energy of Brownian motion or with the potential energy of a barrier typically used to stabilize colloid solutions of NPs' ensembles. In recent studies, the most attention was devoted to the investigation of metallic NPs interacting with light. Particularly, calculation technique for modeling the dynamics of metal NPs was elaborated [4]. High precision manipulation of multiple metallic NPs using optical binding force induced by off-resonant low-power laser was recently demonstrated at distances up to several microns [5]. Alternatively, self-assembly of metal NPS at the subwavelength scale due to plasmonic interaction was obtained under strong off-resonant cw laser illumination, as was deduced from Raman and Rayleigh scattering [6]. Somehow similar result was observed in [7] where hybridization of metal NPs plasmonic resonance was observed in scattering when NPs were confined in an optical trap. Employing the plasmonic resonance of metal NPs with the laser frequency is widely recognized as means for enhancement of optically induced interaction between metallic NPs, as theoretically investigated [8, 9]. Moreover, it was shown in these two papers that formation of NPs' clusters with pre-defined geometry is possible via proper choice of laser wavelength and polarization. Characteristic potential well depths for silver NPs, according to [9], are less than ten energies of thermal motion at laser field strengths close to metal NPs' breakdown threshold. More deep potential wells could be obtained when NPs with narrower resonant widths are under the self-assembly. Resonant widths of excitons in semiconductor QDs are two orders of magnitude narrower than plasmonic resonances in metals [10]. Formation of QDs' structures under optical irradiation due to various non-electrodynamical mechanisms were studied, e.g. in [11-13]. Surprisingly, no experimental attempts were done up to date to perform electrodynamically-driven laser-induced self-assembly of semiconductor nanoparticles, that may be of interest for quantum information, spintronics, single-electron transport, and sensoric devices.

Investigation of laser induced self-assembly is extremely attractive since electrodynamical interactions between nanoparticles are rather universal and in principle allow self-assembly of semiconductor QDs of different kind or self assembly of nanostructures containing both metal and semiconductor constituents ath the sub-wavelength scale. Recent theoretical studies [14, 15] directly addressed to the proposed experiments provide the tool for predicting the results of laser-induced self-assembly within the colloid solutions of QDs. Main predictions of these studies are as follows. 1) Controlled self-assembly of nanoparticles is possible via proper choice of the wavelength of laser inducing the electrodynamical interaction. 2) Efficient self-assembly must be expected in the region of wavelengths redshifted with the respect to excitonic resonance. 3) Efficient self-assembly is possible in the regime of nanosecond laser pulses with high enough repetition rate. The latter feature must minimize the thermal effects that can be expected in case of cw laser irradiation. In the present paper we report the experimental evidence for laser-induced self-assembly of

CdTe QDs illuminated by a sequence of nanosecond laser pulses resulting in formation of stable QD pairs.

2. Theoretical considerations

Theoretical description of laser-induced self-assembly is important both for predictions of optimal self-assembly conditions and for detection of the results of self-assembly via changes in absorption spectra caused by the QD convergence. We use dipole-dipole approximation for calculation of both the potential energy of inter-QD interaction and for the calculation of absorption spectra of a pair of QDs which are dependent on the distance between them. Details of the theoretical model as well as the examples of computer modeling of laser-induced self assembly of metal and semiconductor particles are described in detail in [14, 15]. Under dipole-dipole approximation, the energy W of interaction between dipoles induced on nanoparticles by strong optical radiation with the electric field strength is [6]:

$$W = \frac{1}{2} E^2 \omega_s^2 r^3 \left[\frac{\sin^2 \alpha}{(\Omega + \omega_s)^2 + \Gamma^2} - \frac{2\cos^2 \alpha}{(\Omega - 2\omega_s)^2 + \Gamma^2} \right] \quad (1)$$

where $\omega_s = |d_{12}|^2 / \hbar r^3$ is the frequency shift of the nanoparticle's resonance due to the interaction with the second particle, $|d_{12}|^2$ is the square of the modulus of the matrix element of electric dipole transition of a particle from the ground to the excited state, $\Omega = \omega_0 - \omega$ is the detuning of laser frequency from the resonant frequency of a particle, $\hbar$ is Planck constant, Γ is homogeneous linewidth, r is the interparticle distance and α is the angle between $|\vec{r}|$ and $|\vec{E}|$. Figure 1 illustrates the change of resonance frequency of a pair of QDs in dependence of the pair orientation with respect to the resonance of isolated pair (Fig.1 a, b) and corresponding change of potential energy of electrodynamical interaction in dependence on the laser wavelength and inter-QD distance (Fig.1 c). Calculations are done using numeric values relevant to semiconductor QDs, namely, $|d_{12}|^2 = 2 \cdot 10^{-46}$ J·m^3, $\Gamma = 2.067 \cdot 10^{13}$ Hz, E= $6 \cdot 10^6$ V/m, $|\vec{r}| = 10$ nm.

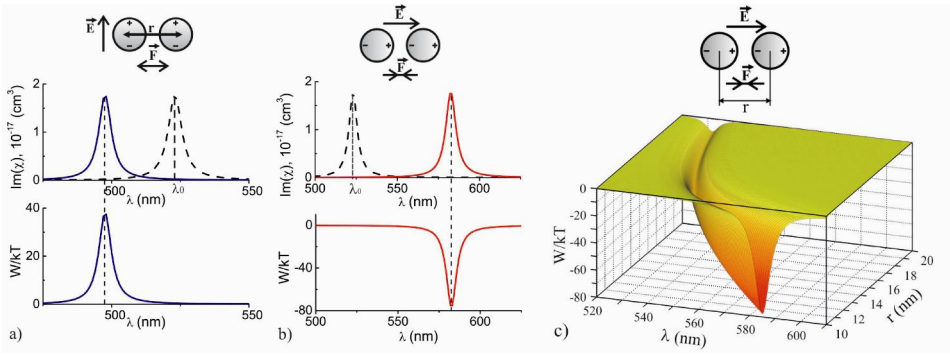

Fig. 1. (a), (b) Concept of electrodynamical interaction of nanoparticles in a laser field: two limiting cases of orientation with respect to electric field vector (upper rows), shift of resonant wavelength (middle rows), potential energy of interaction W (lower rows). λ_0 denotes the position of isolated QD resonance. (c) Potential energy W of laser-induced electrodynamic interaction of two particles as function of laser wavelength (λ) and interparticle distance (r).

3. Experiment

The idea of our experiment is as follows. Let us consider a colloid solution containing an ensemble of QDs which are stabilized against spontaneous aggregation by introducing a potential barrier around each of them. Brownian motion of QDs in the solution might lead to

accidental convergence of QDs to the distance when short-range van der Waals attraction increases, leading to the pair formation, but stabilizing barrier prevents QD from this close approaching. Linearly polarized laser radiation with the wavelength close to the excitonic resonance induces polarization onto QDs. Two QDs positioned along the electric field vector of the laser radiation experience electrodynamical attraction that may overcome both thermal motion and stabilizing potential barrier and enforce convergence of QDs to the distance close enough for the formation of van der Waals pair.

Solution of CdTe particles (average diameter 2.9 nm, purchased from PlasmaChem Gmbh, Berlin, Germany) in water was used as the object for laser-induced self-assembly. Solution of QDs was stabilized against spontaneous aggregation with addition of thioglycolic acid and triethylamine molecules. Combination of these two stabilizers is reliable while working with QDs of several nm size. Molar concentration of QDs in the samples that undergone laser irradiation was $5 \cdot 10^{-2}$ mole/m^3, that corresponds to the mean inter-QD distance 20 nm. Excitonic absorption band of CdTe QDs ensembles in solutions is usually 30 nm wide; however, luminescence measurements show that individual QD linewidth is of order 3 nm [10]. Hence, observed absorption linewidth is due to inhomogeneous broadening caused by the scatter of QDs size. Narrow resonance enables achieving electrodynamical interaction energy of a pair of QDs up to 10^2 kT (Fig.1c) (T is the temperature of solution, and k is Boltzmann constant) at interparticle distance 10 nm and laser intensity 10^6 W/cm^2. For our experiment, absorption spectra (PerkinElmer Lambda 35) and luminescence spectra (Horiba Jobin Yvon Fluorolog 3) of initially prepared QD solution are presented in Fig.2a; experimental exciton peak is at 523 nm in absorption and at 551 nm in the luminescence. These spectra are similar to those typically observed for CdTe QDs [10, 16].

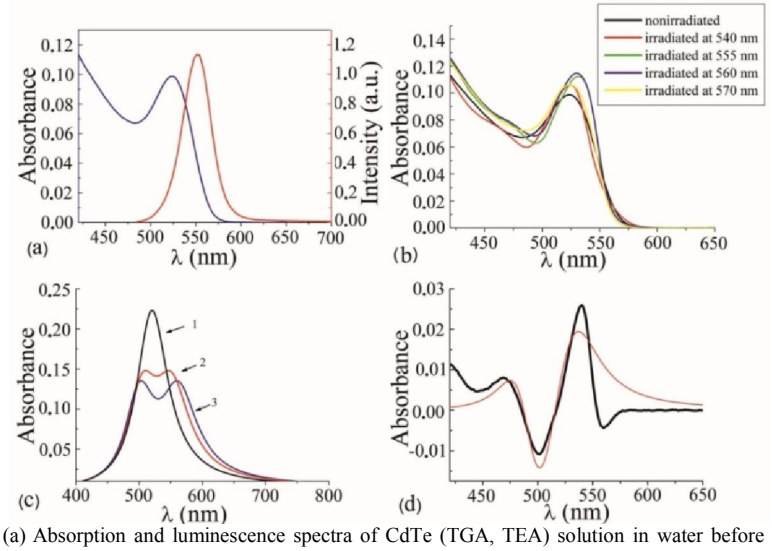

Fig. 2. (a) Absorption and luminescence spectra of CdTe (TGA, TEA) solution in water before intense laser irradiation. Excitation wavelength for luminescence spectrum is 480 nm. (b) Selected absorption spectra of CdTe (TGA, TEA) solutions in water after intense laser irradiation at different laser wavelengths. (c) Calculated shape of first absorption peak of CdTe QDs (2.9 nm diameter) positioned at the interparticle distance larger than 20 nm (curve 1), 12 nm (curve 2) and 10 nm (curve 3). (d) Example of difference absorption spectrum (thick line) obtained by extraction of spectrum of isolated particles from the spectrum of solution after laser-induced self-assembly at 555 nm. Thin line is the best fit simulation of ensemble of paired and isolated QDs' absorption spectra.

Electrodynamical interaction of QDs was induced using Opotec Vibrant 355 optical parametric oscillator by the laser pulses of 10 ns duration with the peak power 1.5 MW at 10 Hz repetition rate. The peak intensity of laser radiation at the irradiated sample was $2 \cdot 10^7$ W/cm^2. Assuming refractive index of the solution n = 1.33, that corresponds to amplitude of

electric field strength 10^7 V/m. Six different samples of the same solution were irradiated at the wavelengths 540, 550, 555, 560, 565 and 570 nm. Each sample was irradiated during 5 minutes by 3000 laser pulses. Absorption spectra of the solutions irradiated at different laser wavelengths are presented in Fig. 2b. The laser irradiation at the wavelengths 555 and 560 nm leads to the noticeable shift of absorption maximum from initial value of 523 nm to the red (531 nm), and to the formation of new maximum in the region 473 nm. Note that absorption spectra changes lie in the region of wavelengths rather far from the acting wavelength. Absorption spectrum of irradiated solution can be analyzed via assumption that it is composed from the contribution from isolated particles that remained unpaired after the irradiation and are still positioned at distance farther than 20 nm (curve 1 in Fig. 2c), and contributions from pairs of more closely spaced QDs (curves 2 and 3 in Fig. 2c).

In comparison with the plasmon hibridization reported by Tong et al [7], our result demonstrates at least two important features. First of all, formation of NPs pairs is stable, and therefore, it can be detected not only in scattering simultaneously to optical trapping, but also in absorption spectra, i.e. long after the laser-induced self-assembly process. Colloid solutions after irradiation at wavelengths 555 and 560 nm were kept for two weeks with 20% drop of maximum absorption coefficient, that coincides with the decay rate of unirradiated solution. However, the change of the spectra shape induced by the irradiation was not changing during that period. Second feature is that the self-assembly can be attained in repetitive pulsed laser regime instead of cw irradiation.

4. Analysis of results

Curves 2 and 3 in Fig.2c are obtained theoretically and are averaged over the orientations of pairs with respect to electric field strength vector[17]. Subtraction of the spectrum of unirradiated sample containing only isolated QDs' allows obtaining orientation-averaged spectra of ensemble containing QDs' pairs and the rest of isolated QDs, as presented in Fig.2d (thick line) for irradiating laser wavelength 555 nm. Thin line shows theoretical best fit to the experimental difference spectra obtained by fitting the interparticle distance and the percentage of QDs assembled into pairs. Different amplitudes of the blue- and redshifted peaks in difference spectra are due to different value of blue and red shifts resulting in the fact that they fall into different parts of the absorption curve of isolated QDs. From the fitting, the average inter-QD distance in pairs can be estimated to be 10 nm for both 555 and 560 nm laser wavelengths. The percentage of QDs in pairs is 47% for 555 nm and 45% for 560 nm. The most prominent discrepancy between fitted and experimental curves lies in the region of inducing laser wavelength, where the dip is observed in experimental spectra. This means that pairs with resonant absorption at the laser wavelength experience strong absorption and are destroyed due to overheating, while all the rest pairs survived the laser exposure. Irradiation at 570 nm induced less efficient self-assembly, and the weakest self-assembly process was induced at 540 nm. The intensity of inducing laser radiation fairly fits theoretical expectations. The wavelength region of efficient self-assembly rather fairly fits predictions presented in Fig.1c for inter-QD distance in the range 10–20 nm.

More detailed picture of the self-assembly process can be understood from the examination of potential energy dependences on the interparticle distance at different laser wavelengths (Fig.3). Maximum attraction at most efficient self-assembling wavelengths is in the range of inter-QD distances 12–14 nm, while at the mean inter-QD distance 20 nm attraction energy is well below kT. At 570 nm attraction is maximum at 11 nm, but the percentage of QDs catched at this distance by the laser pulse is smaller, resulting in less efficient self-assembly. For 540 nm, attraction is maximum for larger part of QDs in the state of Brownian motion, but attraction at distances close to 10 nm is too small, resulting in fail of QDs to form stable van der Waals pair. Hence, efficient self-assembly is result of compromise between the percentage of QDs positioned at distances smaller than mean distance in the solution and the deepness of electrodynamical potential well at the distance of van der Waals

pair formation. Complete approach of QDs to the distance smaller than 10 nm is prevented by the equalization of van der Waals attraction plus laser-induced attraction and the potential barrier produced by QD stabilizer used. Note the laser pulse intensity used in the experiment ($2 \cdot 10^7$ W/cm^2) is considerably higher than that necessary for the formation of potential well deeper than kT at the distance range 10 to 20 nm. This intensity excess not only enables distance-insensitive self-assembly but also prevents possible decrease of the potential well depth due nonuniformity of QDs' size (i.e., deviation of resonant frequencies within QDs ensemble).

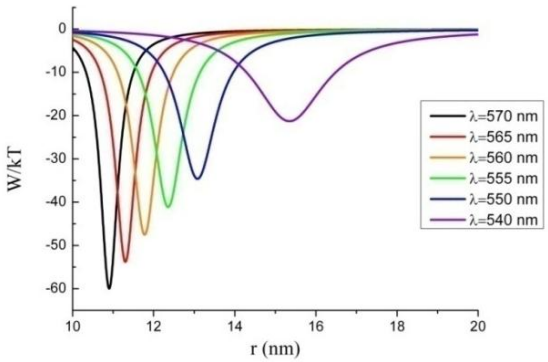

Fig. 3. Potential energy of electrodynamical interaction between CdTe QDs under irradiation at the wavelengths in the range 540 - 570 nm.

Alternative explanation for observed spectra variations could be photochemical processes in the CdTe solution. The influence of several-hour cw 532 nm irradiation of TGA-stabilized 4 nm diameter CdTe QDs' solution was investigated by Ma et al [18], and it was shown that light absorption leads to singlet oxygen formation, detachment of TGA, and aggregation of QDs accompanied by severe drop of luminescence intensity. Absorption spectra were not reported in that paper, but due to variation of diameter and reported luminescence maxima, one must expect that absorption of QDs at 532 nm in experiment of Ma et al was estimatively 10 times higher than in our case. Moreover, the irradiation doze in Ma experiment was 60 to 240 times higher than in our experiment. Therefore, contribution of mechanism outlined by Ma et al must be negligible in our case, and observed spectral changes must be ascribed to electrodynamical attraction of QDs.

5. Conclusion

Presented experimental results show that, under sufficiently intense pulsed laser irradiation with properly chosen wavelength, about a half of quasiresonant isolated QDs initially positioned at the average distance 20 nm are self-assembled into pairs with average distance 10 nm. For CdTe QDs with average diameter 2.9 nm, this effect is efficient in the laser wavelength range 550–565 nm only, and this wavelength range is redshifted from the resonant wavelength of most of isolated QDs as predicted by the theory of electrodynamical interaction of polarizations induced on QDs. The technology under study may allow precise manipulation of QDs not only in the solution, but also on technological substrates. It is featured by the expected universality, since, as theoretically shown in [11], manipulation is possible by not only identical QDs, but also of nanoparticles of different kind, via the proper choice of the wavelength.

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