Chapter 2: Experiments

2. 1 Sample preparation

For the preparation of CdSe nanocrystal, 0.3 g of cadmium oxide (CdO), 1.3 g of tretradecylphosphonic acid (TDPA) and 25.0g of tri-n-octylphosphine oxide (TOPO) were mixed together in a 250 mL reaction flask, and then heated to 320℃ under argon flow. As CdO dissolved totally in TDPA and TOPO, the solution became optically clear. Subsequently, 4.45 mL of 0.5 M selenium stock solution with tributylphosphine (TOP) was rapidly injected into the reaction mixture. The solution was kept at approximately 240℃.

To cover the ZnS layer, 1.5 mL of Zn and S precursor solution was added, with 1.75mL of 2.0M dimethyliznc ($ZnMe_2$) in toluene and bis(trimethylsilyl)sulfide ($(TMS)_2S$) in TOP. A total mole ratio of injected reagent was 1:4 (CdSe: ZnS). After cooled the reaction mixture to room temperature, the QDs were purified by the precipitation with anhydrous methanol. A schematic for the synthesized process steps is shown in Figure 2.1.1. The sample parameters are listed in Table2.1.1

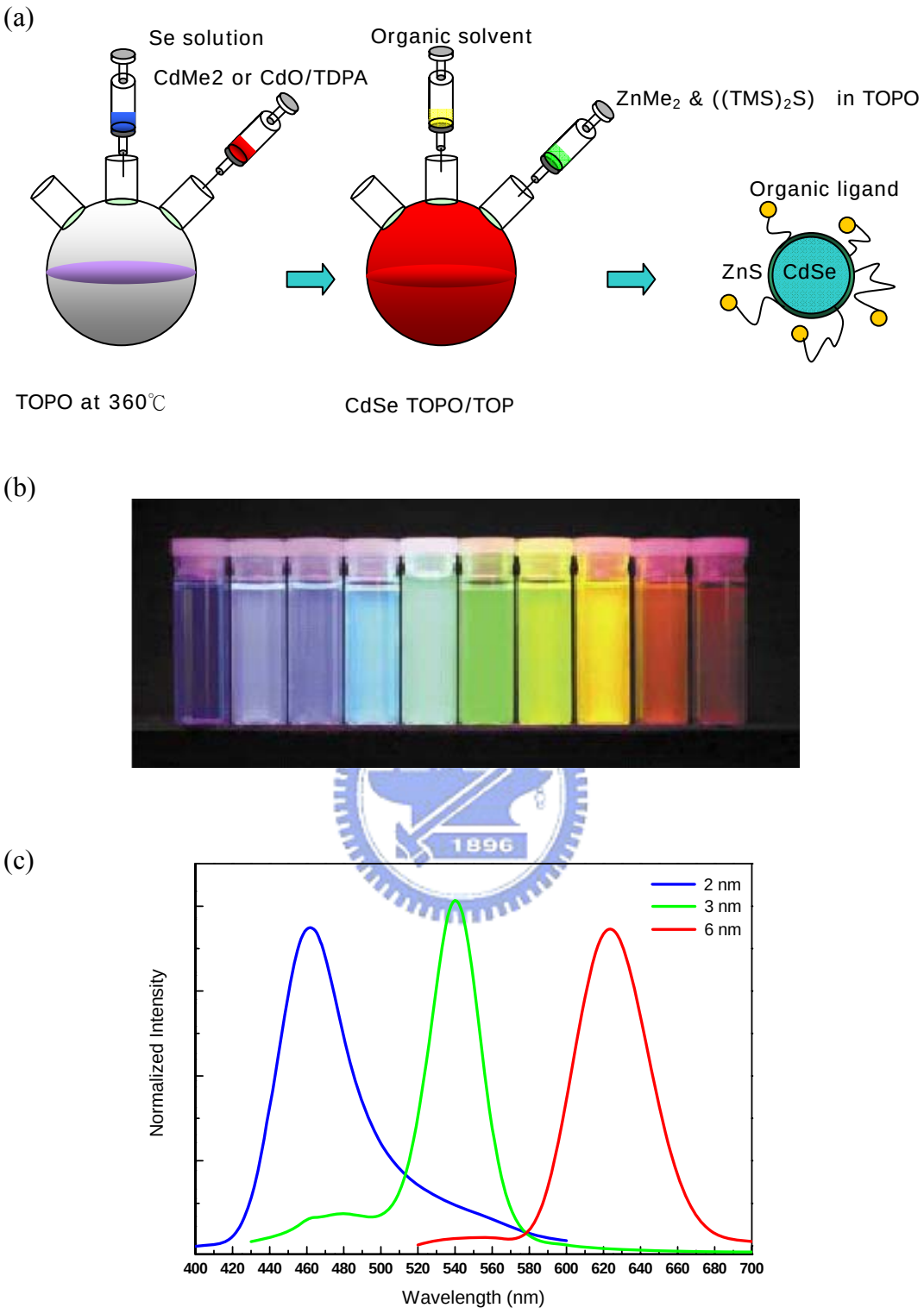

Figure 2.1.1 (a) Synthesis of CdSe colloidal QDs (b) Emission of CdSe QD which is immersed in chloroform solution illuminated by UV light (c) PL spectra for three kinds of QD sizes.

Table 2.1.1 Sample parameters.

Sample	Diameter(nm)	Surface ligand	Solution
CdSe/ZnS	2	-	chloroform
CdSe/ZnS	3	-	chloroform
CdSe/ZnS	6	-	chloroform
CdSe	3	TOPO	chloroform
CdSe	3	TOPO-HDA	chloroform
CdSe	3	TOPO-HDA-PA	chloroform
CdSe	3	TOPO-HDA,PA	chloroform
CdSe/ZnS	3	TOPO	chloroform
CdSe/ZnS	3	TOPO-HDA	chloroform
CdSe/ZnS	3	TOPO-HDA-PA	chloroform
CdSe/ZnS	3	TOPO-HDA,PA	chloroform
Au	13	-	water

※ TOPO (trioctylphosphine oxide) :(CH3-(CH2)7)3-P=O
HDA (hexadecylamine): CH3-(CH2)15-NH2
PA (pylamine): C3H7N

2.2 Measurement techniques

2.21 Photoluminescence

The experimental setup for photoluminescence is shown in Figure 2.2.1 .The high sensitive JASCO FP-6500 spectrofluorometer is mainly utilized for biochemistry performance. The sample is mounted in the water thermal-stable single cell holder. The excitation source is DC-powered 150W Xenon lamp whose wavelength covers 200~750nm. The excitation and emission wavelength is dispersed by holographic concave grating with 1800nm grooves/nm, and the resolution of monochromator is about 1nm to 2nm. The photon signal is collected by photo-multiplier-tube (PMT). Here, the concentration of the sample solutions is all 10^{-5}M, and the light spot is about 10^{-6}L, so the total number of illuminated QD is 10^{11}.

2.22 Time-Resolved photoluminescence system (see Figure 2.2.2)

Excitation Subsystem

The excitation with 50 ps duration, at the wavelength of 400nm is provided by GaN pulsed diode laser. The corresponding controller is PDL 800-B driver. The repetition frequency can be reduced by the divider knob to 1, 1/2, 1/4, 1/8, 1/16 of 40 MHz base frequency either. The beams couple to the main optical unit by the polarization maintaining single mode optical fiber.

Optical Microscope

The Olympus IX71 is a versatile inverted optical microscope. The multi-port design is conventional for adding the equipment. The equipped tungsten lamp is used for transmitted illuminator. The 100× oil objective with 0.13mm working distance and

1.4 numerical aperture has been chosen. The vertical focus position can be tuned manually with 1μm resolution. Specially, the P-733 piezo-scanner provides a positioning and X-Y plane scanning range of $80\times80\mu m^2$ with 1nm resolution.

Main optical unit of MicroTime 200 system (See Figure 2.2.3)

Single Photon Avalanche Photo Diode (SPAD)

The SPAD is usually used for ultra-low light detection (optical power <1 pW), and restricted to operation in UV to infrared part (400nm~1100nm) of spectrum. The SPAD may have great quantum efficiency (about 48% maximum), although it has larger noise than the PMT. At the bias voltage slightly less than the breakdown voltage, the gain represents linear amplification up to 500 times. In the opposite biased condition, which is known as Geiger mode, a single photon will trigger an avalanche of about 10^8 carriers, and thus the gain will be dramatically increased. The later case is more sensitive for single photon detection. The photon arrival timing accuracy may achieve 200 ps or less.

Charged Coupled Device (CCD)

The CCD camera is consisted of few thousand photodiodes (also called “pixel” here). Every photodiode has red, green, blue sensor collectively. Generally, the linear CCD camera is used for wild field imaging. For our request, it is primitively used for optical alignment from the laser beam waist image. The GANZ ZC-F10C2 CCD camera has a 500×582 pixel sensor. There are preset functions including back light compensation mode, auto iris mode, and synchronization mode.

Power Photodiode

The photodiode set in the main optical unit is utilized to measure the excitation throughput.

Optical Components

The selective optical components are as follows: collimating lens, notch filter, tube lens, dichroic mirror, reflection mirror, beam splitter and pinhole. Take the notice of the pinhole behind the detection tube lens. This pinhole with 50 μm diameter is set at the confocal position exactly, and it plays an important role of image resolution.

Computer Driver and Analyzing Software

For time-correlated single photon counting data (TCSPC) acquisition, the powerful and unique board Time Harp 200 is utilized. The pivotal mode in the system is called Time-Tagged Time-Resolved (TTTR). Based on the TTTR data collection, users can perform the complete analysis by the built-in functions, including Time Correlated Single Photon Counting (TCSPC) histogram, Fluorescence Correlation Spectra (FCS) trace, or fluorescence image analysis and so on.

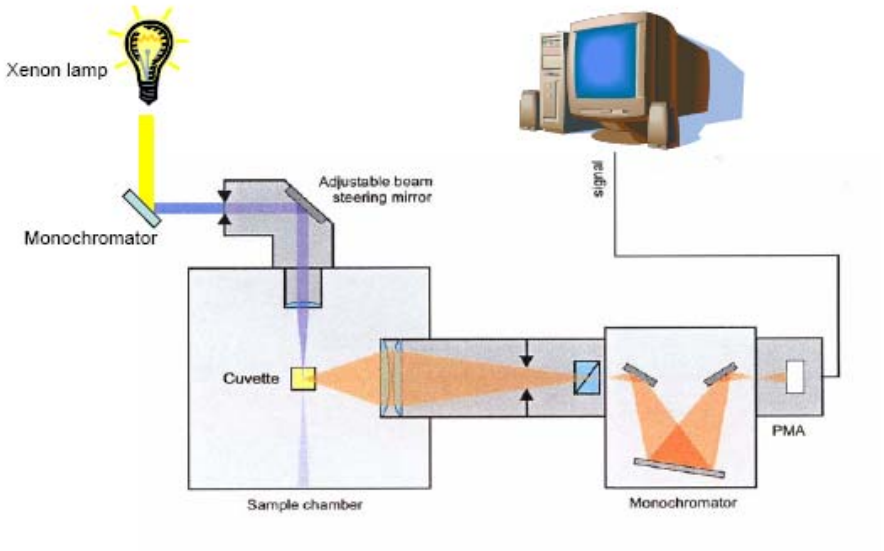

Figure 2.2.1 Photoluminescence system.

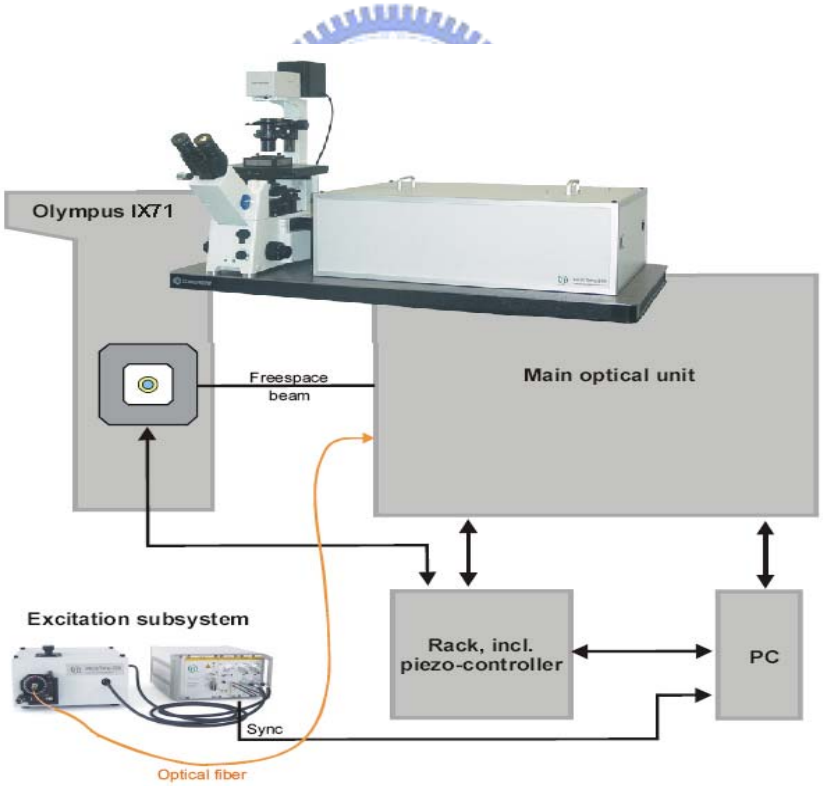

Figure 2.2.2 MicroTime 200 time-resolved photoluminescence system.

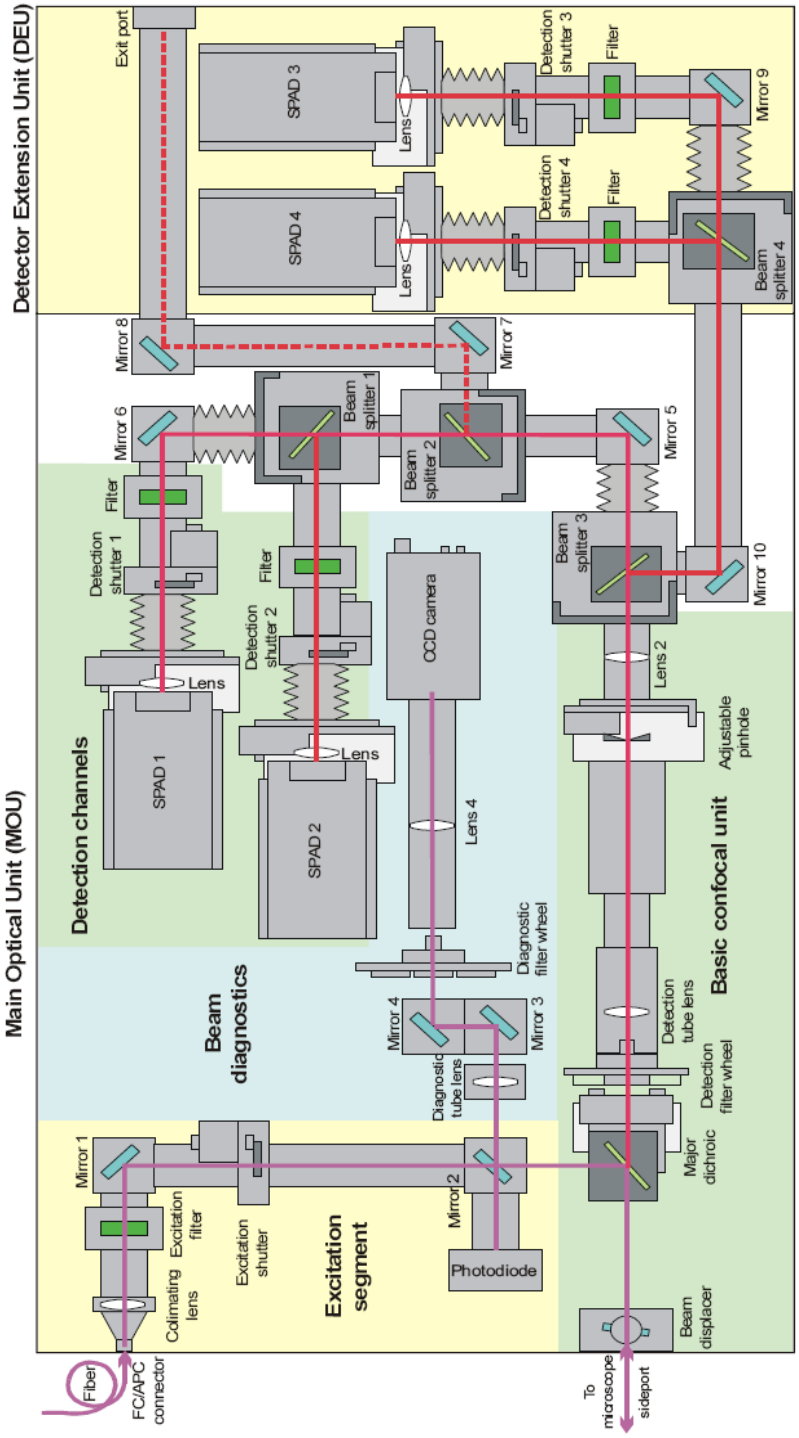

Figure 2.2.3 Main optical units of MicroTime 200.