# SPECTROGRAPHS FOR ANALYZING NANOMATERIALS

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*ABSTRACT*

The optical schemes of high numerical aperture spectrographs based on concave holographic diffraction gratings are described. A calculations of an optical schemes using flat field spectrograph method for analyzing the fluorescence of all kinds of Quantum dots in a wide range of wavelengths with spectral resolution of 6,3 nm are submitted. A special calculation of spectrographs for investigating CdSe/ZnS, InP Quantum dots with high resolution of 1 nm are given because of their wide uses.

An experimental mounting for analyzing Raman scattering in carbon nanotubes is described. Experimental results are given. On the basis of these results the requirements for optical characteristics of a compact specialized spectrograph for analyzing Raman scattering in carbon nanotubes are developed. The calculation of an optical scheme using flat field spectrograph method with spectral resolution of 3.5 $cm^{-1}$ is submitted.

**Keywords:** Quantum Dots, carbon nanotubes, fluorescence, Raman scattering, spectrograph, holographic diffraction gratings, an optical scheme, aberration.

## *INTRODUCTION*

We calculated the various options for optical schemes spectrographs to study the two types of nanomaterials -quantum dots and carbon nanotubes.

Highly and long luminescent lifetime quantum dots (QDs) potentially can overcome the functional limitations encountered with chemical and organic dyes. They are highly stable against photobleaching and have narrow, symmetric emission spectra. In particular, the emission wavelength of QDs can be continuously tuned by changing the particle size or composition, and a single light source can be used for simultaneous excitation of all different coloured dots. In practice, by variation of size and composition of QDs, the luminescence photon energy can be tuned in steps of 30 nm from the IR to the UV. These novel remarkable spectral properties can render QDs ideal fluorophores for sensitive, multicolour, and multiplexing applications in molecular bioengineering, medicine, photonic studies, micro-electronics and optoelectronical devices [1, 2].

The most commonly used to study the carbon nanotubes (CNT) Raman scattering, because this method requires minimal sample preparation and is

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quite informative[3]. To study the possibility of investigating CNT Raman scattering in the spectrograph low resolution, we also developed an experimental mounting to analyze the Raman scattering.

For analysis of the fluorescence spectra and Raman scattering, a high numerical aperture spectral instruments with low level detection and enough high resolution are required. To these conditions satisfy the optical schemes based on concave holographic diffraction gratings with aberration correction.

In this paper we represent calculations of different optical schemes intended for analyzing nanomaterials.

## ***THE OPTICAL SCHEMES SPECTROGRAPHS*** FOR ANALYZING OF QUANTUM DOTS

The wavelength range of QDs fluorescence emission are given in *Table 1* [4].

Table 1. Emission wavelength range of some QDs

| Material of QDs | Emission wavelength range, nm |
|---|---|
| ZnS | 300-380 |
| CdS | 380-460 |
| ZnSe | 360-500 |
| CdSe (CdSe/ZnS) | 480-660 |
| CdTe | 600-1000 |
| CdHgTe/ZnS | 630-860 |
| InP | 650-750 |
| InAs | 830-1350 |
| PbS | 700-1600 |

Taking into account, that as the receiver of radiation in modern devices, mainly, multichannel photo-electric receivers (array) are used, as optical system we have chosen the flat-field spectrograph (*Fig. 1*).

*1. An optical scheme with one grating*

To built one spectrograph to investigate all kind of QDs fluorescence, we need to calculate the parameters of the optical scheme that can detect the fluorescence in a wide range of wavelengths from 300-1600 nm.

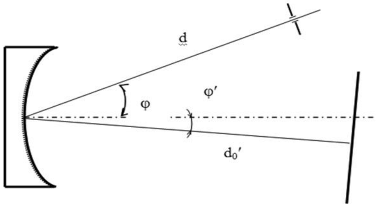


**Fig. 1** - Optical scheme for a flat-field spectrograph

The parameters of the scheme are determined from relationships for “flat-field spectrograph” [5], which provide an aberration correction of coma, defocus and astigmatism. The spectrograph has the following parameters: the spectral range 300-1600 nm, grating curvature radius of 200 mm, ruled surface diameter of 50 mm, the groove density of the grating 110 1/mm, the length of the spectra of 29 mm

$d$ = 197.9 mm, $d_0'$ = 197.842 mm, $\varphi$ = 09° 05' 23", $\varphi'_{950}$ = - 03° 03' 56".

The recording parameters of the grating are:

$d_1$=200.075 mm, $d_2$= 202.007 mm, $i_1$=09° 32' 28", $i_2$= 06° 43' 46".

The aberrations are given in the *table 2*.

Table 2. Aberrations of the spectrograph with one grating

| y | z | λ = 300 nm, y'= -14,23 | | λ = 950 nm, y'= 0 | | λ = 1600 nm, y'= 14,18 | |
|---|---|---|---|---|---|---|---|
| | | δ y' | δ z' | δ y' | δ z' | δ y' | δ z' |
| 25 | 0 | -0,077 | 0 | 0,040 | 0 | -0,077 | 0 |
| 12,5 | 0 | -0,04 | 0 | 0,020 | 0 | -0,039 | 0 |
| -12,5 | 0 | 0,039 | 0 | -0,020 | 0 | 0,042 | 0 |
| -25 | 0 | 0,074 | 0 | -0,040 | 0 | 0,090 | 0 |
| 0 | 12,5 | 0,002 | 0,32 | -0,001 | 0 | -0,002 | -0,32 |
| 0 | 25 | 0,008 | 0,64 | -0,003 | 0 | -0,007 | -0,64 |

The instrumental function when we use entrance slit width of 0,1 mm do not exceed 0,14 mm. As the reciprocal linear dispersion is 45 nm/mm, we obtain a resolution of 6,3 nm. Taking into account that the bandwidth at half maximum of the fluorescence line is 20-25 nm at room temperature, we have a good resolution. Instrumental function for the three wavelengths (the center and the edges of the spectral range) is represented in *figure 2*.

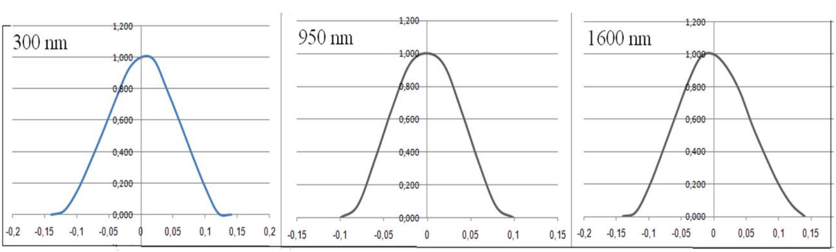


**Fig. 2** - The instrumental function for three wavelengths

*2. An optical scheme with two changeable gratings*

To get a better resolution the spectral range is separated into two sub-ranges with two different gratings, but one optical scheme. First sub-range is 300-700 nm, it is for the ZnS, CdS, ZnSe, CdSe and CdSe/ZnS quantum dots. the second one is 600-1600 nm, it is for the CdTe, CdHgTe/ZnS, InP, InAs and PbS.

The parameters of the scheme are:

$d$ = 197.9 mm, $d_0'$ = 197.977 mm, $\varphi$ = 10° 10' 05", $\varphi'_{500,1100}$ = - 01° 17' 29".

The first grating has a groove density of 308 1/mm, and the following recording parameters:

$d_1$=198,569 mm, $d_2$= 202,14 mm, $i_1$=10° 05' 30", $i_2$= 02° 14' 50".

The aberrations are given in the *table 3*.

Table 3. Aberrations of the spectrograph with changeable gratings – first grating

| y | z | λ = 300 nm, y'= -12,23 | | λ = 500 nm, y'= 0 | | λ = 700 nm, y'= 12,12 | |
|---|---|---|---|---|---|---|---|
| | | δ y' | δ z' | δ y' | δ z' | δ y' | δ z' |
| 25 | 0 | -0,0578 | 0 | 0,032 | 0 | -0,072 | 0 |
| 12,5 | 0 | -0,0309 | 0 | 0,016 | 0 | -0,033 | 0 |
| -12,5 | 0 | 0,0324 | 0 | -0,016 | 0 | 0,031 | 0 |
| -25 | 0 | 0,064 | 0 | -0,032 | 0 | 0,061 | 0 |
| 0 | 12,5 | -0,0013 | 0,2 | 0 | 0 | 0 | -0,2 |
| 0 | 25 | -0,0054 | 0,4 | 0,001 | 0 | 0,001 | -0,4 |

The instrumental function when use entrance slit width of 0,1 mm do not exceed 0,1 mm, as the reciprocal linear dispersion is 14 nm/mm, we obtain a resolution of 1,4 nm.

The second grating has a groove density of 140 1/mm, and the following recording parameters:

$d_1$=199,91 mm, $d_2$= 201,535 mm, $i_1$=07° 57' 59", $i_2$= 04° 24' 10".

The aberrations are given in the *table 4*.

Table 4. Aberrations of the spectrograph with changeable gratings – second grating

| □y | z | λ = 600 nm, y'=-13,9mm | | λ = 1100 nm, y'= 0 | | λ = 1600 nm, y'= 13,88mm | |
|---|---|---|---|---|---|---|---|
| | | δ y' | δ z' | δ y' | δ z' | δ y' | δ z' |
| 25 | 0 | -0,085 | 0 | 0,032 | 0 | -0, 096 | 0 |
| 12,5 | 0 | -0,045 | 0 | 0,016 | 0 | -0,048 | 0 |
| -12,5 | 0 | 0,046 | 0 | -0,016 | 0 | 0,044 | 0 |
| -25 | 0 | 0,092 | 0 | -0,032 | 0 | 0,088 | 0 |
| 0 | 12,5 | -0,002 | 0,227 | 0 | 0 | 0 | -0,228 |
| 0 | 25 | -0,007 | 0,456 | 0 | 0 | -0,001 | -0,458 |

The instrumental function when use entrance slit width of 0,1mm do not exceed 0,1mm, as the reciprocal linear dispersion is 35 nm/mm, we obtain a resolution of 3,5 nm.

*3. Special optical scheme with high resolution*

For more resolution we carried out in special the calculation of the optical schemes for two types of QDs - CdSe/ZnS and InP, the most wide spread QDs.

The parameters of the scheme are determined from empirical relationships for "spectrograph with the extended spectral range" [5], providing a flat spectrum with astigmatism and meridional coma correction for two wavelengths located symmetrically relative to the spectrogram center and edges:

$$d = r(1,01056 - 0,0393k\lambda_{m.}N),$$

$$d'_0 = r[1,0037 - 0,014k\lambda_{m.}N + 0,058(k\lambda_{m.}N)^2],$$

$$\varphi = -0,016 + 0,748k\lambda_{m.}N.$$

$k$ - order of diffraction, $\lambda_m$ - middle wavelength of the spectral range.

The spectrograph for CdSe/ZnS has the following parameters: the spectral range 480-660 nm, grating curvature radius r = 100 mm, ruled surface diameter of 33 mm, the groove density of the grating 500 1/mm, the length of the specter of 9 mm, $d$ = 99,94 mm, $d'$=100,44 mm, φ=11°18′, reciprocal linear dispersion of 20 nm/mm.

The spectrograph for InP has the following parameters: the spectral range 600-780 nm, grating curvature radius of 100 mm, ruled surface diameter of 33 mm, the groove density of the grating 500 1/mm, the length of the spectra of 9 mm, $d$ = 99,7 mm, $d'$=100,58 mm, φ=13°52′, reverse linear dispersion of 20 nm/mm.

The recording parameters of the concave holographic diffraction gratings provide the aberration correction: bandwidth at half maximum of instrumental functions of the spectrographs for an input slit of 0,05 mm on all field does not exceed 0,05 mm and the astigmatic extension do not exceed 0,03 mm.

The calculations were performed for center entrance slit (l = 0). When l = 1mm for an input slit of 0,05 mm on all field does not exceed 0,08 mm and the astigmatic extension do not exceed 0,08 mm for CdSe/ZnS and 0,03 mm for InP. Aberrations of the meridional and sagittal cross sections are practically identical, that allows to relate this schema to the imaging diffraction grating.

A similar method was used to calculate a spectrograph for investigating CdSe QDs. A ultra high resolution of 0.25 nm was obtained using a cylindrical lens to correct the residual aberration in front of the photo-detector [6].

## *THE OPTICAL SCHEME OFSPECTROGRAPH* FOR ANALYZING RAMAN SCATTERING IN CARBON NANOTUBES

*1. The experimental mounting*

To determine the feasibility of developing a compact device on modern element base - compact diode lasers, holographic concave diffraction gratings, and diode arrays as detectors, established the experimental mounting based on the spectrograph Sirius [7]. The unit includes: a source of laser radiation, a collimator, short-throw lens aperture, the substrate to be coated test substance, a spherical mirror that collects the scattered radiation, and sends it to the entrance slit, Notch-filter aperture spectrograph. Spectrographs to study the Raman spectra should be of great luminosity, low levels of ambient light and a large variance. The spectrograph Sirius meets these requirements: it has a relative aperture 1:3, its optical scheme is based on holographic diffraction gratings with correction of aberrations and has a minimal number of optical components. The studies were conducted with a diffraction grating 1153gr./mm, which provides a working spectral range 486-680 nm. The spectrograph is equipped with a multichannel recording system based on the spectrum of the diode line with the number of pixels 2048 and a pixel size of 1914 * 150 microns. To suppress the laser beam in front of the entrance slit set Notch-filter [8]. In the experiments, spectra were obtained by surface-enhanced Raman scattering (SERS) on silver substrate. *Figure 2* shows spectrum of carbon nanotubes obtained under the following conditions: laser power 200 mW at 532 nm with a Notch-filter, the relative aperture of 1:4, the width of the entrance slit of 50 microns.

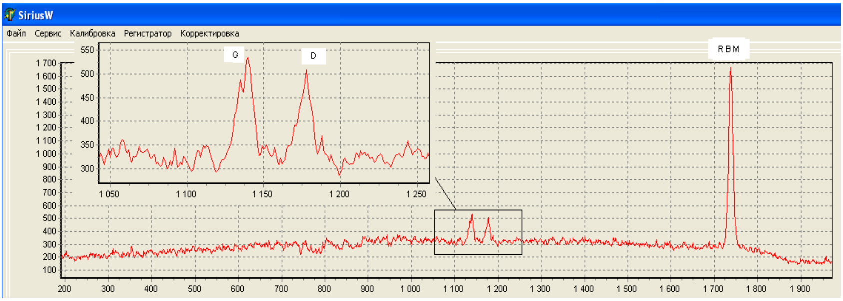


**Fig. 2** – The spectrum of carbon nanotubes

Raman shift Δ ν lines for RBM, D and G was 475 $cm^{-1}$, 1436 $cm^{-1}$ and 1511 $cm^{-1}$, respectively.

*2. The optical scheme of the spectrograph*

Our experiments allowed to form the following requirements for the optical system of the spectrograph: the relative aperture of 1:4, the width of the entrance slit of 50 mm, the working spectral range of 536-622 nm, reciprocal linear dispersion of 3 nm / mm and a length range of 29 mm. In accordance with these requirements was designed optical layout according to the method of calculation of the spectrograph with a flat field.

To obtain a higher resolution before the receiver is a cylindrical concave-plane lens with a radius of curvature of 50 mm. The design parameters of the scheme with the lens have the following meanings: d = 205 mm, d0 '= 205,47 mm, φ = 310 37' 45 '', φ'579 = -160 37 '45'', N = 1400 gr./ mm, and recording parameters of the grating: $d_1$=488,048 mm, $d_2$=211,145 mm, $i_1$=720 39 '34 '', $i_2$ = 190 39' 08''. Instrumental function of the spectrograph across the field does not exceed 0,035 mm, which corresponds to the spectral resolution of 0,1 nm or 3,5 cm-1.

## *CONCLUSIONS*

Thus, using the concave holographic diffraction gratings with aberration correction we can be created compact spectrographs with the high enough optical characteristics to investigate Quantum dots fluorescence and the Carbon nanotubes Raman scattering.

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