

A NEW APPROACH ON SIZE QUANTIZATION AND ELECTRON TRANSPORT IN QUANTUM DOTS.

Dr. Dharmendra Kr. Singh

Deptt. Of Physics,

J. P. University, Chapra.

ABSTRACT

Optical absorption and photoluminescence were first used to study the electronic structure of nanometer sized semiconductor colloids. However, these techniques only provide information about the collective properties of large numbers of QDs and, due to a distribution in particle size, the luminescence signals are inhomogeneously broadened. With Scanning Probe Techniques such as Scanning Tunneling Spectroscopy (STM) and Scanning Near-field Optical Microscopy (SNOM), electrical and optical measurements on individual particles can be performed, avoiding problems arising from polydispersity. In the work described in this thesis the optoelectronic properties of semiconductor quantum dots, and charge transfer between such structures and a conducting substrate were studied in a novel way. For this purpose, metal substrates were provided with a (sub) monolayer of quantum dots; the opto electrical properties of the systems were investigated with time-resolved photoelectron chemistry.

Introduction

A crystalline material which is size-restricted in three dimensions such that the electron wave functions are confined within its volume is called a quantum dot (QD). Due to this confinement the electronic properties of Quantum dots opened on their size in the nanometer regime (1,2). This effect, now called 'size-quantisation', was first observed in 1926 with DdS colloids (3), but was only properly recognised in the 1980's (4,5]. Chemists and physicists have studied nanostructures extensively in the past two decades in order to understand the size-quantisation effects in semiconducting and metal quantum dots.

Due to their extremely small sizes and their interesting electronic properties. quantum dots are promising building blocks for the fabrication of electronic and optoelectronic solid state devices. Integrated circuits (ICs) might be further miniaturised by using nanocrystallites. The II-VI nanocrystals have a bandgap which can be tuned in a

broad range (up to 4 eV) by changing either their size or chemical composition; this makes them suitable candidates for applications as a Light Emitting Diode (LED) [6,7], a Single Electron Transistor (SET) [8-10], chromophores in solar cells [11-15], or as a building block for photonic crystals (16). Recently, a LED with an efficiency of 10 % in a semiconducting polymer matrix, was fabricated [17,18] based on CdSe nanocrystals. The output colour could be tuned in the entire visible range. A critical parameter for the performance of a SET, the principle of which is based on the Coulomb blockade effect, is the capacitance of the quantum dot, which is determined by its size. Quantum dots can be applied as stable fluorescent indicators in biological research; core-shell quantum structures of CdSe/ZnS have a very high luminescence quantum yield (up to 100%). Since they can easily be attached to DNA [19] or proteins by a sulphide bond they can act as a luminescing label to monitor biological reactions. Semiconductor colloids can also be employed in photocatalysis; TiO₂ colloids irradiated with UV-light can photocatalyze organic contaminants [20]. Methods for the preparation of large quantities of well defined nanoparticles have been developed in order to study the size quantisation effect. A technique to grow low dimensional structures, Molecular Beam Epitaxy (MBE) was developed at the end of the 1960's [22,23].

EXPLANATION

Optical absorption and photoluminescence were first used to study the electronic structure of nanometer sized semiconductor colloids. However, these techniques only provide information about the collective properties of large numbers of QDs and, due to a distribution in particle size, the luminescence signals are inhomogeneously broadened. With Scanning Probe Techniques such as Scanning Tunneling Spectroscopy (STM) and Scanning Near-field Optical Microscopy (SNOM), electrical and optical measurements on individual particles can be performed, avoiding problems arising from polydispersity. In the work described in this thesis the optoelectronic properties of semiconductor quantum dots, and charge transfer between such structures and a conducting substrate were studied in a novel way. For this purpose, metal substrates were provided with a (sub) monolayer of quantum dots; the optoelectrical properties of the systems were investigated with time-resolved photoelectron chemistry. The electronic structure of individual nanocrystals was investigated by Scanning Tunneling Spectroscopy at room temperature and at 4 K. This chapter presents an introduction to the size-quantisation effect in semiconductors and

electron transfer between a metal and a semiconductor quantum dot. In the latter sections the principles of the measuring techniques are explained and an outline of this thesis is given.

Size-quantisation in Semiconducting Nanocrystals

Energy Bands in Bulk Semiconductor Crystals

To discuss the origin of energy bands in bulk semiconductors and electron tunneling between two systems, a single electron in a crystal is considered [33]. The time – dependent Schrodinger equation for an electron can be written as,

$$-\frac{\hbar^2}{2m_e} \nabla^2 \Psi(x, y, z) + U(x, y, z) = E \Psi(x, y, z)$$

where m_e the mass: of the free electron, E is the kinetic energy. In the free-electron approach, the potential energy of the electron due to the crystal lattice of core ions $U(x,y,z)$ is neglected, and is taken as a constant (e.g. $U(x,y,z) = 0$).

Quantum Size Effects

Nanocrystals have crystalline order and dimensions corresponding to some tens of a lattice constant in each direction. Electron scattering with the lattice leads to band formation, as for macroscopic crystals. However, the free electron wavelength and the Bohr radius can be comparable to or even larger than the crystal dimensions. This means that the nanocrystal acts as a quantum box for quasiparticles. The symmetry of the box is important for the solution of the Schrödinger equation. In the literature, a spherical symmetry is often used. For simplicity, we consider a rectangular box of dimensions L_x , L_y , and L_z ; surrounded by infinitely high energy walls. Stable solutions of the Schrödinger equation are standing waves. For instance in the x -direction, the free- electron and free-hole standing waves must fulfil.

Brus has modelled electron confinement in a spherical box by using the effective mass approximation [5,34]. When $R \ll a_B$ the confined electron and hole have no bound state as in the definition of an exciton given above and the Coulomb interaction may be ignored to a first approximation. The mathematical treatment is similar to that for an electron in the spherical potential well of a nucleus [35].

In which E_g is the bandgap of the macrocrystalline semiconductor, defined as the energy needed to excite an electron from the top of the valence band to the bottom of the conduction band. X is the n th root of the spherical Bessel function and l the order of the function; for $l=0$ (so-called s- states) x_{n0} an. Weakly quantised quantum dots (with $R \sim a_B$) contain a large number of atoms and unit cells; therefore Bragg reflection at the periodic lattice will lead to the formation of continuous energy bands. Only the levels at the top of the valence band and at the bottom of the conduction band, which correspond to the most delocalised electron wave function, will be discrete. Highly quantised semiconductor quantum dots are sometimes called artificial atoms because they exhibit a discrete optical spectrum determined by their size.

The electron and hole, confined in a space with dimensions smaller than the Bohr radius of the exciton, cannot however be considered as independent particles; the Hamiltonian must be expanded by two-particle kinetic terms and the Coulomb and confinement potential. This leads in the Brus model to an expression for the energy of the ground state of the electron-hole pair ($1s_e 1s_h$ or first excited state).

In which the second term describes confinement and the third the Coulomb electron-hole interaction. The coefficient A corresponds to 1.786 for the $1s, 1s$, state and has values between 1.6 and 1.9 for other states[36]. Equation (4.10) implies that the gap between the filled valence band levels and the empty conduction band levels increases when the radius of the particle decreases. Due to the electron-hole Coulomb interaction, the measured optical band gap has a slightly lower energy than the 'actual' electronic band gap.

The increase of the bandgap and the transition from continuous energy bands to discrete energy levels upon a decrease of particle size has been observed by optical absorption spectroscopy in many colloidal semiconductor systems [30,37]. The absorption and emission spectra of colloidal CdSe quantum dots of different sizes studied in this work (see Figure 4.4) demonstrate these effects. Upon a decrease of the particle radius, the onset of the absorption and the emission maximum shift towards higher energies. A clear structure in the absorption spectra is observed for the smallest particles, corresponding to discrete optical transitions.

Surface States

Although the presence of surface states is by no means a size-quantisation effect, surface states become increasingly important as the size of a structure reduces; the ratio of the number of surface to bulk atoms, which increases with decreasing particle radius, is very large for quantum dots. Surface atoms give rise to electron levels of energy different from those of the bulk levels; these levels can play an important role in light absorption and emission.[38] The importance of surface states in the photoexcited decay dynamics has become clear from time-resolved luminescence spectroscopy on colloidal suspensions of quantised PbS, CdS, CdSe, ZnO, and InP [39-42]. Besides direct conduction-to-valence band recombination, a broad band at lower energy is often observed in emission spectra.

Electron Tunneling

Basic Principles of Electron Tunneling

Metals and semiconductors generally have a high potential energy barrier at surface, which confines the electrons within the solid (44) at room temperature thermally activated escape of the electrons over the surface barrier as very improbable. However, quantum mechanical tunnelling can occur when the interfacial barrier is thin. This is the main mechanism of electron transfer through an insulating layer between two solids in intimate contact.

The free electron model discussed in section 1.2 allows a more quantitative discussion of the probability of finding an electron in a limited region just outside a crystal potential energy in the crystal is set to zero, and that of an electron at rest outside crystal to E_{vac} . The Fermi-energy of the electrons in the crystal is considered as E_F . The work function, $E_{vac} - E_F$ is generally of the order of a few eV. The Schrödinger equation for a single free electron in the region outside the crystal in the x direction is given by, The energy of the electron at rest in vacuum is larger than energy $E(x)$ of the impinging electron.

The wave function of an electron impinging on a surface wall decays exponentially outside the metal. The decay length $1/k_{vac}$ depends on the effective barrier height $E - E(x)$. Tunneling of an electron between two solid phases can occur if these phases are separated

by a distance of the order of $1/K\alpha$ The probability of tunneling is relatively small when $x > 1/K\alpha$.

The dependence tunneling probability is determined by the exponential term, since the prefactor depends only weakly on the effective barrier height.

Electron Tunneling between a Quantum Dot and a Metal

Colloidal semiconductor quantum dots can be adsorbed on a metal electrode by Van der Waals interactions of the capping molecules, which stabilize the dots in the suspension, with the metal surface. Alternatively, covalent anchoring of the dots to the metal is possible with a di functionalised Self-Assembled Monolayer (SAM) [50-55], In addition, QDs can be grown electrochemically on a conductive substrate; the particle size can be controlled by the charge used to electrodeposit the dots [56-58].

A metal coated with a (sub)monolayer of nanocrystals can be used as working electrode in a conventional electrochemical cell. With such electrodes we have performed time-resolved photoelectrochemistry. The metal electrode, coated with a monolayer of dots, can be considered as a 2D array of mutually independent Double- Barrier Tunnel Junctions (DBTJ). The junctions are formed between the metal substrate and the dot and between the dot and the electrolyte. Using a modulated light intensity it is possible to measure the rate of photoinduced tunneling between the dots and the metal or the electrolyte solution.

Photoelectrochemical Measurements

The processes involved in photo induced electron tunneling between a quantum dot and a metal electrode, forming the basis of the photoelectrochemical and electrical measuring techniques, are presented in this and the following section. A quantum dot on a metal electrode, An electron has been excited from a valence band level (HOMO) to a conduction band level (LUMO) of the quantum dot upon absorption of a photon ($h\nu > E_g$). Direct band-band recombination is usually very fast (\sim ps) and returns the system to the ground state. However, trapping of the hole or the electron in a bandgap state may compete with the fast relaxation to the ground state. As a result, an excited state of lower energy is formed. It will become clear in this work that such a photoexcited state can possess a long lifetime, so that photoinduced tunneling between the dot and the metal can occur.

Resonant tunneling of the photoexcited electron to the metal is only possible when the substrate Fermi level ($E_{F,sub}$) is below the electron level (E_n), and an electron can only tunnel from the metal to the unoccupied level in the dot when the metal Fermi level is above this level (E_n). Thus, relaxation of the excited state to the ground state via photoinduced tunneling to and from the metal can only occur when $E_n < E_{F,sub} < E_p$: Decay of the photoexcited state via the metal can be observed by time-resolved measurement of the current in the external electrical circuit. When $E_{F,sub}$ is scanned and the photoinduced tunneling currents are measured in the external circuit, the electronic levels of the long-lived excited state can be resolved. The rate constants of these tunneling processes may be determined by using time-resolved photoelectrochemistry. This technique will be explained in section 4.4. In the presence of either a reducing agent (Figure 4.6(a)) or an oxidizing agent (Figure 4.6(b)), electron transfer may also occur between the dot and the electrolyte. When r_3 is followed by r_2 , a steady-state anodic photocurrent will be observed. Otherwise, when r_1 is followed by r_2 , a steady-state cathodic photocurrent results.

Electrical Measurements with a Substrate/Dot/Tip Configuration

Shows an energy level scheme for a highly quantised semiconductor quantum dot (with discrete energy levels) in contact with a metal substrate. By positioning the STM tip above the particle a DBTJ is formed. For simplicity, we assume that $E_{F,sub}$ is fixed with respect to the energy levels in the quantum dot. At small bias ($\Delta E \ll E_g$) the Fermi levels of the tip and the substrate are located in the bandgap of the nanocrystal and resonant electron tunneling via energy levels of the dot cannot occur. If a bias potential is applied such that $E_{F,tip} > E_{F,sub}$, resonant tunneling of an electron from the tip to the dot and from the dot to the substrate can occur when $E_{F,tip}$ reaches the first discrete conduction band level of the quantum dot. When $E_{F,tip}$ is raised further and reaches the next level, tunneling through this level can also take place. At a bias such that $E_{F,tip} < E_{F,sub}$ an electron can tunnel from the substrate to tip, via the levels of the valence band. In the current-bias plot a zero current range around $\Delta E = 0$ will be found, corresponding to the bandgap of the quantum dot. Steps in the current-bias (I-V) plot or peaks in the conductance-bias plot (dI/dV -V) will appear at bias values corresponding to resonant tunneling through discrete.

Intensity-Modulated Photocurrent Spectroscopy

Intensity-Modulated Photocurrent Spectroscopy (IMPS) is a time-resolved optoelectrical method. In this work the technique is used in a photoelectrochemical context to determine the rate constants of electron tunneling processes between the semiconductor quantum dots and a metal or redox system in the solution. IMPS has previously been used to study recombination processes, majority carrier injection at the bulk semiconductor/electrolyte interface [70], and charge transport in nanoporous semiconductor electrodes [71-73]. In this section the principle of the technique will be briefly described. In IMPS, a small sinusoidal modulation, d , is superimposed on a steady state light intensity, I_0 , giving a photocurrent which also has a sinusoidal contribution (ω is the modulation frequency). The modulated photocurrent j_u is measured using frequencies, ω , lower than $1/RC$. The ratio $j_u(\omega)/j_{dc}$ is called the optoelectrical transfer function. Slow processes contributing to the total photocurrent will lead to a phase shift, ϕ , between j_u and j_{dc} . The transfer function, determined by the amplitude ratio and the phase shift, can be plotted in the complex plane (imaginary component vs real component) or in a Bode plot (imaginary or real component vs frequency).

References

1. S. V. Gaponenko, Optical properties of semiconductor Nanocrystals 1998, Cambridge University Press, United states of America.
2. MRS Bulletin, February 1998
3. G. Jaeckel, Z. Tech. Phys. 1926, 6, 301
4. A. Henglein, J. Phys. Chem. 1982, 86, 2291-2293
5. L. Brus, J. chem. Phys. 1984, 80, 4403
6. H. Mattoussi, L.H. Radzilowski, B.O. Dabbousi, D.E. Fogg, R.R. Schrock, E.L. Thomas, M.F. Rubner, and M.G. Bawendi, J. Appl. Phys. 1999, 46, 4390
7. Y. Yang, S. Xue, S. Liu, J. Huang, and J. Shen, Appl. Phys. Lett. 1996, 69, 377
8. D.L. Klen, P.L. McEuen, J.E. Bowen Katari, R. Roth, and A.P. Alivisatos, Appl. Phys. Lett. 1996, 68, 2574
9. M.A. Kastner, Nature 1997, 389, 667
10. H. Weller, Advanced Materials 1993, 5, 88.