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Integration Of Organic Electronic Materials With Semiconductor Nanoparticles

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INTEGRATION OF ORGANIC ELECTRONIC MATERIALS WITH SEMICONDUCTOR NANOPARTICLES

A Thesis Presented

by

TONGXIANG LU

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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Chemistry
INTEGRATION OF ORGANIC ELECTRONIC MATERIALS WITH SEMICONDUCTOR NANOPARTICLES

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CHAPTER 1

INTEGRATION OF ORGANIC ELECTRONIC MATERIALS WITH SEMICONDUCTOR NANOPARTICLES

1.1 Introduction

There is growing demand to fabricate low cost and/or high density electronic components, which has led to exploration of new materials as alternatives to more traditional inorganic materials (silicon based). These new materials generally fall into three classes:

a) Semiconductor and metallic nanoparticles (NPs) building blocks.

b) Organic semiconductors building blocks.

c) Hybrid organic-inorganic materials.

1.1.1 Semiconductor and metallic NPs building blocks

Current research on nanoparticles can be classified into two main categories. The first involves manipulation and exploration of single nanoparticles in devices, for example, single electron transistors (SET) (Figure 1-1). The second category focuses on the application of nanoparticle assemblies to produce a new generation of devices, such as optoelectronics and photonics devices. Moreover, the nanoparticles can also be divided into two classes based on the surface capping ligands: first class composed of metallic NPs with electronically active organic ligands on the surface – NPs in such systems act as a conducting scaffold. The second class is composed of semiconductor nanoparticles that are stabilized with long alkyl chains (which are electronically insulating) ligands and are used for construction of superlattices and glassy solids.
Communication, coupling, and coherence between semiconductor nanoparticles, also known as quantum dots (QDs) are central themes for fabrication of electronic devices. Recent investigation of two coupled quantum dots has shown coulomb blockade and electron pairing. Furthermore, it has been demonstrated that electronic energy transfer in mixed size quantum dot solids arises from dipole-dipole interactions. For example, quenching of the luminescence (lifetime) of the small dots accompanied by enhancement of the luminescence (lifetime) of the large dots is consistent with long-range resonance energy transfer of electronic excitations from the more electronically confined states of the small dots to the higher excited states of the large dots. Recently, Talapin and Murray have showed that initially poorly conducting PbSe NPs solids assembled on a field effect transistor (FET) platform can be chemically activated, by exposure to hydrazine vapors, for fabricating n- and p-type channel transistors. The original NP arrays were insulating because of the 1.5 nm oleic acid ligands coating the particles, and showed a 10 fold increase in conduction after thorough washing that removed some of the ligands.

**Figure 1-1.** CdSe quantum dots single electron transistor (SET) device. Adapted from reference 1a.
1.1.2 Organic semiconductor building blocks

Organic electronics, or plastic electronics, is a branch of electronics that deals with conductive organic molecules. This is as opposed to traditional electronics which relies on inorganic semiconductors such as copper or silicon. There are three major classes of conjugated organic materials: (a) organic charge-transfer complexes, (b) various conjugated polymers derived from polyacetylenes, polyphenylenes, polypyrroles and polyanilines, and (c) pentacene and sexithiophene of the small conjugated molecules or oligomers.

Organic conductive materials are lighter and more tunable than inorganic conductors. In addition, the flexibility of organic synthesis enables the formation of organic molecules with useful luminescent and conducting properties and thus their usage as materials in organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs) and photovoltaic cells. However, in general, the organic conductive materials have a higher resistance and therefore conduct electricity poorly and inefficiently as compared to inorganic conductors.

1.1.3 Hybrid organic-inorganic materials

Hybrid organic-inorganic materials take advantage of the merits of both organic and inorganic components. One approach to achieve the composite materials is to fill conductive polymer matrices, such as polyaniline or polythiophenes with semiconductor nanoparticles: CdS, CdSe or CuS NPs, thus providing access to peculiar morphologies, such as interpenetrating networks, p-n nanojunctions, or “fractal” p-n interfaces, not by traditional microelectronic technology. A significant feature which makes the composite materials different to fully organic or inorganic based materials is the improved long-term stability. For example, recently Bawendi and Rubner reported the tunable electroluminescence of CdSe
poly (phenylene vinylene) heterostructures, while Alivisatos has shown incorporation of CdSe nanorods composites for fabrication of photovoltaic cells. In both cases there is no real electronic coupling, achieved through covalent bonding, between the polymer matrixes and the NPs and control of phase segregation and morphology are very difficult. The second approach is to directly coat the NPs with electronically active ligands. Alivisatos and Fréchet have reported the synthesis of a pentathiophene phosphonic acid ligand that facilitates electron transfer between a CdSe NPs and an organic semiconductor polymer for the construction of a composite organic-inorganic LED. Following this report a number of papers appeared in the literature showing the exchange of insulating ligands with conjugated ligands. Advincula and colleagues have synthesized and used oligothiophene dendrons with varying size to coat CdSe NPs for construction of photovoltaic cells. In another example, a CdSe–tetraaniline hybrid influences the band structure of the nanocrystal and in particular shifts the band ascribed to the HOMO level towards higher potentials and that originating from the LUMO level towards lower potentials. These recent studies mark the first attempts in achieving real molecular-NP hybrids but lack addressing problems of NPs assembly and segregation and deserve further research.

Here, we will explore the fabrication of hybrid organic-inorganic field effect transistors (OIFETs) by assembly of quantum dots coated with electronically active organic ligands. Towards this goal, the semiconductor nanoparticles (QDs) will be synthesized first which will then be coupled to the organic semiconductor such as tetrathiafulvalene (TTF).
Figure 1-2. OFET based on CdSe coated with electron-donor TTF derivatives.

1.2 Synthesis of semiconductor quantum dots

In recent years semiconductor quantum dots have found many new applications and play an important role in interdisciplinary research. Quantum dots have unique physical and photoemission effects; interest has arisen for a functional application of these nanocrystallites. First, CdSe is a highly fluorescence material and is interesting because it shows no photobleaching. This is an important property because in most organic fluorophores there is photobleaching that occurs. Since CdSe does not photobleach they can be used as biomarkers. The ability to tune the fluorescence properties by external stimuli (energy transfer or electron donation) allows one to custom design a sensor for a specific application. Second, QDs also have tunable band gaps. These tunable band gaps lead to opportunities for harvesting light energy in the visible and infrared regions of solar light. Owing to these special properties, the research of quantum dots is focused on two aspects:
a) Addressing the large potential for using luminescent colloidal QD as labeling reagents in biosensing, biomarkers, and biotechnological applications.\textsuperscript{17}

b) Designing and developing QD based solar cells and light emitting devices.

The quantum dots, in general, can be synthesized using various methods including a) arrested precipitation in solution\textsuperscript{18} b) molecular precursor route\textsuperscript{19} and c) synthesis in a structured medium.\textsuperscript{20} For device application crystalline material with ordered structure is preferred and the molecular precursor route is an ideal choice as the particles synthesized using this method are, in general, nanocrystalline. The use of coordinating solvents and high temperature leads to the synthesis of nanocrystalline materials with well defined sizes and shapes, while making them soluble in either non-polar or polar solvents.\textsuperscript{21} (Figure 1-3)

![Figure 1-3. TEM image of CdSe nanoparticles coated with pyridine which have an average size of 6nm.](image)

1.3 Synthesis of tetrathiafulvalene (TTF) derivatives and functionalization of quantum dots

To fabricate efficient, low operating voltage OIFETs based on quantum dots, the capping ligand of the QDs needs to be exchanged from electronically insulating to electronically conductive or at least semiconductive. The ligand chosen for this purpose is
derived from tetrathiafulvalene (TTF). Tetrathiafulvalene (TTF) is a well studied redox material, and the ability to electron donation allows for the modulation of the TTF by chemical and electrochemical methods. TTF also has the ability to respond to external stimuli in the presence of different ligands. TTF is the important component of charge transfer complexes that can be applied in numerous fields of scientific research and applications. The ability of TTF moieties as redox centers have been demonstrated and also extensively researched.

Scheme 1-1 shows the synthesis of TTF derivative, a ligand that consists of TTF and two pyridine “legs” that will allow binding to the surface of quantum dots. Next, through one step place exchange with TOPO ligands the electronically active ligands were coated onto quantum dots.

Scheme 1-1. Synthesis route of TTF derivatives.
1.4 Manipulation of cadmium selenide quantum dots to facilitate the “On/Off” switching of fluorescence

The fluorescence of quantum dots coated with TOPO was taken and demonstrated a significant fluorescence on its own. Then the fluorescence of CdSe with electron donation ligands-TTF was recorded (Figure 1-4). The complex demonstrated 2-fold decrease in the fluorescence due to electron transfer between CdSe and TTF.

**Figure 1-4.** Fluorescence of CdSe-TOPO (red line) and CdSe-TTF (blue line) in THF. Excitation at 380 nm. Both of them have the same optical concentration.

Fluorescence studies were done on the CdSe quantum dots upon addition of numerous oxidants. The oxidants used were FeClO₄, PbClO₄, and NOBF₄. The spectra did
not show significant change after the mixture of FeClO$_4$ with CdSe-TTF in THF. However, the intensity of fluorescence increased partially after the addition of PbClO$_4$. (Figure 1-5) More importantly, the best recovery was seen with 2-fold increase in the fluorescence intensity when NOBF$_4$ was incubated with CdSe-TTF. This is due to its ability to withdraw electrons from the present TTF molecule (Figure 1-6). Therefore, the quenching and recovery of fluorescence of quantum dots leads to a synthetic “ON/OFF” fluorescence switch. (Figure 1-7)

**Figure 1-5.** Titration of PbClO$_4$ (9.65 mM) against CdSe-TTF in THF. Excitation at 380 nm.

**Figure 1-6.** The recovery of fluorescence of CdSe-TTF with addition of NOBF$_4$ in THF. Excitation at 360 nm.
1.5 Fabrication of hybrid organic-inorganic FETs based on the modified QDs

1.5.1 Quantum dots Assembly.

Having achieved the synthesis of the semiconductor NPs with the appropriate electronically active ligands, we will optimize and address the issues of NPs assembly on the device platforms. Assembly and superstructure of NPs on surfaces/platforms can be achieved using conventional techniques such as spin coating, dip coating, drop casting, inkjet printing or the Langmuir-Blodgett technique (LB). We will employ the drop casting and controlled evaporation techniques. These techniques are simple but still allow very controlled assembly of the QDs. Our goal will be to make the structured assembly as high a degree as possible.

1.5.2 Device platform fabrication

Device platforms will be fabricated using two major techniques – standard photolithography (PL) following metal deposition and lift-off, and nanoimprint lithography (NIL). Although the standard PL is the work horse of the semiconductor industry, the
simplicity and diversity of the NIL technique is much more appealing, especially for constructing devices on flexible plastic substrates. For this project we have chosen to work simultaneously with PL and NIL in order to gain more diversity of structures and electrode materials. Recently, we have been testing our ability to replicate available device electrodes platforms. Processes include the fabrication of a negative mold, a positive mold and the final imprinting of the pattern followed by metal deposition and lift off. The photo-polymer formulation used in the NIL process is a combination of 61% ethoxylated bisphenol A dimethacrylate, 18.5% 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate, 18.5% N-vinyl pyrrolidone and 2% 2,2-dimethoxy-2-phenylacetophenone. Figure 1-8a shows preliminary results of a two step NIL replication process of devices and figure 1-8b shows PL prepared devices. Devices are designed to have a variety of channel width (W) and length (L) allowing the understanding of grain size effect and optimization.

Figure 1-8. Examples of a device platform produced by a) NIL replication of electrodes. b) Photolithographically fabricated interdigitated electrodes.
1.6 Conclusions

Quantum dots coated with electronically active ligands-TTF derivatives were synthesized through one step place exchange reaction. The fluorescence of quantum dots can be manipulated through electron transfer between quantum dots and ligands. Therefore, a functional “ON/OFF” fluorescence switch was achieved. Furthermore, quantum dots coated with TTF derivatives will be assembled on device platforms, which will bridge between inorganic semiconductor nanoparticles and organic conductors/semiconductors, with the ultimate goal being the fabrication of devices.

1.7 Experimental methods

1.7.1 Syntheses

1.7.1.1 4, 5-bis-(benzylthio)-1, 3-dithiole-2-one (1)

A boiling solution of mercuric acetate (2.1g, 6.56mmol) in 20ml of acetate acid was slowly added with stirring to a red solution of 4, 5-bis-(benzylthio)-1, 3-dithiole-2-thione (1g, 2.6mmol) in 80ml of chloroform. After vigorous stirring for 15min at room temperature, the white precipitate was filtered off and washed with chloroform (3*10ml). The filtrate was washed with water (4*50ml), and a red precipitate was filtered off and then washed with water again to neutralize any acetate acid in the organic phase (chloroform). The solution was dried over MgSO₄ overnight. After filtration and removal of the solvent, a yellow crystalline solid was obtained.

Yield: 0.7g, 70%

¹H-NMR (400 MHz, CDCl₃, TMS): δ=7.45-7.98 (m, 10H); UV-Vis (CH₃OH, λ_max) spectra: 248.7nm. MS (EI): m/e 390.
1.7.1.2 4, 5-bis (3-Picolythio)-1, 3-dithiole-2-one (2)

4, 5-bis (Benzoylthio)-1, 3-dithiole-2-one (1) (500 mg, 1.28 mmol) was dissolved in 20 ml of anhydrous methanol under argon at room temperature. A solution of sodium methoxide prepared from sodium (58.8 mg, 2.56 mmol) in 5 ml of anhydrous methanol was added to the above solution slowly within 20 min under N₂ atmosphere. With the reaction proceeding, the color of the reaction mixture changed from pale yellow to reddish due to the generation of air-sensitive dithiolate ions. To the above reaction vessel a mixture of 3-picolyl chloride hydrochloride (419.9 mg, 2.56 mmol) and K₂CO₃ (177.9 mg, 2.56 mmol) in 21 ml of anhydrous methanol was added. Then, the reaction mixture was stirred at room temperature for 6 h. After removing the solvents, column chromatography of the crude reaction mixture on silica gel with dichloromethane/methanol (30:1, v/v) afforded compound 2 as brown solid.

Yield: 250 mg, 53.5%

¹H NMR (400 MHz, CDCl₃, TMS): δ=3.83 (s, 4H, -SCH₂), 7.17-7.15 (m, 4H, pyridine ring), 8.54–8.56 (m, 4H, pyridine ring).

1.7.1.3 4, 5-Bismethylthio-4′,5′-(3-picolythio) tetrathiafulvalene (3)

Compound 2(250 mg, 0.69 mmol) and 4, 5-bismethylthio-1, 3-dithiole-2-thione (468 mg, 2.1 mmol) were suspended in triisopropyl phosphite (3 ml) under argon. The resulting mixture was heated over an oil bath up to 120–130 °C, and kept at this temperature for 3 h. Evaporation of the excess of triisopropyl phosphite from the mixture afforded an oily black residue, which was subjected to chromatography on silica gel with
dichloromethane/methanol (30:1, v/v) as the eluant. The compound 3 was obtained as red solid.

Yield: 85mg, 26%

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta=2.43\) (s, 6H, -SCH\(_3\)), 3.79 (s, 4H, -SCH\(_2\)), 7.17–7.19 (m, 4H, pyridine ring), 8.55–8.57 (m, 4H, pyridine ring).

1.7.1.4 Preparation of CdSe nanoparticles

A typical synthesis for CdSe nanocrystals: 0.0514 g of CdO, 0.2232 g of tetrade-cylphosphonic acid (TDPA) and 3.7768 g of trioctyolphosphine oxide (TOPO) were loaded into a 25 mL flask. The mixture was heated to 300-320 °C under Ar flow, and CdO was dissolved in TDPA and TOPO. The temperature of the solution was cooled to 270 °C; selenium stock solution (0.0664 g of selenium powder dissolved in 2 g of trioctylphosphine (TOP)) was injected. After injection, nanocrystals grew at 250 °C to reach desired size.

1.7.1.5 Preparation of CdSe nanoparticles coated with compound 3.

The CdSe nanoparticles (7 mg) and compound 3 was dissolved in 15ml dichloromethane under argon. The mixture was heated around 40 °C for 6 days. After removal of excess dichloromathane, the mixture was precipitated into 30ml of methanol. The precipitate was collected after centrifugation. The ratio of compound 3 to TOPO is around 1 to 2 according the integral of \(^1\)H NMR.
$^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$=1.25 (bs, 104H, TOPO) 2.43 (bs, 6H, -SCH$_3$), 3.79 (bs, 4H, -SCH$_2$), 7.17(bs, 4H, pyridine ring), 8.55 (bs, 4H, pyridine ring); UV-Vis (DCM, $\lambda_{\text{max}}$) spectra: 508 nm.

### 1.7.2 Conditions for fluorescence spectroscopy

The fluorescence spectroscopy studies were performed at Jasco FP-6500 Spectrofluorometer. The experiment conditions in figure 1-4 are given below.

Excitation: 380 nm, emission range: 450-700 nm, response: 2 sec, sensitivity: high, band width (Ex) 1 nm, band width (Em) 3 nm, data pitch: 0.5 nm, scanning speed: 200 nm/min.
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(7) Talapin, D.V.; Murray, C.B. Science, 2005, 310, 86.


