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Theoretical Investigation of Optical Detection and Recognition of Single Biological Molecules Using Coherent Dynamics of Exciton-Plasmon Coupling

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Abstract

We use quantum coherence in a system consisting of one metallic nanorod and one semiconductor quantum dot to investigate a plasmonic nanosensor capable of digital optical detection and recognition of single biological molecules. In such a sensor the adsorption of a specific molecule to the nanorod turns off the emission of the system when it interacts with an optical pulse having a certain intensity and temporal width. The proposed quantum sensors can count the number of molecules of the same type or differentiate between molecule types with digital optical signals that can be measured with high certainty. We show that these sensors are based on the ultrafast upheaval of coherent dynamics of the system and the removal of coherent blockage of energy transfer from the quantum dot to the nanorod once the adsorption process has occurred.

Keywords

Quantum dots; quantum coherence; metallic; nanorods; nanosensors; dynamics

Introduction

The rarity and very small sizes of biological molecules with significant clinical and health importance are major obstacles for their accurate and fast detections. Metallic nanoparticles (MNPs) can be used to detect such molecules via monitoring the MNPs' plasmon resonance shift.^{1,2} When it comes to the detection of single molecules, however, the sensitivity of this technique is not enough. To detect single molecules using MNPs, one needs to amplify the plasmon shift using a highly polarizable label,^{3,4} or localized precipitation reaction on the particle's surface.⁵ Without such amplification, the sensitivity of MNP-based sensors only allows statistical detection of single molecules.⁶ A recent technique has used a single gold nanorod coated with biotin receptors. Here binding of single proteins was detected by monitoring the plasmon resonance of the nanorod with a sensitive photothermal assay.⁷

In this paper we study plasmonic quantum nanosensors that not only hold the promise of digital detection and recognition of single biological molecules, offering significantly high certainty, but also allow counting of these molecules one at the time. The core aspect of

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these sensors is the fact that they have a unique response to the presence of a specific molecule once they interact with an optical pulse of a certain intensity and temporal width adjusted for that molecule (called here biologically designated optical pulse). Such quantum nanosensors have the capability to translate specific but minute changes in the environmental parameters into very noticeable, easily measurable, and well-defined digital optical events.

Unlike conventional nanosensors,^{1,2} the quantum nanosensors studied in this paper are not based on plasmons or excitons. Therefore, their signal transduction is not based on collorimetrics via Foster resonance energy transfer (FRET) or wavelength shift of the plasmons. Rather, they are based on ultrafast upheaval of the coherent dynamics of a system consisting of a metallic nanorod (NR) and a QD which happens when a biological molecule is adsorbed onto the NR. We show these dynamics include the removal of the coherent blockage of FRET from the QD onto the NR induced by exciton-plasmon coupling. The principles of operation of such sensors are schematically shown in Fig.1. Here, for example, we consider the QD-NR system interacting with three optical pulses (A, B, and C) with widths and intensities specified for detection and counting of a specific biological molecule. When no molecule is adsorbed to the NR, the response of this system to these optical pulses consists of three QD emission pulses a, b, and c, corresponding to its interaction with pulses A, B, and C, respectively (Fig.1a). When one molecule is adsorbed to the NR, the system does not emit pulse a (Fig.1b). When two molecules are adsorbed, both a and b are disappeared (Fig.1c) and etc. We show such responses correspond to a transition between the collective states of the QD-NR system triggered by the adsorption of single molecules.

A major feature of this paper is that it addresses ultra-fast polarization dephasing (or short decoherence time) of QDs, which for sensor applications is a prominent feature. Additionally, we show that the characteristic decay length of the plasmonic field of the NR in the QD-NR system can be dynamically suppressed, making it less than half of its intrinsic value when the NR is isolated. This feature may have additional applications for biological sensing. Moreover, the results of this paper are related to previous reports investigating the possibility of using quantum coherence in QD-MNP systems for sensing applications.⁸⁻¹⁰ In those reports, the impact of changes in the refractive index around the QDs or MNPs on the coherent dynamics of the excitons were investigated in a generic way. None of them addressed detection of small single biological molecules, as discussed in this paper, and the impact of the ultra-fast dephasing times of the QDs was not included.

Interaction of QD-NR systems with short optical pulses

To study quantum nanosensors based on QDs, a major issue is how to deal with the impact of their ultra-fast polarization dephasing or very short decoherence times. In fact, practical applications of these sensors mostly require room temperature operation. At such a temperature it is known that ultra-short decoherence times of the QDs smear out quantum coherence effects. To tackle this issue we use the results of a recent study that showed quantum coherence effects in QD-MNP systems can sustain themselves at elevated temperatures even when the pure dephasing times of the QDs are on the order of several hundreds of femtoseconds.¹¹ Considering this and the requirement for functionalization of MNPs by a receptor for selective detection of biological molecules, in this paper we study a structure as depicted in Fig.2. This system includes a QD and a silver nanorod (AgNR) with semimajor and semiminor radii given by a_s and b_s , respectively. The center-to-center distance between the QD and AgNR is R . The AgNR is exposed to the environment (analyte) while the QD is considered to be made of CdSe-based material with dielectric constant $\epsilon_s=6.25$ and embedded in ZnSe with dielectric constant $\epsilon_0=7.1$.^{12,13} Note that this is an optimized design of the structure and materials that allows the quantum coherence

effects needed for quantum nanosensors discussed in this paper to happen when the rate of the pure dephasing process in the QD (γ_{dep}^p) is 1 ps^{-1} . This rate is about three orders of magnitude larger than those considered in reports that studied quantum effects in a QD-MNP system.¹⁴⁻¹⁸ The pure dephasing rate is caused by an elastic interaction of excitons with phonons.¹⁹

As schematically shown in Fig.3, in this paper the exciton transition of the QD with frequency ω_0 (the $|1\rangle$ - $|2\rangle$ or 1-2 transition) is considered to be driven near resonance by a laser beam with the frequency $\omega_l(E(t) = E_0 \cos(\omega_l t))$. This laser is polarized along the z-axis (Fig.2) and its amplitude is modulated to form a train of return-to-zero optical pulses. We consider that the excitons are strongly confined in the QD and have a large energy separation. Under these conditions, as shown before,¹⁹ the diagonal electron-phonon interactions determine the pure dephasing process and the Hamiltonian involving the QD and phonons can be diagonalized. Considering this, we adopt a semiclassical approach wherein the NR and interaction of the QD-NR system with the laser beam are treated classically, while the QD is addressed quantum mechanically. In our treatment we ignore time-dependent phonon-carrier coupling and the impact of pure dephasing is treated in a phenomenological way.^{19,20}

Note that, as schematically shown in Fig.3 and discussed in the following, the rate of FRET from the QD to the NR (lines 3 and 3') is synchronized with the optical pulses. Before the absorption, the FRET process is nearly completely blocked (line 3) and the QD emits efficiently (line 1). Because of the lack of FRET, the rate of non-radiative decay of excitons caused by such a process (γ_{nr}) is also suppressed (line 2). When a biological molecule is adsorbed onto the NR, the FRET blockage is removed (line 3'). Under this condition the emission of the QD (the downward dashed arrow) is suppressed (line 1') and the rate of γ_F increases significantly (line 2').

The AgNR is considered to be in an environment with an effective dielectric constant ϵ_{eff} . As will be shown in the following, ϵ_{eff} depends on the plasmonic field of AgNR normalized by the coherent exciton-plasmon coupling, the dielectric constants of the receptor (ϵ_{sam}), the biological molecules (ϵ_{sa}), and the background environment ($\epsilon_b = 1.77$) which is considered to be water. Having these in mind, the key feature of our analysis is to find the electric field associated with the normalized plasmonic field of the AgNR. Note that at any point around AgNR, in addition to the applied field ($E(t)$), we have the field generated by the QD-AgNR system. One of the main contributors to the field of the QD-AgNR is the field generated by direct excitation of plasmons in the AgNR by the applied laser field, given by:

$$E_{plas}(z) = \frac{\gamma a_s b_s^2}{\epsilon_{eff} z^3} E_0 e^{-i\omega_l t} \quad (1)$$

The other contributor is the plasmonic field induced by the electric dipole of the QD. For this the laser field interacts with the QD and the induced electric dipole, in turn, excites plasmons in AgNR. The field induced by such plasmons is influenced by quantum coherence and is given by the following:

$$E_{plas}^{QD}(z) = \frac{2\gamma a_s b_s^2}{\epsilon_{eff} z^3} \frac{\mu_{12} \rho_{21}}{\epsilon_{eff1}} \frac{1}{R^3} e^{-i\omega_l t} \quad (2)$$

In this equation $\epsilon_{eff1} = (2\epsilon_{0q} + \epsilon_s)/3$, ϵ_{0q} and μ_{12} is the dipole moment associated with the 1-2 transition. Additionally, we approximate the shape of the AgNR with a spheroid having polarization ϵ_s as

$$\gamma = \frac{[\epsilon_m(\omega) - \epsilon_{eff}]}{[3\epsilon_{eff} + 3\kappa(\epsilon_m(\omega) - \epsilon_{eff})]}. \quad (3)$$

Here γ is the depolarization factor of the spheroid when the incident electric field of the laser is polarized along its semimajor diameter.¹⁴ We describe Ag with the local dynamic dielectric function $\epsilon_m(\omega) = \epsilon_B(\omega) + \epsilon_D(\omega)$, which is a combination of the contribution of d electrons ($\epsilon_B(\omega)$) and s electrons ($\epsilon_D(\omega)$). Having Eqs.(1) and (2), the total field along the axis of the AgNR (z axis) at a point $\mathbf{P}$ can be calculated using:

$$E_{plas}^c(z) = E_{plas}(z) + E_{plas}^{QD}. \quad (4)$$

In Eq (2) ρ_{21} is the off-diagonal element of the density matrix of the QD. To obtain this we need to solve the following set of equations:

$$\dot{\rho}_{21} = -4\text{Im}[\Omega_{eff}\rho_{21}] - 2\Sigma_F + \dot{\rho}_{21}|_{\text{relax}}, \quad (5)$$

and

$$\frac{\partial \rho_{21}}{\partial t} = -[i(E_p - \hbar\omega) + \Lambda_F + \gamma_{12} + \gamma_{dep}^p]\rho_{21} - i\Omega_{eff}\delta. \quad (6)$$

In Eq. (6) $E_p = E_0 - \text{Re}[\eta_{NR}]$ and $\Lambda_F = \text{Im}[\eta_{NR}]$ with $\eta_{NR} = \eta_{11} - \eta_{22}$ where η_{NR} is given by:

$$\eta_{NR} = \frac{\gamma\mu_{12}a_sb_s^2}{\pi\hbar\epsilon_{0q}\epsilon_{eff}^2R^6} \quad (7)$$

Here E_p is the normalized energy of the QD and Λ_F is the contribution of FRET from the QD to AgNR to the polarization dephasing rate of the QD (Fig.3). The fact that both E_p and Λ_F are normalized by γ_{12} indicates how the combined effects of quantum coherence and plasmons influence the interaction of the laser field with the QD-AgNR system. In Eq. (6) $\gamma_{12} = \gamma/2$ is the polarization dephasing rate induced via radiative decay of excitons with rate γ .

In Eqs. (5) and (6) $\Omega_{eff} = \Omega_{12}^0 \left(1 + \frac{2\gamma a_s b_s^2}{R^3}\right)$ and $\Omega_{12}^0 = \frac{\mu_{12}E_0}{2\hbar\epsilon_{eff1}}$ are, respectively, referring to the Rabi frequency of the QD in the presence of pure plasmonic effects (without any coherence effects) and in the absence of the AgNR (very large R). Additionally, these equations show that the FRET process can act as a non-radiative decay channel for the excitons in the QD (Fig.3), which is represented by

$$\Sigma_F = 2\text{Im}[\eta_{NR}]|\rho_{21}|^2 \quad (8)$$

This suggests that in the presence of quantum coherence FRET happens efficiently only when $|\rho_{21}|^2$ has noticeable values.

Note also that, considering Eq. (2), we can calculate the plasmonic enhancement factor as

$P_{coh}(z) = |E_{plas}^c(z) + E_0/2\epsilon_{eff}|^2 / |E_0/2\epsilon_{eff}|^2$. P_{coh} represents the ratio of the field intensity at the location of z in the presence of AgNR (I_{eff}) to that in the absence of it (I_0), i.e., $I_{eff} =$

$P_{coh}I_0$. To calculate the plasmonic field enhancement of AgNR when it is isolated (P_{enh}) we use the same expression as that of P_{coh} but consider very large R . Under this condition

$$P_{enh} = |\Omega_{eff}/\Omega_{12}^0|^2. \quad (21)$$

Quantum nanosensor for single biological molecule detection

For biological sensing applications, one needs to functionalize the AgNR with a receptor (e.g., biotin) with the effective thickness of d_{SAM} and refractive index n_{SAM} . We consider in the following that $d_{sam}=0.5$ nm and $n_{SAM}=1.5$.⁷ Single protein molecules, such as streptavidin, can bind to such a receptor. We consider the refractive index of such a molecule to be $n_{sa}=1.46$ (hydrated protein) and its effective thickness after adsorption is d_{SA} .⁷ To calculate the effective refractive index experienced by the AgNR (n_{eff}) we need to consider the spatial extension of E_{plas}^c . n_{eff} is given by²²

$$n_{eff} = \frac{2}{l_d} \int_{a_s}^{\infty} n(z) \widehat{E}_{plas}^c(z) dz \quad (9)$$

where l_d is the characteristic decay length of $\widehat{E}_{plas}^c$, which is obtained after normalizing E_{plas}^c to one. $n(z)$ is the refractive index profile along the axis of the AgNR (z axis), obtained as follows:

$$n(z) = n_{SAM} \quad a \leq z \leq d_{SAM}, \quad (10)$$

$$= n_{SA} \quad d_{SAM} \leq z \leq d_{SA} \quad (11)$$

$$= n_b \quad d_{SA} \leq z \leq \infty \quad (12)$$

One of the main results of this paper is that l_d associated with E_{plas}^c depends on the collective states of the QD-AgNR system and can be very different from the intrinsic field of the AgNR in isolation. To see this we consider $a_s=7$ and $b_s=3$ nm. We also consider $\hbar\omega_0=2.69$ eV, which is the same as that of the plasmonic absorption peak of AgNR, and $\tau_2 = 0.6$ ns⁻¹. The center-to-center distance between the QD and AgNR (R) is also considered to be 10 nm. Fig.4 shows the results for variations of P_{coh} as a function of z for two different intensities of the applied laser. This figure also represents the results for P_{enh} under the same conditions as P_{coh} but in the absence of any quantum coherence (circles). These results indicate that P_{coh} strongly depends on the laser intensity. For $I_0=271$ W/cm² (the laser field intensity inside the NR environment) P_{coh} (squares) is comparable for P_{enh} (circles) while for $I_0=255$ W/cm² it reduces significantly (triangles). In fact, our results show that, for given parameters of the QD-AgNR system, there is a critical laser intensity where P_{coh} is switched between the two values reported in Fig.4. Based on the results, shown in Fig.4, we found that when $I_0=271$ W/cm², the decay length $l_d=3$ nm. When $I_0=255$ W/cm², l_d reduces to 1.5 nm. The value of l_d for the intrinsic field of the AgNR is obtained at 3.3 nm, which is about half of the semimajor radius of the NR, as expected.⁷

Note that the QD-AgNR supports two states characterized by the value of P_{coh} . When P_{coh} is significant (Fig.4, squares), the QD experiences a significant amount of field and, as shown in the following, it does not efficiently transfer its energy to AgNR. Therefore, it is quite emissive. We call this state of the QD-AgNR the bright state (B state). On the other hand, when P_{coh} is small (Fig.4, triangles), the optical excitation in the QD is weak. Under this condition, as described in the following, the rate of FRET from the QD to AgNR rate is

significantly higher. As a result, despite the presence of the applied field, the QD remains non-emissive. We refer to this state as the dark state (D state).

To discuss a quantum sensor application of the system studied above, we consider a return-to-zero optical pulse train, as shown in Fig.5a, that interacts with the QD-AgNR described above. We consider three pulses (A, B, and C) with peak intensities of $I_0=290, 270$, and 255 W/cm^2 , respectively. These field intensities are such that they can induce a transition between D and B states of the QD-MNP system with integer variations of d_{SA} , which can be associated with the adsorption of one, two, or three specific molecules to the AgNR.

As mentioned before, we consider that the AgNR is conjugated with a receptor with $d_{SAM}=0.5$ and $n_{SAM}=1.5$. Figs.5b-5d show how P_{coh} (i.e., the effective field experienced by the QD) is changed when the effective thickness of the adsorbed molecule (d_{SA}) is equal to 0, 0.1, 0.2, or 0.3 nm, corresponding to $n_{eff}=1.3784, 1.3844, 1.3900$, and 1.3953 . The case shown in Fig.5b shows that the QD emits light for all three optical pulses. In other words, the QD-AgNR system is in B state for these pulses. When $n_{eff}=1.3844$, however, the QD does not emit light when the system interacts with pulse A (Fig.5c). This suggests that the peak intensity of pulse A is such that when n_{eff} becomes 1.3844 the QD-AgNR system switches to the D state. When $d_{SA}=0.2$ nm and n_{eff} becomes 1.3900 (Fig.5d), the response of the system to pulse B disappears. A similar event happens for $d_{SA}=0.3$ nm for pulse C (Fig. 5e).

The sensor system discussed in this paper can be used to recognize biological molecules based on their sizes. To show this, we consider in Fig.6 a case where the applied field consists of two biologically designated optical pulses (A and B). Pulse A is designed to switch off the emission of the QD when $n_{eff}=1.3900$ or $d_{SA}=0.2$ nm. On the other hand, the pulse B peak intensity and pulse width are adjusted such that the QD-AgNR is transferred to its D state when $d_{SA}=5$ nm or $n_{eff}=1.4680$. This corresponds to the case where a relatively large biological molecule is adsorbed onto the NR.

Coherent dynamics of QD-NR system triggered by molecular adsorption

To explain the results seen above, note that based on Eq. (4) the effective field of the AgNR (E_{plas}^c) is influenced by γ_{21} . On the other hand, from Eqs. (5) and (6) it is clear that γ_{21} depends on the effective linewidth ($\gamma_{eff}=E_p - \gamma_0$), FRET-induced broadening (γ_F), and exciton population (or ρ_{11}). The ways these parameters evolve with time determine the state of the QD-AgNR system and its response to the adsorption of biological molecules. Using these facts, in this section we study the mechanism behind the results shown in the preceding section. The outcomes of this section show that a signal transduction in the proposed sensors is based upon upheaval in the collective exciton-plasmon coupling of the QD-AgNR and the way FRET is blocked by such a coupling.

To begin, we consider in Fig.7 the case of the pulse train studied in Fig.5. The results in Fig. 7b show that during the troughs, where the laser intensity is nearly zero, γ_F is significant ($\sim 18 \text{ ps}^{-1}$). This is a simple indication of the fact that when the laser intensity is zero (no coherent effect), $\gamma_F = \text{Im}[\gamma_{NR}]$ ($\gamma_{NR} = 1$); representing the FRET rate from the QD to the AgNR in the absence of quantum coherence. This is a rather standard feature of hybrid QD and MNP (or metallic NR) systems, wherein a dipole-dipole interaction induces such an energy transfer process. The rate of this process peaks at the same frequency as that of the plasmon peak.²¹

As shown in Fig.7b, during all three optical pulses, when $d_{SA} = 0$ and the QD-AgNR is in the B state (Fig.5b), γ_F is very small. As schematically shown in Fig.3, this means that in

the absence of adsorption of biological molecules, the energy transfer from the QD to AgNR is significantly suppressed (line 3). This phenomenon can be seen more clearly if we consider the fact that FRET only happens when optical excitation occurs in the QD, i.e., excitons are generated. This feature is embedded in the values of F (Eq. (8)). The results presented in Fig. 7b (dashed line) show F is mostly zero in the absence of molecular adsorption, as schematically shown in Fig. 3 as well (line 2). Comparison of these results with those in Fig. 5b indicates that $F \sim 0$ when P_{coh} is significant and the QD is emissive. This suggests a near complete blockage of FRET from the QD to the AgNR in the absence of molecular adsorption.

As shown in Figs. 7c-7d, the situation changes significantly with the adsorption of biological molecules to the NR. The results show that when d_{SA} increases to 0.1 nm or n_{eff} becomes 1.3844 the values of F and F during the optical pulse A become significant (Fig. 7c). Under the conditions considered in this paper, F can reach 10 ps^{-1} and F becomes about 2.2 ps^{-1} . As schematically shown in Fig. 3, these suggest that with the adsorption of biological molecules the coherent blockage of FRET is removed and energy transfer happens in the form of pulses with the same temporal width as the optical pulses (lines 2 and 3) while the molecule(s) remained attached to the NR.

To provide a clearer picture of the physical mechanisms behind the results reported above, in Fig. 8 we study the impact of QD transition energy (ϵ_0) on F for the same optical pulse train as that in Fig. 5a. The results presented in Fig. 8 are obtained considering $d_{SA} = 0$ or $n_{eff} = 1.3784$ nm. These results show that in the troughs of the pulse train F peaks when $\epsilon_0 = 2.69 \text{ eV}$, i.e., at the NR plasmonic peak, as expected in hybrid QD-MNP (or NR) system in the absence of quantum coherence.²¹

During the optical pulses, however, depending on the intensity of each pulse and ϵ_0 , F changes in a more complex way. The overall results in Fig. 8 suggest abrupt changes in the values of F . This can be clearly seen in Fig. 9a, where we show the contour plots of Fig. 8. Here one can see, depending on the value of the laser intensity, the sudden changes happen at different value of ϵ_0 . For the case of $\epsilon_0 = 2.69 \text{ eV}$ (dashed line) and $d_{SA} = 0$, as that considered above, we can see the values of F for the three peak intensities are nearly zero during the pulse train maxima, suggesting efficient blockage of energy transfer from the QD to the AgNR. Under this condition the system is in the B state. This corresponds to the results shown in Fig. 5a. As Fig. 9b shows, for $d_{SA} = 0.3 \text{ nm}$, the resonances where transition between B and D happens are shifted. Under these conditions, for all three peaks at $\epsilon_0 = 2.69 \text{ eV}$ (dashed line) the rates of F are enhanced. Suggesting the system transition to B state. This corresponds to the case of Fig. 5e.

As mentioned before, F is good indicator of coherent blockage of FRET and its removal once adsorption happens. Fig. 10 shows a contour plot of how this parameter is changed as a function of ϵ_0 (transition energy of the QD). The results are compatible with those in Fig. 8, suggesting when F is large F is also large. This means when FRET is significant, the non-radiative decay rate of excitons caused by such a process is also high. The dashed line here represents $\epsilon_0 = 2.69 \text{ eV}$ and corresponds to the results shown in Fig. 7b (dashed line).

F and F are both entangled with each other and with the exciton population. Fig. 11 shows the variation of γ_{22} under the same conditions as those in Fig. 8. Note that for large ϵ_0 the value of γ_{22} is very low. This corresponds to the case where the QD transition energy is well above the plasmon peak of AgNR. On the other hand, for low ϵ_0 , the value of γ_{22} is nearly at its maximum. As ϵ_0 increases, the rise of γ_{22} does not happen at the same time as the edges of the pulses. A ϵ_0 passes a critical value, which is different for different pulses, γ_{22} does not rise at all.

The mechanism behind the B-D switching process seen in this paper can be explained considering the fact that before the risetimes of the optical pulses reach the QD-AgNR system or during troughs of the pulse train that $I_0=0$ and, therefore, ~ 1 . Because of this F is significantly large (Fig.7b) and the laser detuning from the QD transition or ω_{eff} is also very large (not shown). As a result, the QD is not able to engage efficiently with the laser field, at least initially, when the optical pulses reach the system. This hampers the rise of the exciton population or, equivalently, the reduction of ω_{eff} . Therefore, the plasmonic broadening and the laser detuning persist for a while, causing a delay in the optical excitation. Such a time delay can be seen in Fig.7b, wherein we predict F rises for very short periods of time (arrows). The time delay is also shown in Figs.8-10 as a function of ω_0 . For a given ω_0 , as seen in Fig.7b, the amount of the delay is smaller for pulses with higher peak intensities. This is because of the fact that when I_0 is large, the exciton population reaches its maximum faster; allowing earlier reduction of ω_{eff} and, therefore, faster suppression of F and ω_{eff} . The results in Figs.7d show that with the adsorption of the biological molecules the time delay associated with pulses A and B becomes larger than the width of the optical pulses. This leads to the removal of the emission of the QD in the presence of these pulses.

Note that the results shown in Figs.8-11 are further indication of similar dynamics, but in the frequency domain. Inspection of these results shows that, as ω_0 increases at the beginning of each pulse, F and ω_{eff} are augmented. With the increase of ω_0 , the period of time where this process happens increases. When ω_0 reaches a critical value, F and ω_{eff} are increased abruptly, suggesting transition from B to D state.

The results presented in this paper are based on single QD-MNP systems. Such systems can be fabricated using biolinkers which provide a high degree of control over the spacing between the QDs and the MNPs.²³⁻²⁵ Some recent reports have also shown the possibility of fabrication of MNPs inside epitaxial structures,²⁶ formation of epitaxial QDs very close to the surface,²⁷ and deposition of Ag MNPs close to the epitaxially grown QDs.²⁸ These techniques can support exciton-plasmon coupling, which is needed for practical implementation of the results presented in this paper. Note also that coherent coupling of excitons and plasmons is scaled by the polarization dephasing rate and transition energy of the QDs, R , laser intensity, and type or shapes of the MNPs. For the parameters considered in this paper, Fig.4 shows that even when R reaches 12 or 13 nm we expect to see distinct differences between B and D states. Additionally, the results presented in Fig.8 show the sensitivities of the results to the variation of the size (or transition energy) of the QD. Considering these, when the structural parameters of the QD-AgNR system vary within the ranges seen in Figs.4 and 8, one can adjust the intensity of the laser field to reach similar results as those presented in this paper. Such a capability is very important, as it allows us to address the random fluctuations of the sizes and shapes of the MNPs and R which will happen when such systems are fabricated.

Conclusions

We showed that quantum coherence in a hybrid system consisting of a AgNR and a QD can act as a quantum nanosensor; offering a significantly high certainty for detection of ultra small changes in the refractive index. The key feature of these sensors is their ability to convert these changes to digital optical processes. These sensors were studied in the presence of ultra-fast polarization dephasing of the QD which is a necessary condition to developing real-world applications.

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Figure 1.

Schematic illustration of quantum nanosensors based on a QD-NR system. A, B, and C are three incoming optical pulses (biologically-designated optical pulses) interacting with this system. a, b, and c are the corresponding emission pulses of the QD caused by such interaction. In (b) one biological molecule is adsorbed to the functionalized NR, removing a. In (c) two of such molecules are absorbed, leading to the suppression of a and b.

Figure 2.

Schematic illustration of quantum nanosensors based on a QD-NR system. R is the center-to-center distance of the NR and the QD, and a_s and b_s are the semimajor and semiminor radii of the NR, respectively. The NR is assumed to be functionalized with a receptor with refractive index n_{SAM} and effective thickness d_{SAM} . Biological molecules (target molecules) with refractive index n_{SA} and effective thickness d_{SA} are considered to be selectively adsorbed to such a receptor.

Figure 3.

Schematic illustration of the electronic structure of the QD-AgNR system and energy transfer paths in the absence (left panel) and presence (right panel) of molecular adsorption. The optical pulse is nearly resonant with the transition from ground ($|1\rangle$) to the excited states ($|2\rangle$) of the QD. Σ_F refers to the FRET-induced electron-hole non-radiative recombination rate. Lines 1 (1'), 2 (2'), and 3 (3') show the QD emission, Σ_F and energy transfer from the QD to the AgNR in the absence (presence) of adsorption of a biological molecule.

Figure 4.

Variations of P_{coh} for two different intensities of the applied field (in W/cm^2) as a function of z . The circles refers to the plasmonic field enhancement of the intrinsic field of AgNR (P_{enh}).

Figure 5.

Variations of P_{coh} for three optical pulses with the same temporal widths but different peak intensities (I_0), as shown in (a). (b), (c), and (d) show P_{coh} as we consider the effective thickness of the adsorbed molecules (d_{SA}) are 0, 0.1, 0.2, and 0.3 nm, respectively.

Figure 6.

Variations of P_{coh} for two biologically designated optical pulses, as shown in (a). Pulse A is used to detect a molecule with $d_{SA}=0.2$ nm or $n_{eff}=1.3900$ (c) and pulse B allows sensing of a larger molecule with $d_{SA}=5$ nm or $n_{eff}=1.4680$ (d). (b) shows the case when $d_{SA}=0$.

Figure 7.

Variations of Λ_F (solid lines) and Σ_F (dashed lines) under the conditions of Fig.5. (a) represents the optical pulses train and (b), (c), and (d) show the results corresponding to the cases when $d_{SA}=0, 0.1$, and 0.2 nm.

Figure 8.

Variations of E_F as a function of the QD transition energy (E_0). Here all other specifications are the same as those in Fig.5b

Figure 9.

Contour plots of F as a function of the QD transition energy and time when $d_{sa} = 0$ (a) and $d_{sa} = 0.3$ nm (b). All other specifications are the same as those in Fig.5. The dashed lines represent $\epsilon_0 = 2.69$ eV.

Figure 10.

The contour plot of variation of F under the same conditions as those in Fig.8.

Figure 11.
Variations of ρ_{22} under the same conditions as those in Fig.8.