Lesson 7
Case Studies

You Will Learn Instrumentation for:

- **A. Monitoring synthetic procedure *in situ***
- **B. Electrochemistry**
- **C. Spectroelectrochemistry**

- **As well as data treatment and presentation**

A. Monitoring synthetic procedure *in situ*

It is known that the smaller the size of the nanoparticle, the shorter the wavelength they absorb. ---Quantum Confinement (http://pubs.acs.org/cgi-bin/archive.cgi/jacsat/1993/115/i19/pdf/ja00072a025.pdf)

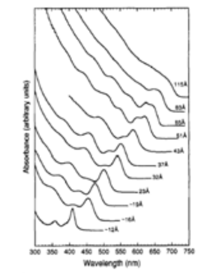
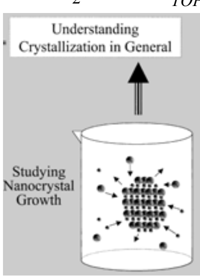


Figure 3. Room temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from ~12 to 115 Å.

C. B. Murray, D. J. Norris, M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites", *Journal of the American Chemical Society* 115 (1993) 8706-8715.

Preparation of monodispersed CdSe nanoparticles is desirable. Peng et al reported that these nancrystals can be made in a benign way:

$$CdAc_2 + Se \xrightarrow[TOP/\Delta]{TOPO} CdSe$$



L. Qu, X. Peng, "Control of Photoluminescence Properties of CdSe Nanocrystals in Growth", *Journal of the American Chemical Society* 124 (2002) 2049-2055.

L. Qu, W. W. Yu, X. Peng, "In Situ Observation of the Nucleation and Growth of CdSe Nanocrystals", *Nano Letters* 4 (2004) 465-469. (http://pubs.acs.org/cgi-bin/asap.cgi/nalefd/asap/html/nl035211r.html)

Post-measurements by Peng et al in 2002

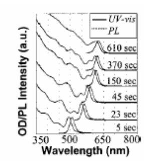
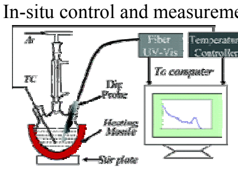
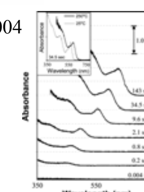


Figure 1. Temporal evolution of UV−vis and PL spectra of a growth reaction of CdSe nanocrystals. See the typical synthesis for details.

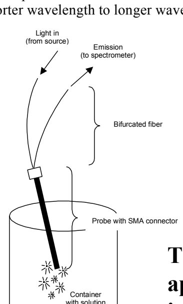
In-situ control and measurements by Peng et al in 2004





Instrumentation:

A dip probe immersed in the reaction solution can be connected with a cost-effective hand-held spectrometer (From Ocean Optics Inc or Aventes), to monitor the UV-VIS absorption spectrum with LabVIEW and to watch absorption peak wavelength shifting from shorter wavelength to longer wavelength, i.e. the particle size becomes larger and larger.

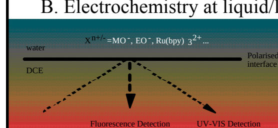


A lamp and a spectrometer interfaced by LabVEW can be connected.

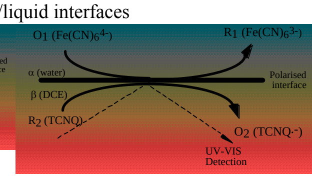
At desired wavelength (i.e. desired size), the reaction can be stopped.

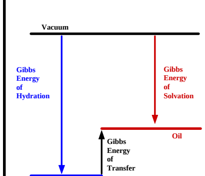
The same principle can be applied for a dip probe in situ infrared spectrometer.

B. Electrochemistry at liquid/liquid interfaces



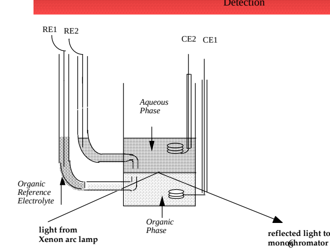
Thermodynamics of Ion Transfer





Gibbs Energy of Transfer

$$\Delta G_{tr,i}^{o,w\to o} = \tilde{\mu}_i^o - \tilde{\mu}_i^w$$



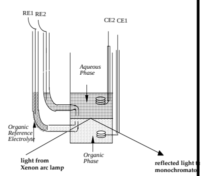
C. Spectroelectrochemistry

1. Introduction

The absorbance of species in solution measured by reflection can be estimated by integration of the Beer-Lambert expression over the distance (x) from the reflecting surface,

$$A^{\mathrm{TIR}} = 2\varepsilon\int_0^\infty \frac{c(x)}{\cos\theta}dx \qquad \int_0^\infty c(x,t)dx = \frac{1}{zFS}\int_0^t I(\tau)d\tau$$

where θ is the angle of incidence of the light beam at the interface, ε is the molar absorption coefficient of the transferring ion in the phase of higher refractive index and $c(x)$ its concentration at a distance x from the interface.



Theory of in-situ UV-VIS and Fluorescence Spectroscopies

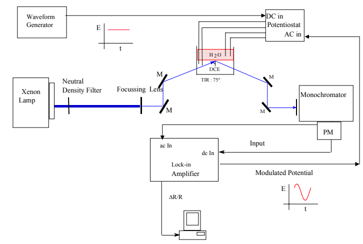
$$A^{\mathrm{TIR}} = \frac{2\varepsilon}{zFS\cos\theta}\int_0^t I(\tau)d\tau \qquad F^o = \frac{2\varepsilon\Phi I_{\mathrm{incid}}}{zFS\cos\theta}\int_0^t I(\tau)d\tau$$

$$\frac{dA^{\mathrm{TIR}}}{dt} = \frac{2\varepsilon}{zFS\cos\theta}I(t) \qquad \frac{dF^o}{dt} = \frac{2\varepsilon\Phi I_{\mathrm{incid}}}{zFS\cos\theta}I$$

2. Instrumentation:

Instruments: waveform generator+potentiostat+Lamp+spectrometer or monochromator PMT

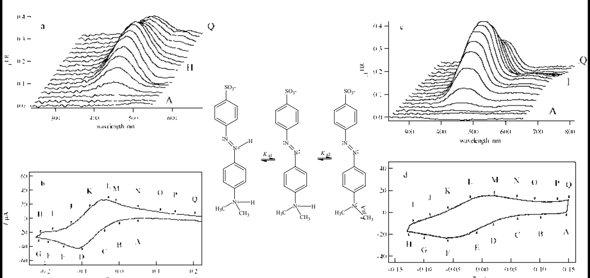
LabVIEW for data acquisition



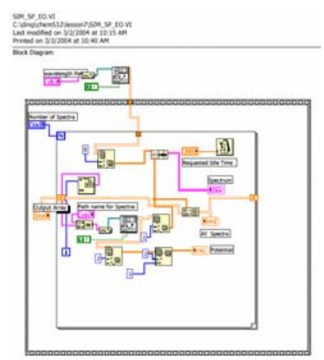
3. Voltabsorptommetry on transfer of methyl and ethyl oranges

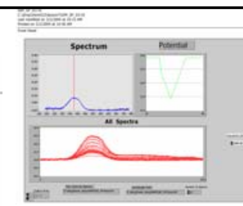
Z. Ding, F. Reymond, P. Baumgartner, D. J. Fermin, P.-F. Brevet, P.-A. Carrupt, H. H. Girault, "Mechanism and dynamics of methyl and ethyl orange transfer across the water/1,2-dichloroethane interface", *Electrochimica Acta* 44 (1998) 3-13.

(http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TG0-3VGV20K-2&_coverDate=09%2F01%2F1998&_alid=152032082&_rdoc=1&_fmt=&_orig=search&_qd=1&_cdi=5240&_sort=d&view=c&_acct=C000048763&_version=1&_urlVersion=0&_userid=940030&md5=eae917920b982fc9a0f06cb8880fa607)



Let's examine SM_SP_EO.vi



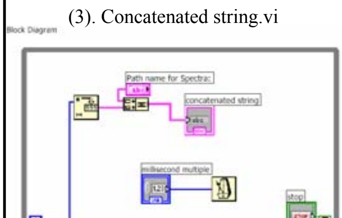


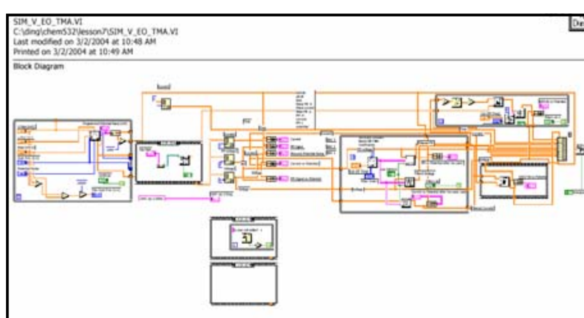
Digestion of the VI

(1). Read From Spreadsheet.vi

(2) How do data flow in LabVIEW----Index Array, Subarray

(3). Concatenated string.vi





For single wavelength (monochromator +PMT):

(1) How to read a spreadsheet file into LabVIEW

(2) How do data flow in LabVIEW

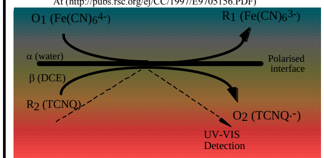
(3) How to filter out noise in LabVIEW

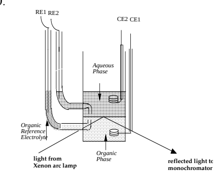
1. Find the **VI from Help»Find Examples...»Search**
2. Type in "lowpass" and **search**
3. Choose EquiRipple Filter Design**.vi**

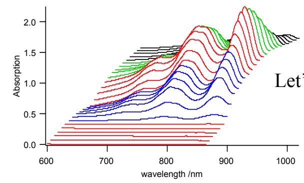
4. Voltabsorptommetry of electron transfer at liquid/liquid interfaces

Z. Ding, P. F. Brevet, "Heterogeneous electron transfer at the polarized water/1,2-dichloroethane interface studied by in situ UV-VIS spectroscopy and differential cyclic voltabsorptometry", *Chemical Communications (Cambridge)* (1997) 2059-2060.

At (http://pubs.rsc.org/ej/CC/1997/E9705156.PDF)







Let's examine SM_SP_TCNQ.vi

References

1. C. B. Murray, D. J. Norris, M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites", *Journal of the American Chemical Society* 115 (1993) 8706-8715.
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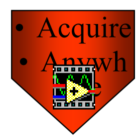
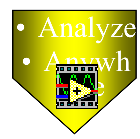
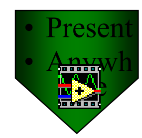
4. Z. Ding, F. Reymond, P. Baumgartner, D. J. Fermin, P.-F. Brevet, P.-A. Carrupt, H. H. Girault, "Mechanism and dynamics of methyl and ethyl orange transfer across the water/1,2-dichloroethane interface", *Electrochimica Acta* 44 (1998) 3-13.
5. Z. Ding, P. F. Brevet, H. H. Girault, "Heterogeneous electron transfer at the polarized water/1,2-dichloroethane interface studied by in situ UV-VIS spectroscopy and differential cyclic voltabsorptometry", *Chemical Communications (Cambridge)* (1997) 2059-2060.
6. Z. Ding, D. J. Fermin, P.-F. Brevet, H. H. Girault, "Spectroelectrochemical approaches to heterogeneous electron transfer reactions at the polarized water/1,2-dichloroethane interfaces", *Journal of Electroanalytical Chemistry* 458 (1998) 139-148.

Summary







In-situ reaction monitoring, electrochemistry, spectroelectrochemistry can easily be done.