Effects of Size on the Optical Properties of Organic Semiconductors: Copper (II) Phthalocyanine Nanoparticles

M. M. AL-Amar, C. A. Burns
Department of Physics, Western Michigan University
Center for the Advancement of Printed Electronics
Kalamazoo, MI 49009-5252 USA

Abstract

Organic materials are of great interest for use as electronic and optoelectronic devices. Currently, solar cells are in limited use, due to their relatively high cost. Solar cells based on organic semiconductors are promising as low-cost alternatives to current technologies; for example, low cost printed solar cells may be possible. However, significant frequency ranges in the solar spectrum are not absorbed. Expanding the absorption-spectrum bandwidth for the organic materials by varying the band gap can lead to improved efficiency for solar cells based on organic semiconductor inks. Here we test the possibility of using nanoparticles with different sizes to increase the absorption efficiency.

Copper Phthalocyanine (CuPc) nanoparticles have been prepared by a Liquid–Liquid Interface Recrystallization Technique (LLIRCT), and deposited on substrates using a dip-coater at room temperature. The size of the nanoparticles is measured by transmission electron microscopy (TEM). Particle size and morphology are mainly determined by the preparation time. Optical proprieties were measured using UV-VIS spectroscopy from 350 to 1000 nm. The spectra show a shift in the peak positions as the particles become smaller. The band gap increases with the particle size.

Introduction

Metal Phthalocyanines (MPcs) are organic semiconductor materials and well-known pigments. These materials are low cost, chemically and thermally stable [1], and can easily form ordered thin films [2]. Important applications include gas sensors [3], photoconductivity, [4], solar cells [5] photonics and optoelectronics [6], organic light emitting diodes, (OLED) [7], and transistors [8]. CuPc is one of the most extensively studied materials in this class [9, 10].

Since the properties of materials often change as their size approaches the nanoscale [11], it is valuable to study the structural, electronic and optical properties of metal Phthalocyanine (MPc) nanoparticles. Properties can depend on the substrate, the deposition technique, and the method of heat-treatment.

Recently, a new method for the preparation of pure nanoparticles of CuPc was reported [12, 13]. The primary objective of this work is to study the size dependence of the optical absorption spectra of CuPc nanoparticles deposited by LLIRCT in the UV-VIS region.

Experimental details

Chemicals

CuPc powder (purity level 95%) was purchased from Alfa Aesar and used without further purification. Other chemicals - liquid carbon tetrachloride (90% purity level) and potassium hydroxide (KOH purity level 85%) were used as purchased from Sigma-Aldrich.

Synthesis of CuPc Nanoparticles

CuPc nanoparticles synthesis was performed following the established LLIRCT [12, 13]. CuPc powder is insoluble in most organic and dilute inorganic solvents but is soluble in a mixture of Carbon tetrachloride (CCl_4) and a strong alkali. This mixture of CCl_4/alkali dissolves the CuPc and forms a homogeneous CuPc solution in CCl_4/alkali as revealed by the color developed in the solution.

The procedure of film formation is somewhat similar to the Langmuir–Blodgett technique. A solution of CuPc in CCl_4/alkali was prepared as follows: 0.15g CuPc was dissolved in 20ml of CCl_4 and 0.35g of potassium hydroxide (KOH). The solution was sealed and stirred for one day at room temperature. A small amount of this CuPc/ CCl_4/KOH solution was spread (1 - 20 drops) on a water surface of area ~70 cm^2. After the CCl_4 evaporates, spontaneously self-assembly of CuPc occurs on the water surface leading to the formation of nanoparticles as CuPc is insoluble in dilute alkali solutions. The growth process occurs in two dimensions which leads to relatively uniform size particles.

The as-formed film was transferred onto a microscope slide (1×1×0.25 cm) which had previously been cleaned by ethanol, and rinsed with distilled water. A NIMA D1L Dip-Coater was used to coat the slides as well as TEM grids. The film was created by immersing the substrate vertically in the solution at a constant rate of 0.5 cm/min and lifting it vertically at the same rate so that the film covers the dipped area (Blodgett technique). This operation was repeated multiple times to get the desired film thickness. We have processed films with 1, 5, 10, and 20 dips.

The shapes and size of CuPc nanoparticles were analyzed using a JEOL Model JEM-1230 TEM. The film thickness and roughness were measured with a WYKO RST-Plus instrument that uses optical interference techniques to measure the thickness, and roughness. A UV-VIS scanning double beam spectrophotometer (Perkin-Elmer Lambda 20) in near normal incidence was used to record the absorption spectra from 300-1000 nm.

Results and discussion

Transmission electron microscopy (TEM)

We found that different size particles grew depending on the number of dips. The average size was calculated by randomly selecting and measuring 300 nanoparticles. For samples made with 1, 5, 10, and 20 dips the average size was found to be 38, 43, 45, and 48 nm respectively. **Figure 1** a-d shows the TEM images and the histogram of the width as function of dips. The standard deviations of the width as function of dip are 16, 21, 18, and 19. The ratio of the length to width for CuPc nanoparticles is around 2.5. One question that arises is how the number of dips can affect the size. One likely possibility is that the time required instead of the number of dips is the important factor. The thickness of these samples 1, 5, 10, and 20 dips were measured and the average thicknesses are 3, 5.5, 7.5, and 7 µm, and the roughness R_a, which is the arithmetic average are 940, 626, 537, and 650 nm respectively.

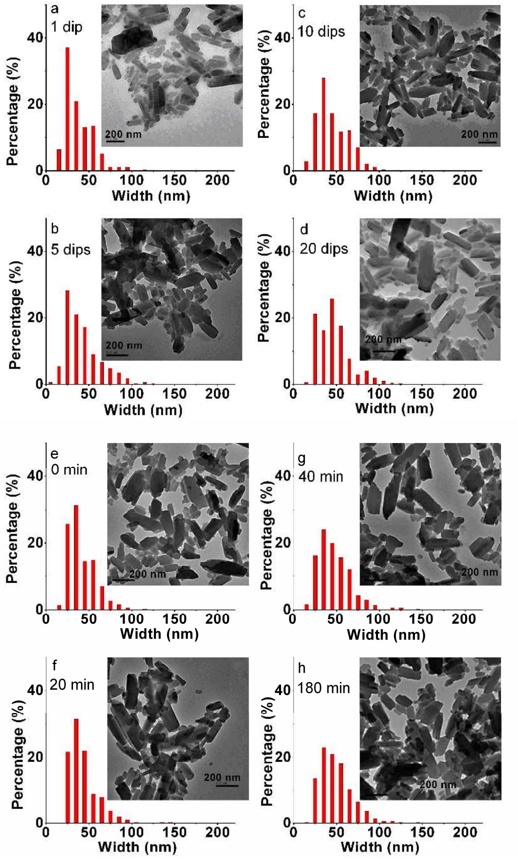


Figure 1 TEM images and the width distribution analysis for CuPc nanoparticles deposited at room temperature, (a) 1 dip (b) 5 dips (c) 10 dips (d) 20 dips (e) 0 min (f) 20 min (g) 80 min (h) 180 min.

The dip-coater at typical speed of 0.5 cm/min takes about 40 minutes to make 20 dips. The deposition period may allow the nanoparticles to grow to a larger size by combining together. To test this idea, four different nanoparticle samples were deposited on glass substrates using just a single dip after waiting 0, 20, 80, and 180 minutes after preparation. The average width sizes were 43, 45 48, and 50 as the time was increased. For this experiment the same LLRCT sample was used. **Figure 1** e-h show the TEM images and histograms of CuPc nanoparticles deposited at different dip times. Standard deviations of the width as function of time are 15, 18, 19, and 19. **Figure 2** shows that the average width of the nanoparticles increases with the number of the dips or time.

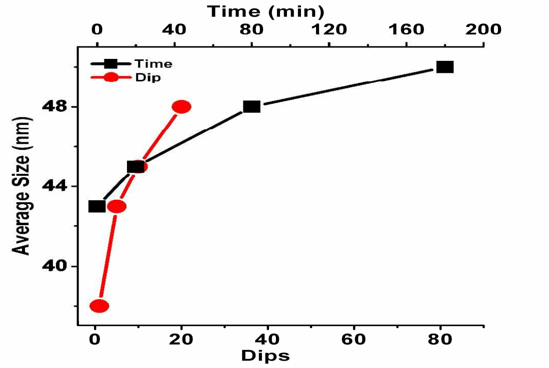
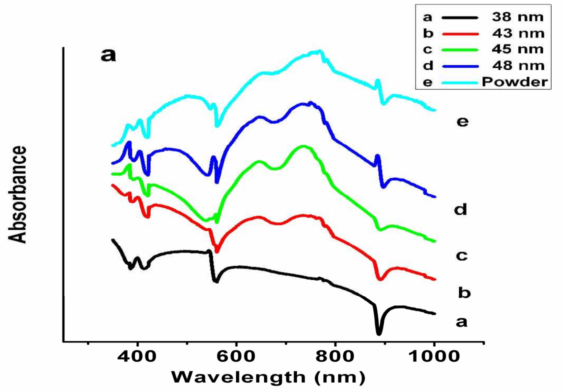


Figure 2 The average width of the CuPc nanoparticles as a function of time and dips.

Optical spectra

There are five known absorption bands for CuPc and most of metal Phthalocyanines (MPcs) Q, B, N, L, and C bands which are owing to $\pi-\pi^*$ and n–π^* transitions. However, there are two strong absorption bands in the visible region for the CuPc [14-16]. The first band (Q-band) is in the range of 600–700 nm and is related $\pi-\pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Phthalocyanine ring. The second band (B-band or soret band) is in the range of 300–450 nm, which is related to direct electronic transition from d–π^* transitions that associated with the central metal atom [14-16].

We took measurements of the absorption spectra of CuPc nanoparticles deposited on glass substrates with the procedure described above. **Figure 3** shows the absorption spectrum of CuPc nanoparticles for different size and the powder. The nanoparticles show optical absorption peaks near 400, 545, 630, and 735 nm. Data in the figure show shifts in the peak positions for both the B-band and the Q-bands. To make this clear, we show the regions of the peaks in **Figure 3** and give the data **Table 1**. The position and relative intensity of the peaks depends on the average size. The wavelength increases as the size increases. The instrumental uncertainty was determined by repeating the measurement on the sample several times also shown in **Figure 3**.



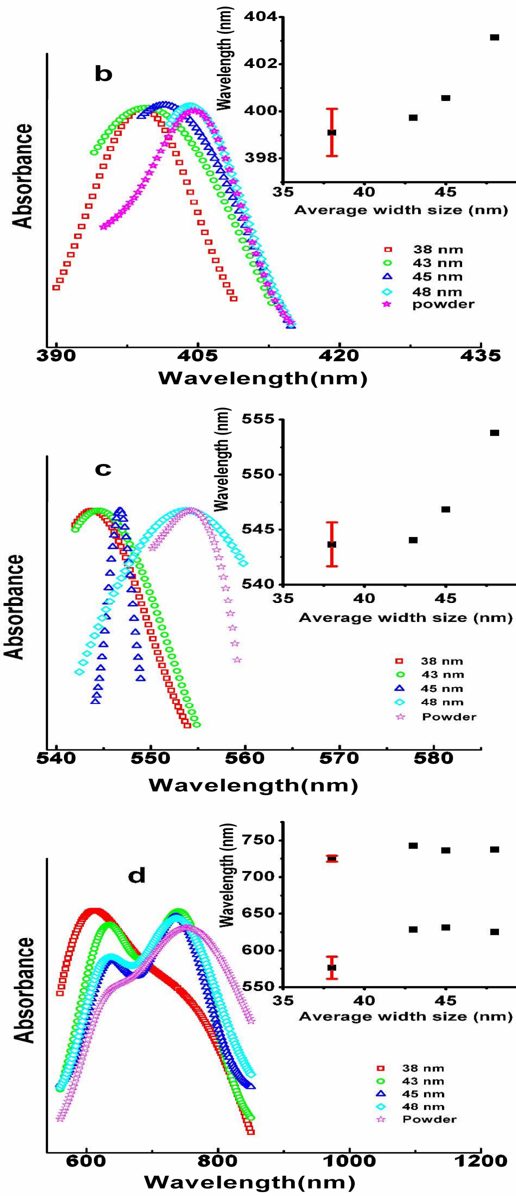


Figure 3 *Optical absorption spectra and the change of wavelength for CuPc nanoparticles, Curves been normalized and offset by hand (a) Range 350-1000 (b) Range 386-415 nm, and (c) Range 540-560 nm (d) Range 560-850 nm. For b, c and d showed the instrumental uncertainty for each wavelength.*

The absorption coefficient (α)

For an electron to leave the valence band and become a free electron in the conduction band, it needs to acquire energy equal to the energy gap. If the electron and hole remain bound they form an exciton and their binding energy reduces the energy that must be absorbed. While the binding energy of exciton is relatively small in classical semiconductors (~meV), it can be significantly larger in certain organic semiconductors (~eV).

The bad gap can be measured by determining the absorption coefficient α from equation (1):

$$I = I_0 \exp(-\alpha t) \tag{1}$$

Here, I and I_0 are the intensities of the incident and transmitted beam, and t is the thickness of the sample. The band gap of the CuPc nanoparticles in the wavelength range where the gap exists (380-420 nm) has been calculated using the equation 2.

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \tag{2}$$

Here, *hv* is the photon energy, E_g is the band gap energy, A and n are constants. For allowed direct transitions n = 1/2, 2 and for allowed indirect transitions n = 3/2 [17]. By far the best fit was obtained for n = 2. The energy gap for the different size particles is determined by graphing the normalized (*áhv*)$^{1/2}$ vs. (*hv*) data as shown in **Figure 4**. The linear nature of the plots indicates the band excitation is a direct transition. The band gap E_g is determined by extrapolating the straight portion of the plot to (áhv)$^{1/2}$ =0 on the energy axis. Also **Figure 4** shows the variation of the band gap energy with particle average width size. Table 1 shows that the band gap increased from 3.02 to 3.1 ± 0.005 eV as the size decreased from 48 nm to 38 nm. As results the optical absorption shows a shift with increasing particle size, indicating a change in E_g

Table 1 Variation of the positions of absorption peak, and the band gap Eg as a function of gain size

<table>
<tr><th rowspan="2">Average width Size (nm)</th><th colspan="4">Absorption Peak (nm)</th></tr>
<tr><th>± 1</th><th>± 2</th><th>±15</th><th>± 4</th></tr>
<tr><td>38</td><td>399</td><td>543</td><td>576</td><td>724</td></tr>
<tr><td>43</td><td>399</td><td>544</td><td>628</td><td>743</td></tr>
<tr><td>45</td><td>400</td><td>546</td><td>631</td><td>736</td></tr>
<tr><td>48</td><td>403</td><td>553</td><td>625</td><td>737</td></tr>
<tr><td>Powder</td><td>403</td><td>554</td><td>622</td><td>752</td></tr>
<tr><th colspan="5">Band Gap E_g (eV)</th></tr>
<tr><th colspan="2">Measurement</th><th colspan="3">Calculation</th></tr>
<tr><td colspan="2">3.1</td><td colspan="3">3.020029</td></tr>
<tr><td colspan="2">3.09</td><td colspan="3">3.020023</td></tr>
<tr><td colspan="2">3.06</td><td colspan="3">3.020021</td></tr>
<tr><td colspan="2">3.05</td><td colspan="3">3.020018</td></tr>
<tr><td colspan="2">3.02</td><td colspan="3"></td></tr>
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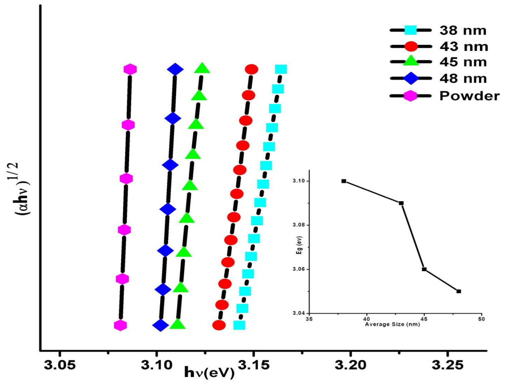

Figure 4 *Plots of (αhv)$^{1/2}$ vs. (hv) and the variation of the optical band gap (Eg) vs. different width size for CuPc nanoparticles*

Exciton energies will also change with particle size. The average distance between the electron and the hole is the exciton

Bohr radius. In bulk materials this radius is small compared to crystal dimensions. In a quantum dot or nanoparticles, the exciton Bohr radius can be the same order as the nanoparticles or even smaller, so exciton energy levels can be significantly altered. In a semiconductor the exciton Bohr radius (r_B) is

$$r_B = \varepsilon(\frac{\hbar^2 n^2}{e^2}) * \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \qquad (3)$$

Here n is the state number, m^*_h and m^*_e are the effective masses of holes and electrons, respectively, and ε is the relative dielectric constant. For CuPc $m^*_e = 2.2\ m_0$ [18], and $m^*_h = 6.6\ m_0$ [19], where m_0 is the standard electron mass, ε is 3.4 [20]. Therefore, the Bohr radius for this exciton in CuPc is 0.11 nm. In our case R >> r_B where R is the average width size for CuPc nanoparticles. This is the regime of weak confinement and the Coulomb interactions term can be neglected [21].

The system can be analyzed [21, 22] based on the Schrödinger equation, with the electrons and holes described by the Hamiltonian:

$$\hat{H} = -\frac{\hbar}{2m_e^*}\nabla_e^2 - \frac{\hbar}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon\left|r_e - r_h\right|} \qquad (4)$$

Here kinetic and Coulomb energies are included. There is also a polarization term which can be ignored because it is small in comparison with the kinetic and Coulomb interactions [23]. As we point out above, this is the regime of weak confinement and the dominant energy is the Coulomb term. Therefore, the energy of the lowest excited states becomes

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2R^2(m_e^* + m_h^*)} \qquad (5)$$

This equation describes the effect of the nanoparticles size on the energy gap of the absorption spectrum. The first term is the bulk energy gap, the second term is the kinetic term, and R is the average width size for CuPc nanoparticles. The calculated and the measured values of the band gap are shown in **Table 1** but the observed effect is much larger than the calculation.

So the cause of the shift in the energy gap must have another explanation. One possibility is that the excitation is more sensitive to size effects than predicted by the simple model used above. While band gaps may depend on the orientation of the materials, the TEM pictures do not seem to indicate any preferred orientation. It is also possible that there are varying amounts of strain in the materials which can alter the band gap [24]. In our case this would imply that the amount of strain varied with the particle size. Further investigation will be necessary to determine the cause.

Future work will involve reducing the size of the CuPc nanoparticles. This reduction should result in more significant shifts and expand the absorption-spectrum bandwidth of the CuPc which could be useful for organic photovoltaic (OPV) devices. Other work will involve replacing the donor layer in the bilayer OPV solar cells with layer of CuPc nanoparticles which can lead to improve the OPV performance.

Conclusions

CuPc nanoparticles were grown and deposited on glass substrates at room temperature by LLIRCT. We find that CuPc nanoparticles grow in size with increasing deposition time. The optical properties of these CuPc nanoparticles depend on the size of the particles. The band gap increases as the size decreases. Further reduction in size of the particles may result in more significant shifts which could be useful for altering the properties of electronic and optoelectronic devices.

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Author Biographies

Mohammad AL-Amar *received his B.Sc in Physics from Yarmouk University in Irbid, Jordan. He received another B.Sc in Electronic Engineering technology and Computer Information system from Minnesota State University in Mankato, Minnesota. He received his MS in Physics and is currently enrolled in PhD program at Western Michigan University. His research interests are in Organic semiconductor materials, Nanoparticles and Solar cells.*

Clement Burns *is Professor in Physics at Western Michigan University. He received his Ph. D. in Physics from the University of California at San Diego. His research includes studies of organic semiconductors for solar cell applications and x-ray scattering studies of highly correlated systems.*