

Recent Research in Science and Technology 2012, 4(8): 109-111
 ISSN: 2076-5061
 Available Online: <http://recent-science.com/>



UV-VIS spectroscopy as a nondestructive and effective characterization tool for II-VI compounds

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Abstract

The characterization of size dependent optical properties of Group II-VI semiconductor particles provide a lot of qualitative and quantitative information about them like size, quantum yield, monodispersity, shape and presence of surface defects. Presently a review of UV-vis optical absorption spectroscopy is described for extracting useful information about these nanomaterials for the analysis of their optical properties with special reference to semiconducting quantum dots.

Keywords: UV-VIS spectroscopy, nondestructive and effective characterization

INTRODUCTION

Absorption spectroscopy, in general, refers to characterization techniques that measure the absorption of radiation by a material, as a function of the wavelength. Depending on the source of light used, absorption spectroscopy can be broadly divided into infrared and UV-visible spectroscopy. The minimum energy required to excite an electron from the valence states of the semiconductor QDs to its conduction states, lies in the UV-visible region. This is also a reason why most of the Group II-VI semiconductor quantum dot solutions are colored. This technique is complementary to fluorescence spectroscopy, in that UV-visible spectroscopy measures electronic transitions from the ground state to the excited state, whereas fluorescence deals with the transitions from the excited state to the ground state. The UV-visible absorbance spectroscopy is a characterization technique in which the absorbance of the material is studied as a function of wavelength. The UV-visible spectrophotometer analyzes over the wavelength range 200 – 900 nm. A quantum dot can absorb energy in the form of light over a range of wavelengths, to excite an electron from the ground state to its excited state. The minimum energy that is required to excite an electron, is dependent on the band gap of the quantum dot. Thus, by making accurate measurements of light absorption at different wavelengths in the ultraviolet and visible spectrum, a correlation can be made between the band gap and size of the quantum dot. II-VI semiconductor quantum dots are of particular interest, since their band gap lies in the visible region of the solar spectrum.

Instrumentation and procedure:

A working schematic of the UV-visible spectrophotometer is shown in Fig.1. A combination of a deuterium lamp for the UV region of the spectrum and tungsten or halogen lamp for the visible region is used to cover the entire visible and the near ultra-violet region (200 - 900 nm). This output is then sent through a diffraction grating as shown in the schematic. The beam of light from the visible and/or UV light source is then separated into its component wavelengths (like a very efficient prism) by a diffraction grating. Following the slit is a slit that sends a monochromatic beam into the next section of the spectrophotometer.

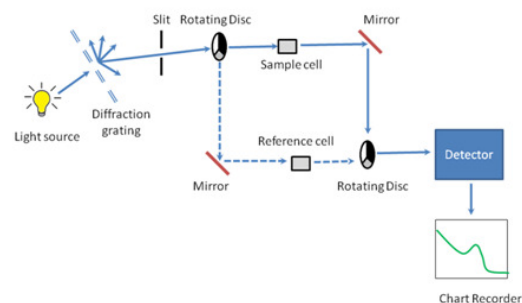


Fig 1. Schematic of UV-visible spectrophotometer.

Light from the slit then falls onto a rotating disc. Each disc consists of an opaque black section, a transparent section and a mirrored section. If the light hits the transparent section, it will go straight through the sample cell, get reflected by a mirror, reaches the mirrored section of a second rotating disc, and then collected by the detector. If the light hits the mirrored section, gets reflected by a mirror, passes through the reference cell, hits the transparent section of a second rotating disc and then collected by the detector. Finally if the light hits the black opaque section, it is blocked, thus enabling the system to make corrections for any current generated by the detector in the absence of light.

Sample cell, reference cell and sample preparation

For liquid samples, a square cross section tube sealed at one end is used. The best cuvettes need to be very clear and have no impurities. Defects on the cuvette such as scratches, can scatter light and hence should be avoided. For Group II-VI semiconductor nanoparticles prepared in organic solvents, the quartz cuvette is chosen. The choice of cuvette depends on the following factors:

Solvent - For aqueous samples, specially designed rectangular quartz, glass or plastic cuvettes are used. For organic samples glass and quartz cuvettes are used.

Excitation wavelength – Depending on the size and thus, bandgap of the II-VI semiconductor nanoparticles, different excitation

wavelengths of light are used. Depending on the excitation wavelength, different materials are used

Cost – Plastic cuvettes are the least expensive and can be discarded after use. Though quartz cuvettes have the maximum utility, they are the most expensive, and need to be reused. Generally, disposable plastic cuvettes are used when speed is more important than high accuracy.

In the sample cell the quantum dots are dispersed in a solvent, whereas in the reference cell the pure solvent is taken. It is important that the sample be very dilute (maximum first exciton absorbance should not exceed 1 au) and the solvent is not UV-visible active. For these measurements, it is required that the solvent does not have characteristic absorption or emission in the region of interest. Solution phase experiments are preferred, though it is possible to measure the spectra in the solid state also using thin films, powders, etc.

Detector converts the light into a current signal that is read by a computer. Higher the current signal, greater is the intensity of the light. The computer then calculates the absorbance using the following equation, where A denotes absorbance, I is sample cell intensity and I_0 is the reference cell intensity.

$$A = \log_{10}(I/I_0) \quad (1)$$

The following cases are possible:

- Where $I < I_0$ and $A < 0$. This usually occurs when the solvent absorbs in the wavelength range. Preferably the solvent should be changed, to get an accurate reading for actual reference cell intensity.
- Where $I = I_0$ and $A = 0$. This occurs when pure solvent is put in both reference and sample cells. This test should always be done before testing the sample, to check for the cleanliness of the cuvettes.
- When $A = 1$. This occurs when 90% of the light at a particular wavelength has been absorbed, which means that only 10% is seen at the detector. So I_0/I becomes $100/10 = 10$. \log_{10} of 10 is 1.
- When $A > 1$. This occurs in extreme case where more than 90% of the light is absorbed.

The output is the form of a plot of absorbance against wavelength,

Analysis of data

The data obtained from the spectrophotometer is a plot of absorbance as a function of wavelength. Quantitative and qualitative data can be obtained by analysing this information

Quantitative Information

The band gap of the semiconductor quantum dots can be tuned with the size of the particles. The minimum energy for an electron to get excited from the ground state is the energy to cross the band gap. In an absorption spectra, this is given by the first exciton peak at the maximum wavelength (λ_{max}).

Size of the quantum dots

The size of quantum dots can be approximated corresponding to the first exciton peak wavelength. Empirical relationships have been determined relating the diameter of the quantum dot to the wavelength of the first exciton peak. The empirical relationships are determined by fitting experimental data of absorbance versus wavelength of known sizes of particles. For example, if the first exciton peak of a CdSe quantum dot is 500 nm, the corresponding diameter of the quantum dot is 2.345 nm and for a wavelength of 609 nm, the corresponding diameter is 5.008 nm.

Concentration of sample

Using the Beer-Lambert law, it is possible to calculate the concentration of the sample if the molar absorptivity for the sample is known. The molar absorptivity can be calculated by recording the absorbance of a standard solution of 1 mol/dm³ concentration in a standard cuvette where the light travels a constant distance of 1 cm. Once the molar absorptivity and the absorbance of the sample are known, with the length the light travels being fixed, it is possible to determine the concentration of the sample solution. Empirical equations can be determined by fitting experimental data of extinction coefficient per mole of Group 12-16 semiconductor quantum dot. The concentration of the quantum dots can then be determined by using the Beer Lambert law.

Qualitative Information

Apart from quantitative data such as the size of the quantum dots and concentration of the quantum dots, a lot of qualitative information can be derived from the absorption spectra.

Size distribution

If there is a very narrow size distribution, the first exciton peak will be very sharp. This is because due to the narrow size distribution, the differences in band gap between different sized particles will be very small and hence most of the electrons will get excited over a smaller range of wavelengths. In addition, if there is a narrow size distribution, the higher exciton peaks are also seen clearly.

Shaped particles

In the case of a spherical quantum dot, in all dimensions, the particle is quantum confined. In the case of a nanorod, whose length is not in the quantum regime, the quantum effects are determined by the width of the nanorod. Similar is the case in tetrapods or four legged structures. The quantum effects are determined by the thickness of the arms. During the synthesis of the shaped particles, the thickness of the rod or the arm of the tetrapod does not vary among the different particles, as much as the length of the rods or arms changes. Since the thickness of the rod or tetrapod is responsible for the quantum effects, the absorption spectrum of rods and tetrapods has sharper features as compared to a quantum dot. Hence, qualitatively it is possible to differentiate between quantum dots and other shaped particles.

Crystal lattice information

In the case of CdSe semiconductor quantum dots it has been shown that it is possible to estimate the crystal lattice of the quantum dot from the adsorption spectrum and hence determine if the structure is zinc blend or wurtzite.

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