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The Effect of Chemisorbed Quantum Dot Size at Graphene on the Charge Transfer

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Abstract—The size of quantum dots significantly influences the chemisorption process at graphene surface, affecting adsorption strength, interaction dynamics and overall performance in various applications. This relationships is primarily driven by quantum confinement effects and surface area variation. Chemisorption of quantum dots onto graphene introduces new pathways for charge transfer, where electron flow can occur due to differences in the Fermi level of graphene and the energy states in the QDs. Based on Newns—Anderson model, the chemical adsorption of spherical quantum dot at graphene depending on its size and normal distance between them were examined. Through a self-consistent computational scheme, the determination of occupation numbers, energy-level positions solved numerically.

Keywords: Anderson impurity, quantum dot size, graphene, chemisorption, quantum confinement

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INTRODUCTION

The chemisorption of a spherical semiconducting QD on graphene is strongly dependent of the distance and the presence of external electric fields and also large QDs exhibit different occupation number and the character of interaction based on different factors such as size of QDs, surface chemistry of QDs and electronic properties of graphene [1]. The electronic energy levels in the QDs had a direct effect on their properties as electron donors or acceptors; a smaller QD, with a higher band gap, naturally traps electrons more tightly and is less likely to donate electrons. On the other side, the bigger QD and the smaller band gap, the more efficient transfer of charge between an adjacent substrate (graphene) [2].

One important part of designing graphene-based hybrid systems is understanding how external nanoparticles, like quantum dots, interact with the surface. Chemisorption is key to these interactions. The size of the quantum dots greatly affects the chemisorption process at the graphene surface, influencing factors such as adsorption energy, charge transfer, and bonding mechanisms [3].

The tunable charge transfer properties in quantum dots graphene hybrid systems open the door to a variety of applications: in the solar cells, the efficient electron transfer from QDs to graphene can improve charge separation and collection, enhancing the performance of photovoltaic. The ability to control charge transfer through the size of QDs opens up other possibilities in designing advanced materials and devices such as photodetectors and sensors, optoelectronics, catalysis and energy storage [4, 5].

For large impurity concentrations, the interchange of the symmetries blocking the localization at the Dirac point, that gives a quantum confinement to a critical regime of charge exchange [6, 7] in which the graphene conductivity is can be constant based on the distribution of adsorbants between distinguished sublattices of graphene sheet [8, 9].

In this work, there are two main pathways of study: First, the computation of density of states for pristine graphene, broadening, and quantum shift depending on energy and direct distance between adsorbed Q.D and graphene. Second, the self-consistently calculations of the occupation numbers and energy levels of the adsorbed Q.D.

THEORTICAL APPROACH

The calculations which can examined with chemisorption process is about the electronic structure. However, it can creat a simple model that stands only basic physics [10, 11]. It can write the physical characteristics that taken into account for the quantum dot chemisorbed on graphene: the quantum coupling effects and the quantum shift. The Anderson model [12] that described a Q.D. as two energy levels with a hybridization with graphene. Coulomb barriers segregate the adsorbed Q.D. energy level from graphene. The hybridization function $V(Z)$ represents the coupling strength. Intra-dot Coulomb correlation (U) separates the spin-down localized level from the spin-up level. The Hamiltonian of the system is:

$$H = H_{\mathrm{Q.D}} + H_{\mathrm{G}} + H_{\mathrm{hyb}}, \tag{1}$$

$$H_{\mathrm{Q.D}} = \sum_{\sigma} E^{\sigma}_{\mathrm{dot}} n^{\sigma}_{\mathrm{dot}} + U n^{+\sigma}_{\mathrm{dot}} n^{-\sigma}_{\mathrm{dot}}, \tag{2}$$

$$H_{\mathrm{G}} = \sum_{\vec{k}\sigma} E^{\sigma}_{\vec{k}} c^{\sigma\dagger}_{\vec{k}} c^{\sigma}_{\vec{k}}, \tag{3}$$

$$H_{\mathrm{hyb}} = \sum_{\vec{k}\sigma} \left(V^{\sigma}_{\vec{k}} c^{\sigma\dagger}_{\vec{k}} d^{\sigma} + V^{\sigma^{*}}_{\vec{k}} c^{\sigma}_{\vec{k}} d^{\sigma\dagger} \right). \tag{4}$$

where, $H_{\mathrm{Q.D}}$ the Hamiltonian describes the isolated Q.D, $E^{\sigma}_{\mathrm{dot}}$ the adsorbed energy level of spin (up/down), the second term is the local-Coulomb-repulsion (U), $n^{\sigma}_{\mathrm{dot}}$ is the occupation number of the Q.D. energy levels: $n^{\sigma}_{\mathrm{dot}} = d^{\dagger}d$ and $d^{\dagger}(d\ )$ the creation (annihilation) operator of the electronic state on Q.D., H_{G} is describe pristine graphene sheet, $c^{\dagger}\ (c)$ the creation (annihilation) operator of the electronic state with the wave vector k in the energy $E^{\sigma}_{\vec{k}}$ on graphene sheet. H_{hyb} the coupling interaction between Q.D and graphene, $V^{\sigma}_{\vec{k}}$ the hybridization energy $V(Z) = V_{\mathrm{o}} e^{-\alpha Z}$ as a function of normal distance Z, where V_{o} is the hybridization at $Z = 0$ and α is an adjustable factor. The important point is that the Q.D. adsorbed hybridizes on top of a carbon atom.

The problem's difficulty stems from adsorbant's twofold occupancy, U, which has an inversely proportion with quantum dots radius, i.e. $U \propto \frac{1}{R}$. From the adsorbent's perspective, graphene acts to dampening the adsorbant's electrical mobility. Resulting the confined electrons to create a self-energy $\sum(E,Z)$ that proportional to the system of energy and distance [13]:

$$\sum(E,Z) = |V(Z)|^{2} \int \frac{\rho_{\mathrm{G}}(E')}{\left(E - E'\right)^{2} + i\lambda^{2}} dE', \quad \lambda \to 0 . \tag{5}$$

The real part of self-energy is correlated to the quantum shift caused a change in the adsorbed energy level:

$$Re\sum(E,Z) = \Lambda(E,Z) = |V(Z)|^{2} \int \frac{\left(E - E'\right)\rho_{G}\left(E'\right)}{\left(E - E'\right)^{2} + \lambda^{2}} dE'. \tag{6}$$

The broadening determined by an imaginary component of the self-energy, given by:

$$\mathrm{Im}\sum(E,Z) = \Delta(E,Z) = -|V(Z)|^{2}\, \pi\, \rho_{\mathrm{G}}(E). \tag{7}$$

While $\rho_{\mathrm{G}}(E)$ represents the DOS for graphene [14]:

$$\rho_{G}(E) = \begin{cases} 0 & E < -3t \\ -\dfrac{\rho_0 t}{E} & -3t < E < -t \\ \dfrac{\rho_0}{t}|E| & -t < E < t \\ \dfrac{\rho_0 t}{E} & t < E < 3t \\ 0 & E > 3t \end{cases}, \quad \rho_0 = \frac{2}{(1 + 2\ln 3)t}, \tag{8}$$

t is the hopping energy (= 2.8 eV [15]) for graphene's nearest-neighbor carbon atoms, the width of the valence and conduction bands is (3t), furthermore the energy at Dirac point (Fermi Level) is $E = 0$.

The electron—electron interaction, ΔE, caused the energy levels of the Q.D shift toward each other as approaching to graphene sheet [16]. The image interaction between electrons in Q.D and graphene is defined as $\Delta E(Z) = \frac{e^{2}}{4\left(Z + Z_{\mathrm{o}}\right)}$, where Z_o denotes the graphene sheet's closest approach. The adsorbed Q.D energy level can now be written as:

$$E^{\pm\sigma}_{\mathrm{dot}}(E,Z) = \varepsilon_{\mathrm{dot}} + U n^{\mp\sigma}_{\mathrm{dot}}(E,Z) + 2\Delta E(Z), \tag{9}$$

$\varepsilon_{\mathrm{dot}}$ denotes to the isolated Q.D energy level and $n^{\mp\sigma}_{\mathrm{dot}}$ is the occupation number [17]:

$$n^{\pm\sigma}_{\mathrm{dot}} = \int_{u_{\mathrm{o}}}^{E_{\mathrm{F}}} \rho^{\mp\sigma}_{a}(E,Z) f(E,Z)\, dE, \tag{10}$$

$\rho^{\mp\sigma}_{a}(E,Z)$ Localized DOS on the adsorbed Q.D. $f(E,T) = \frac{1}{1 + e^{\frac{E}{k_{\mathrm{B}}T}}}$ is the Fermi function, k_{B} is Boltzmann constant and T is a temperature. The DOS associated with each adsorbed energy level is a Lorentizian distribution centered at $E^{\sigma}_{\mathrm{dot}}\left(E^{-\sigma}_{\mathrm{dot}}\right)$ as,

$$\rho^{\sigma}_{\mathrm{dot}}(E,Z) = \frac{1}{\pi} \frac{\Delta(E,Z)}{\left(E - E^{\sigma}_{\mathrm{dot}}(E,Z) - \Lambda(E,Z)\right)^{2} + \Delta^{2}(E,Z)}. \tag{11}$$

CALCULATIONS AND DISSCISION

All of the above equations are solved numerically and that an importance to remember that Eqs. (9) and (10) are solved self-consistently. The initial temperature taken as $T = 300$ K, $\alpha = 0.018$ Å^{-1}, $Z_0 = 3.6$ Å, $Z = 10$–0 Å, $\varepsilon_{\mathrm{dot}} = -0.75$ eV. The functions that explain the chemisorption process for any spherical semiconducting Q.D adsorbed on graphene are included in the self-consistent solution when employing an impurity Anderson-model. The correlation

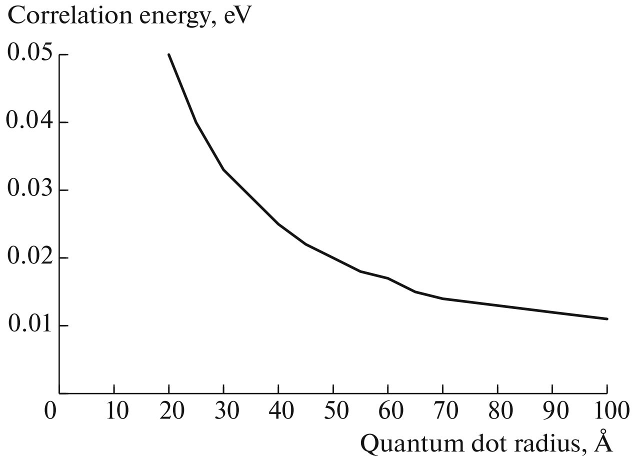

Fig. 1. The correlation energy U of adsorbed quantum dot as a function of its size (radius R).

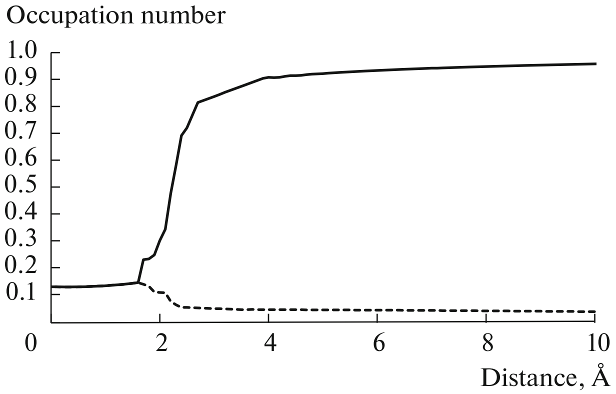

Fig. 2. The occupation numbers n_{dot}^{σ} (solid line) and $n_{\text{dot}}^{-\sigma}$ (dashed line) of adsorbed quantum dot as a function of distance (Z).

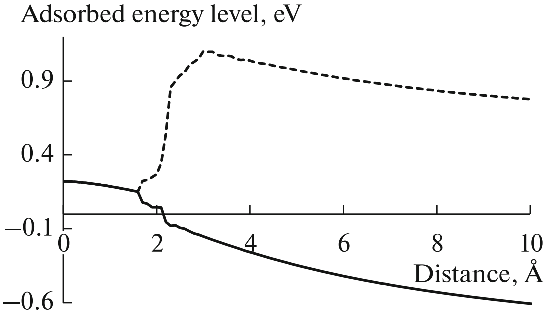

Fig. 3. The energy levels E_{dot}^{σ} (solid line) and $E_{\text{dot}}^{-\sigma}$ (dashed line) of adsorbed quantum dot as a function of distance (Z).

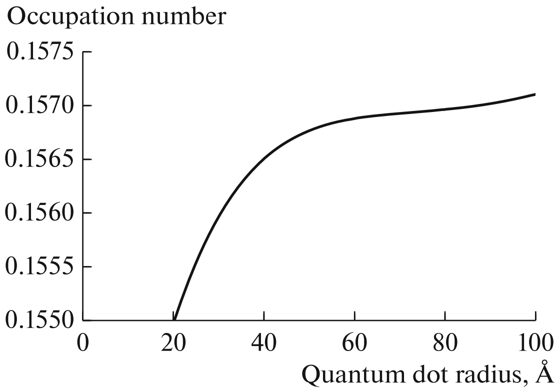

Fig. 4. The occupation number n_{dot}^{σ} of adsorbed quantum dot at graphene surface ($Z = 0$) as a function of its size (R).

related with Q.D dots size is represented by Fig. 1, the occupation numbers and energy level of adsorbed QD, as shown in Figs. 2 and 3, for all distances the solution is the magnetic state ($n_{\text{dot}}^{\sigma} \neq n_{\text{dot}}^{-\sigma}$), while the solution exchange from magnetic state ($n_{\text{dot}}^{\sigma} \neq n_{\text{dot}}^{-\sigma}$) to non-magnetic state ($n_{\text{dot}}^{\sigma} = n_{\text{dot}}^{-\sigma}$) or vice versa at the normal distance from the graphene surface (exchange point Z_{0h}). Also, the occupation number and energy level at the graphene surface (distance $Z = 0$) for various values of quantum dots radius (that represents its size) $R$are showen in Figs. 4 and 5. There is a strong interaction in the adsorption region at graphene sheet, which leads to increasing the coupling and charge exchange. Table 1 explains these results.

The electronic coupling between QDs and graphene depends on how closely the energy levels of the QD align with the Dirac point of graphene. The size of the quantum dot directly influences this alignment. This suggests that smaller QDs form stronger chemical bonds with graphene due to enhanced charge transfer and interaction between the QD and graphene's π-electrons. When a QD is in contact with graphene, the alignment between the QD's conduction band and graphene's Fermi level determines the direction of charge transfer. If the QD has a higher conduction band energy compared to the graphene Fermi level, electrons will transfer from the QD to graphene. Conversely, if the QD has lower conduction band energy, graphene can donate electrons into the QD. These results make an ability to list the following remarks:

Small Quantum Dots

Smaller quantum dots can induce a more significant shift in the electronic properties of graphene, such as opening a bandgap or modifying conductivity, depending on the strength of the interaction during chemisorption because more localized charge distributions might enhance van der Waals forces or even promote covalent bonding with graphene if chemical functionalization occurs. That type of QDs tend to

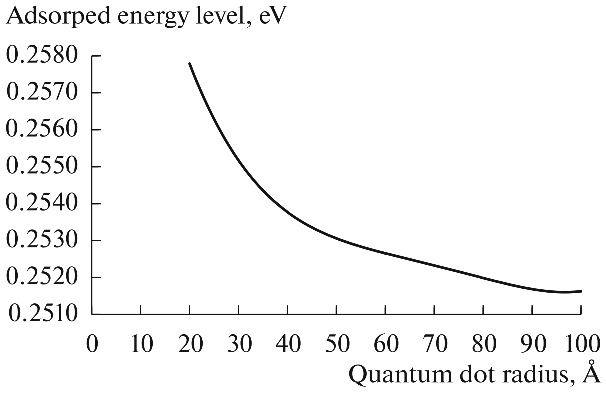

Fig. 5. The energy level E^{σ}_{dot} of adsorbed quantum dot at graphene surface ($Z = 0$) as a function of its size (R).

have a larger ratio of surface area and volume meaning that more of surface atoms are readily available for binding with the graphene sheet. For those smaller than 30 Å, high surface interaction would give rise to a large number of possible chemisorption bonding sites, which would improve the adsorption, and consequently the strength of the bonds formed would be higher. Smaller quantum dots have higher energy conduction bands due to the increased quantum confinement effect. The conduction band edge of the quantum dot may lie above the Fermi level of graphene, facilitating electron transfer from the quantum dot to graphene. The reduced size also leads to stronger Coulombic interactions between the electrons in the dot, affecting the rate of charge transfer.

Table 1. The occupation number, energy level and correlation energy of quantum dot adsorbed at graphene surface for various values of size (radius R)

R, Å	U, eV	E^{σ}_{dot}, eV	n^{σ}_{dot}
100	0.011	0.2516	0.15711
90	0.012	0.2518	0.15700
80	0.013	0.2520	0.15698
70	0.014	0.2522	0.15694
65	0.015	0.2524	0.15690
60	0.017	0.2526	0.15687
55	0.018	0.2530	0.15685
50	0.020	0.2531	0.15672
45	0.022	0.2533	0.15669
40	0.025	0.2539	0.15648
35	0.029	0.2545	0.15632
30	0.033	0.2550	0.15600
25	0.040	0.2560	0.15545
20	0.050	0.2580	0.15500

Large Quantum Dots

In larger quantum dots, a decreased surface area to volume ratio may result in fewer atoms interacting with graphene. This leads to weaker or less extensive chemisorption. The size of the quantum dots also affects how they diffuse on a graphene surface. Larger quantum dots might face limited diffusion, which could influence their adsorption dynamics and how strongly they bind to graphene.

CONCLUSIONS

Understanding how quantum dot size relates to chemisorption on graphene is key to improving the design of graphene-based materials for applications like sensors, catalysis, electronic devices, and optoelectronics. Quantum dots have special electronic properties due to quantum confinement. This occurs when the motion of charge carriers is restricted to a small space, changing the material's bandgap and its interaction with outside surfaces. As the size decreases, the energy levels of the quantum dot become more distinct, leading to a larger bandgap. This change in electronic structure influences how quantum dots interact with the graphene surface. Smaller quantum dots show stronger chemisorption because they have a higher surface-to-volume ratio. This allows more atoms on the surface of the quantum dot to engage with the graphene sheet, resulting in higher adsorption energies. In contrast, larger quantum dots tend to have lower energy levels and a narrower bandgap. This variation in electronic states affects how well quantum dots can transfer charge to and from the graphene surface, which in turn influences the strength of chemisorption. In the case of larger QDs, a few number of atoms interacting with graphene, resulting in a weaker or less extensive chemisorption. The diffusion of quantum dots across a graphene surface is influenced by their size. Larger quantum dots may experience limited diffusion, which could affect their adsorption dynamics and the strength of their binding to graphene.

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CONFLICT OF INTEREST

As author of this work, I declare that I have no conflicts of interest.

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