



# Synthesis and Characterisation of CdSe Quantum Dots

Alana Concannon and Angze Li

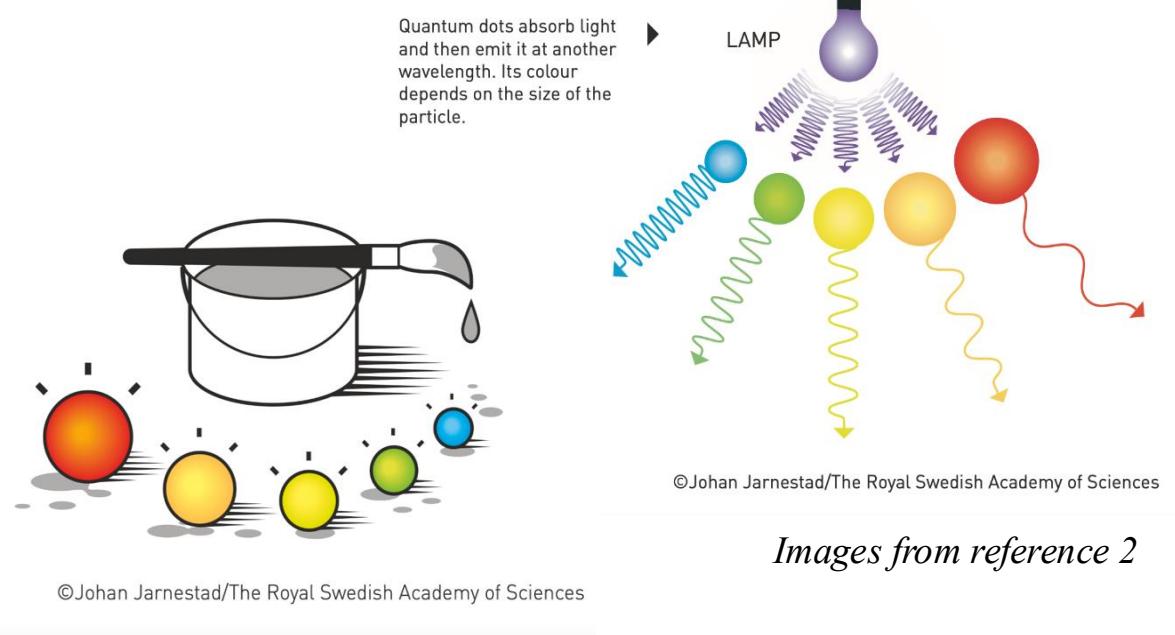
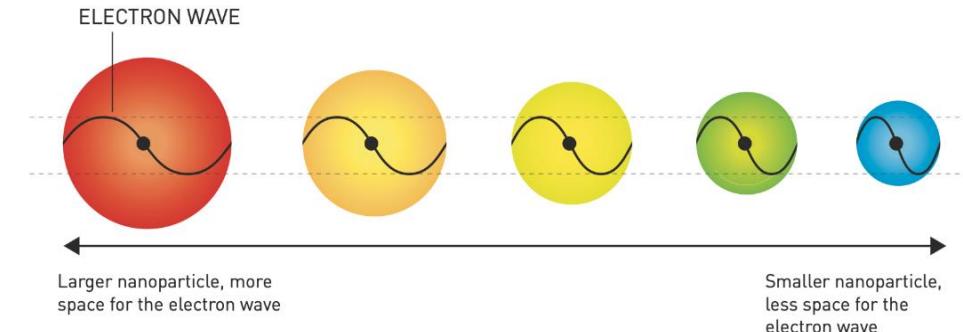


# Introduction

- Quantum dots: unique opportunity for great control over band gap of nanomaterial
- Applications in LEDs, lasers, solar cells, etc.
- CdSe quantum dots show strong confinement of electrons and holes<sup>1</sup>

Quantum effects arise when particles shrink

When particles are just a few nanometres in diameter, the space available to electrons shrinks. This affects the particle's optical properties.



*Images from reference 2*

# Aims of the experiment

1. To synthesise CdSe quantum dots from Cd(oleate) and SeTOP stock solutions
2. Characterise dots using UV-vis and fluorescence spectra and determine dot size using the Brus equation
3. Test different molar ratios of Cd:Se to determine effect on optical properties
4. Determine optimal reaction conditions for controlled particle growth and quantum efficiency

# Methodology

- 10 mL of Cd(oleate) solution with different concentration (diluted by octadecene) heated to 215 °C under reflux, stirring at 650 rpm
- 1 mL of SeTOP then added
- Aliquots (full pipette squeeze) every 30 seconds for the first 8 minutes and at 9:30 and 10:00
- Each aliquot immediately quenched with ~1.5 mL toluene
- Each reaction condition repeated at least twice
- UV-Vis and fluorescence spectra recorded and analysed in python

Run	1	2	3	4	5	6	7	8	9
Cd:Se	1.33:1	1.33:1	1.33:1	1:3	1:5	1.33:1	1:3	1:5	1.33:1
[Cd]	9.18 mM	9.18 mM	9.18 mM	2.31 mM	1.39 mM	9.18 mM	2.31 mM	1.39 mM	9.18 mM
[Se]	6.92 mM	6.92 mM	6.92 mM	6.93 mM	6.93 mM	6.92 mM	6.93 mM	6.93 mM	6.92 mM

# Spectrometer info

## Thermo Unicam UV 500 spectrometer

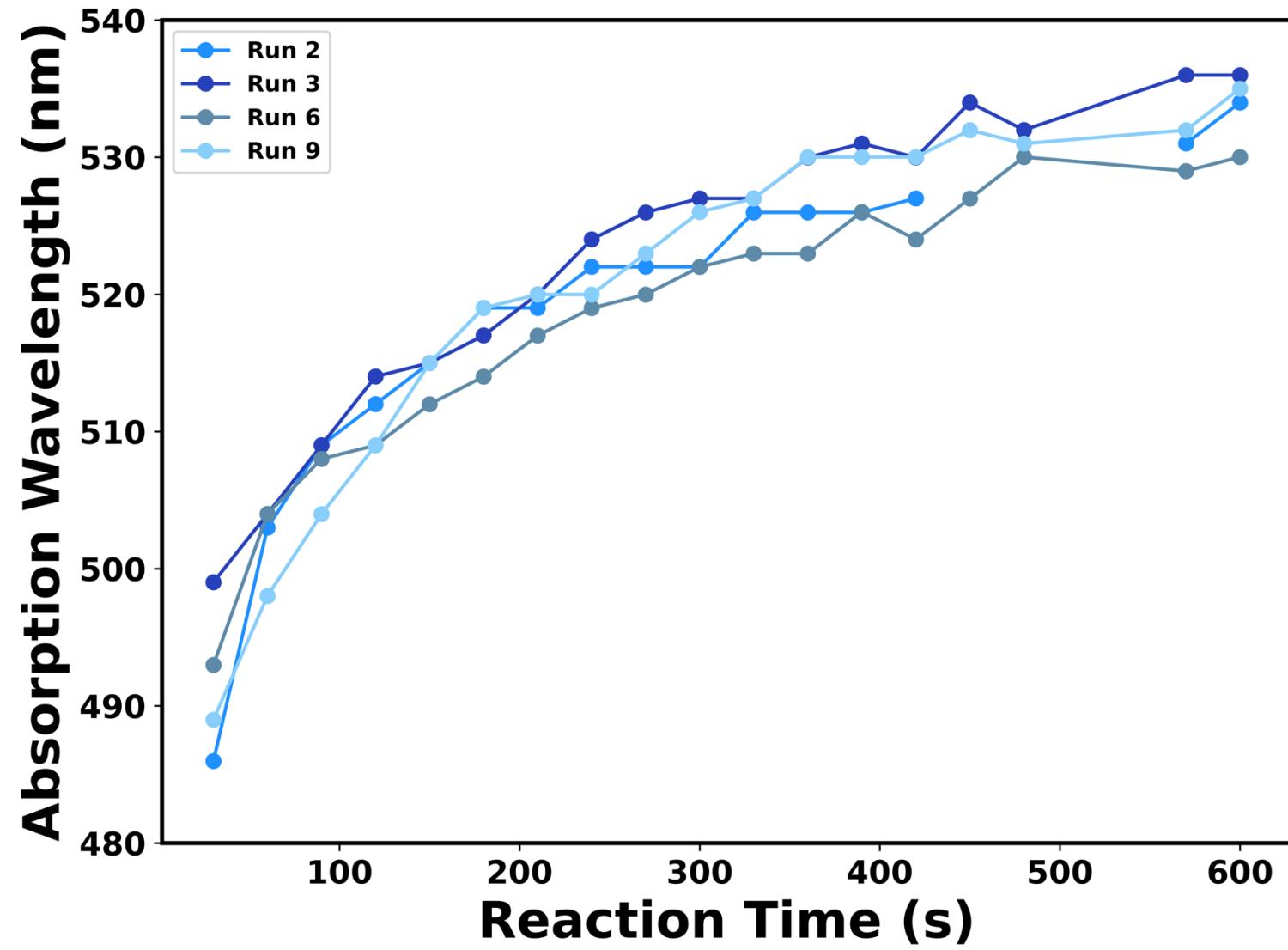
- 0.1 s average time
- 600 scan rate nm/min
- 1 min data interval
- Background (toluene) subtracted

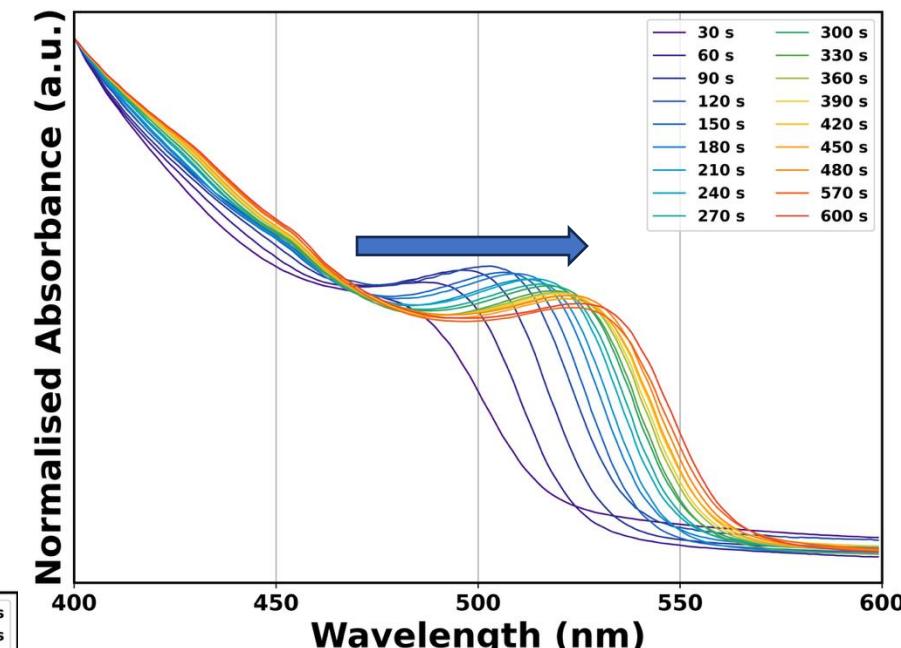
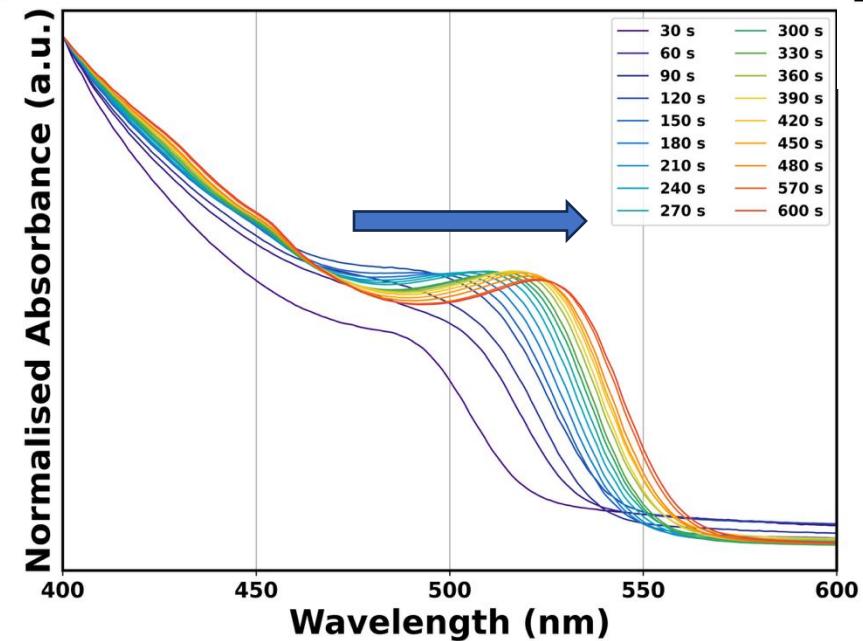
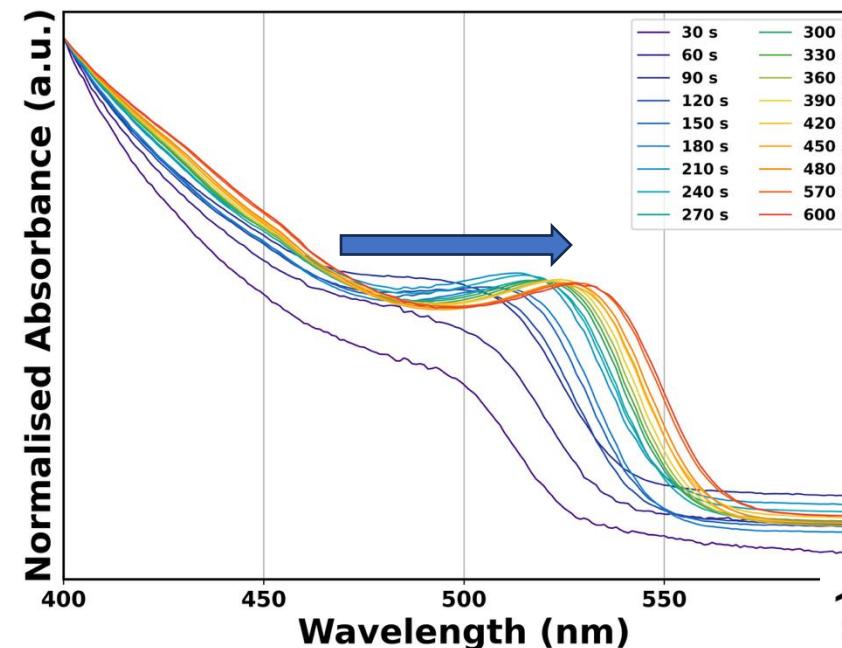
## Shimadzu RF- 5301PC fluorescence spectrometer

- Emission and Excitation slit width: 5 nm
- 0.1 s average time
- 600 scan rate nm/min
- 1 min data interval

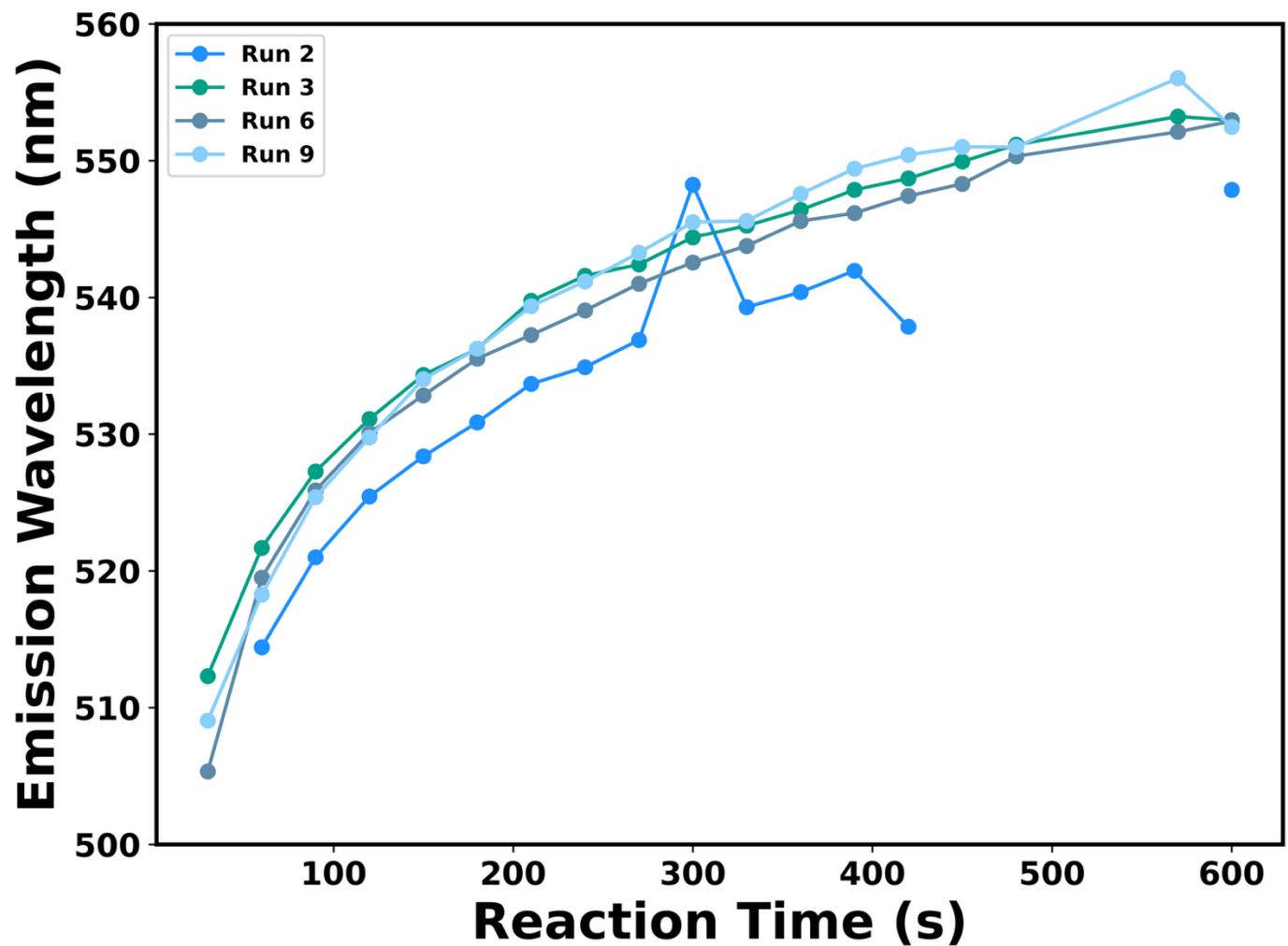
Ratio	Set Wavelength (nm)	Emission Spectra		Excitation Spectra	
		Min (nm)	Max (nm)	Min (nm)	Max (nm)
1.33:1	460 / 470	470/480	600	250	460/450
1:3	440	450	600	300/250	430
1:5	420	430	600	250	410

UV-Vis  
absorption  
peak wavelength  
vs.  
Reaction time



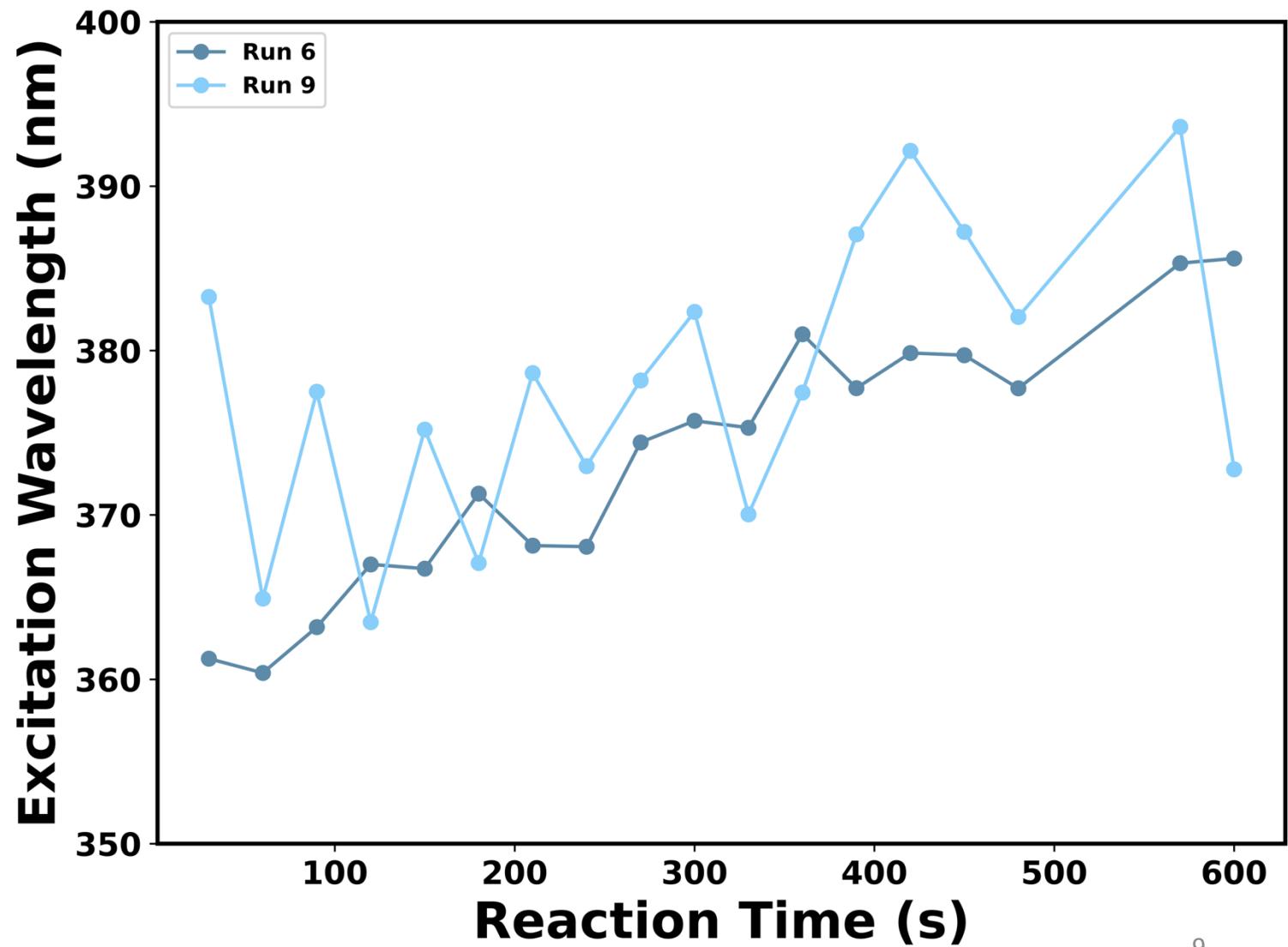


Emission  
peak wavelength  
vs.  
Reaction time

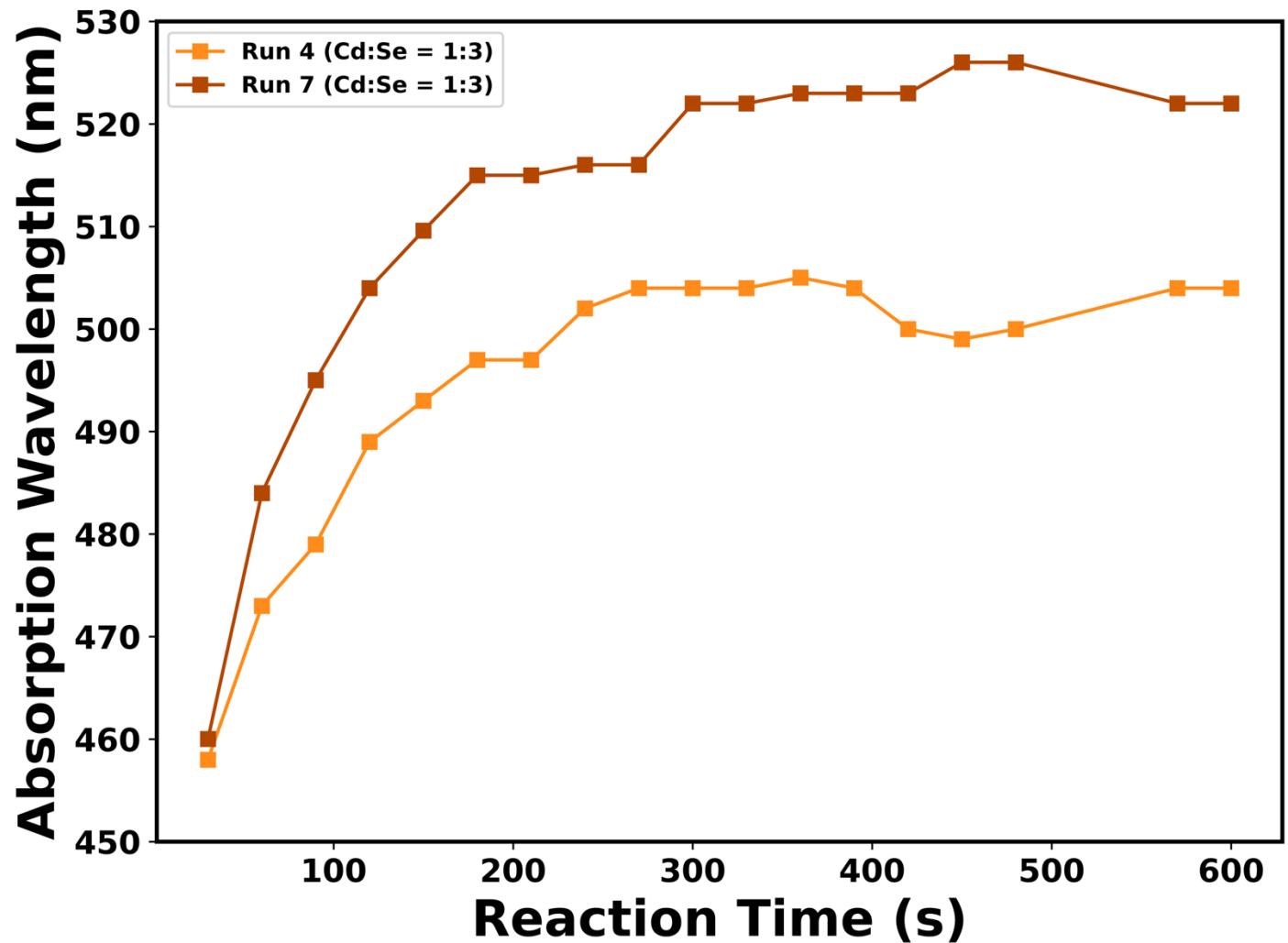


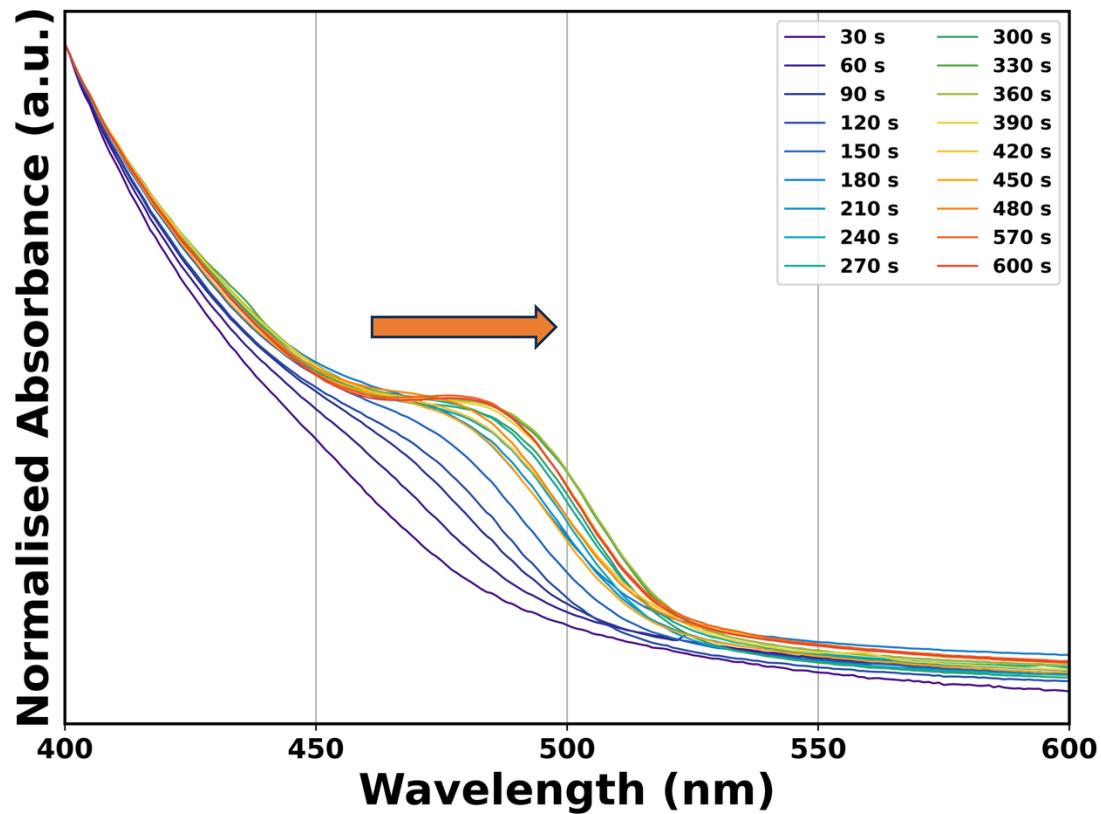
Note: some of the data are not recorded in run 2.

Excitation  
peak wavelength  
vs.  
Reaction time

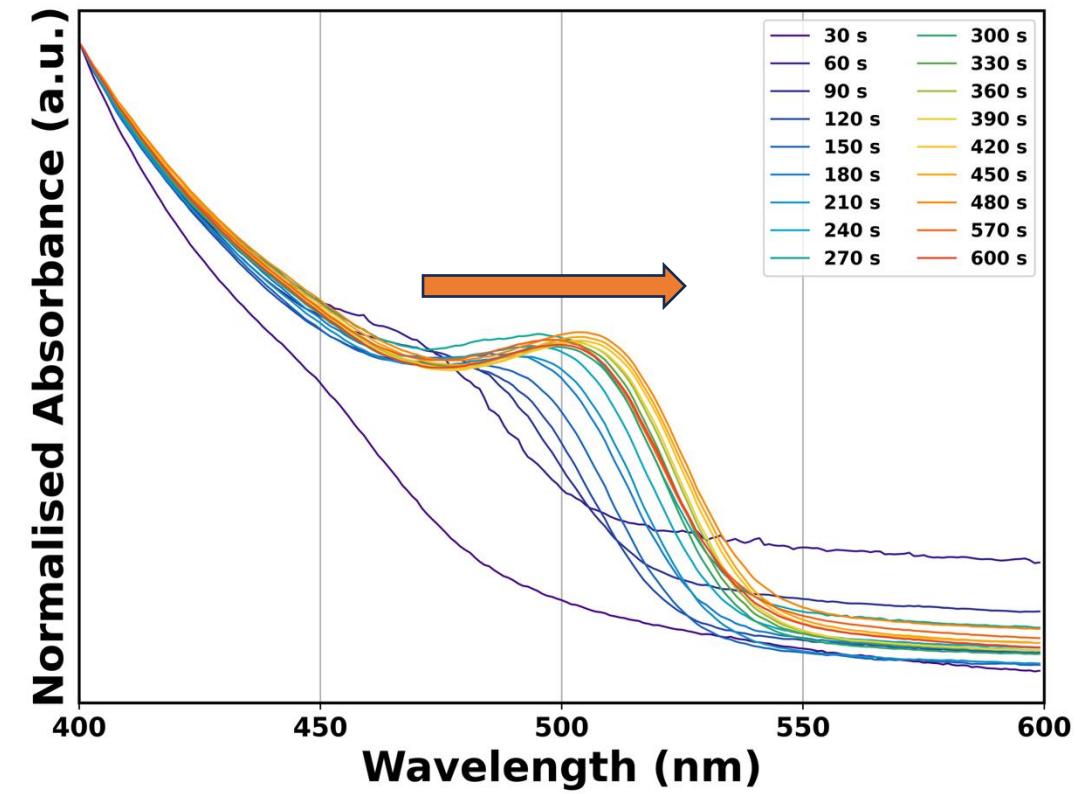


UV-Vis  
absorption  
peak wavelength  
vs.  
Reaction time



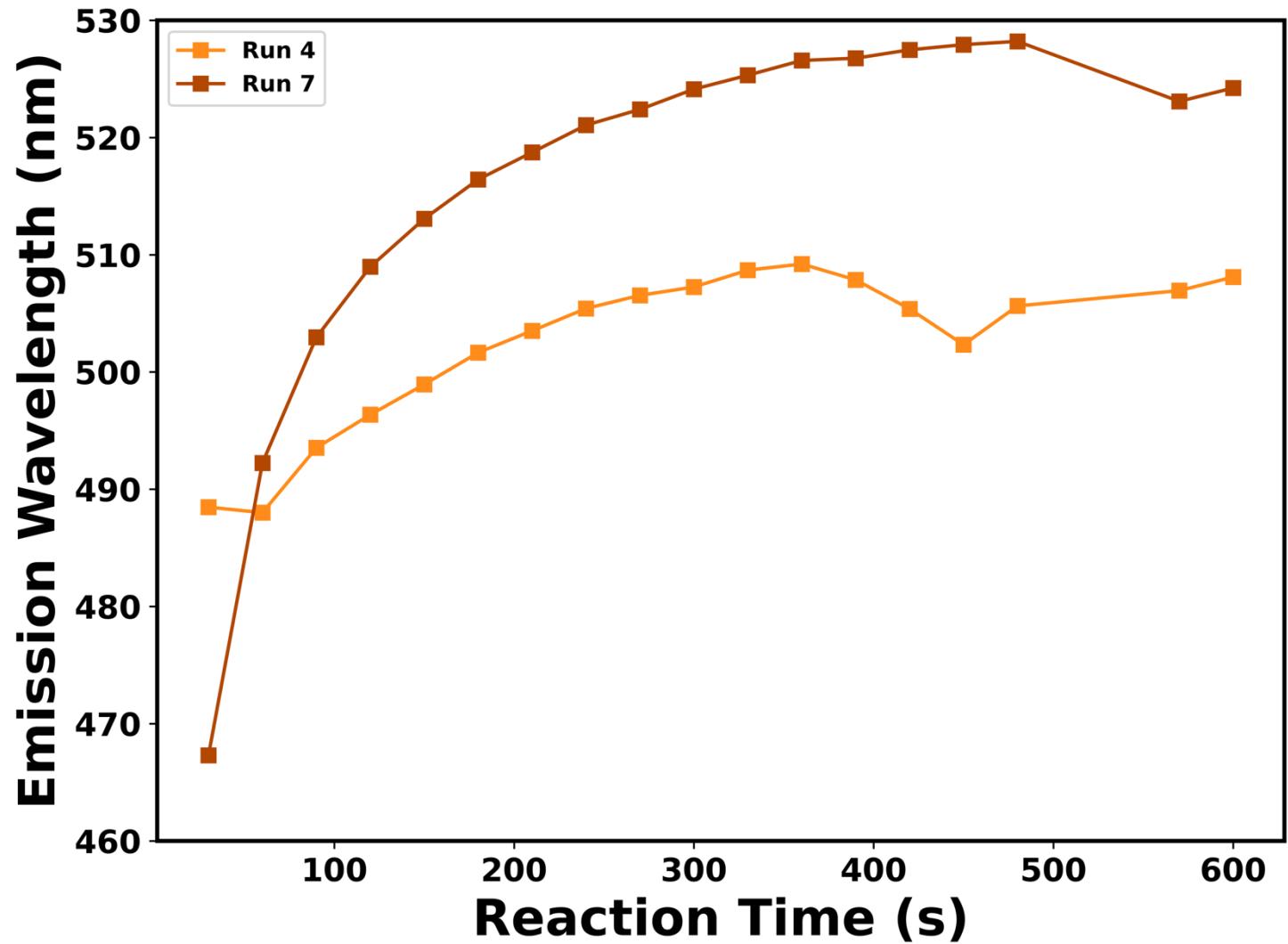


Run 4

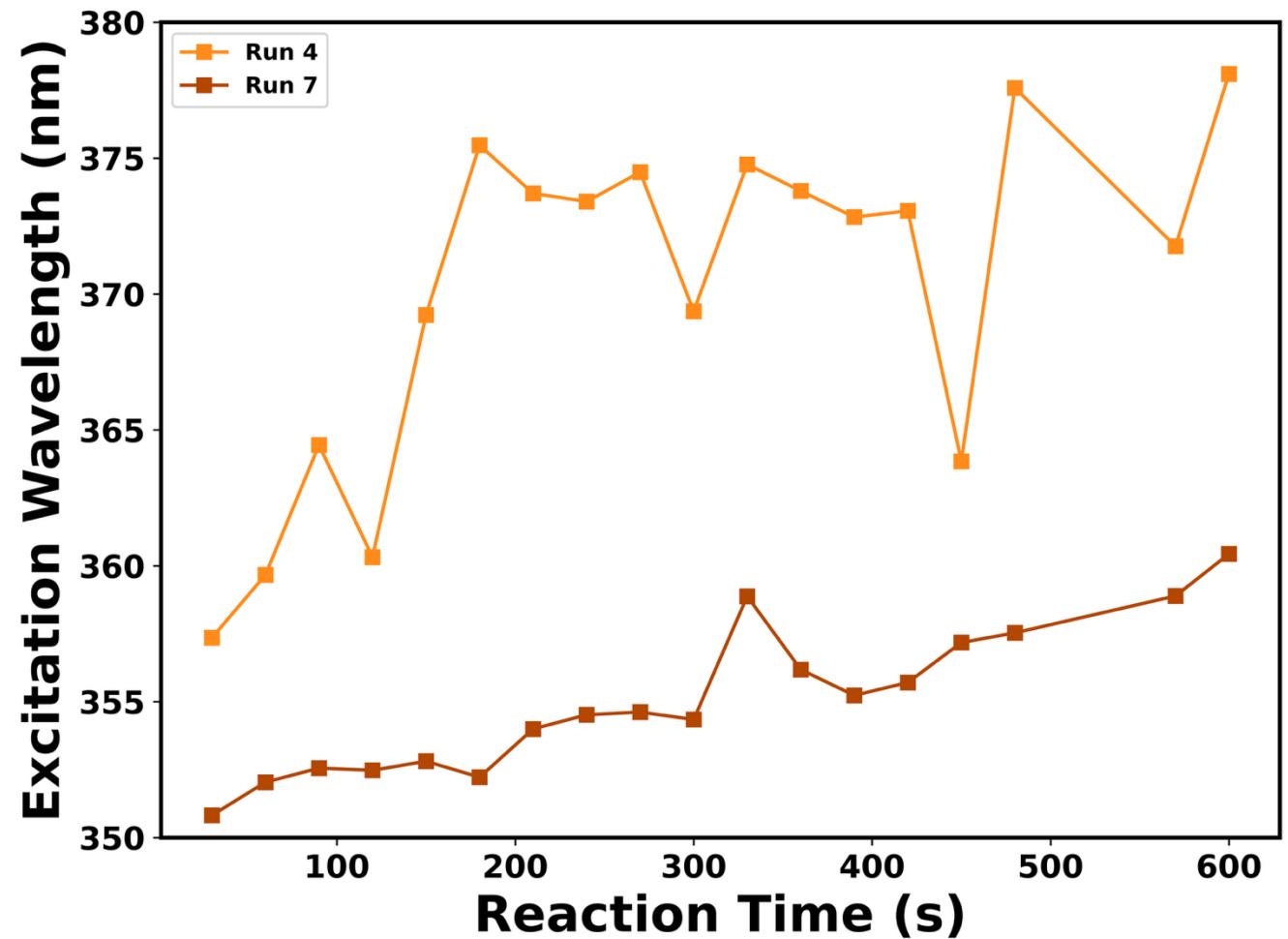


Run 7

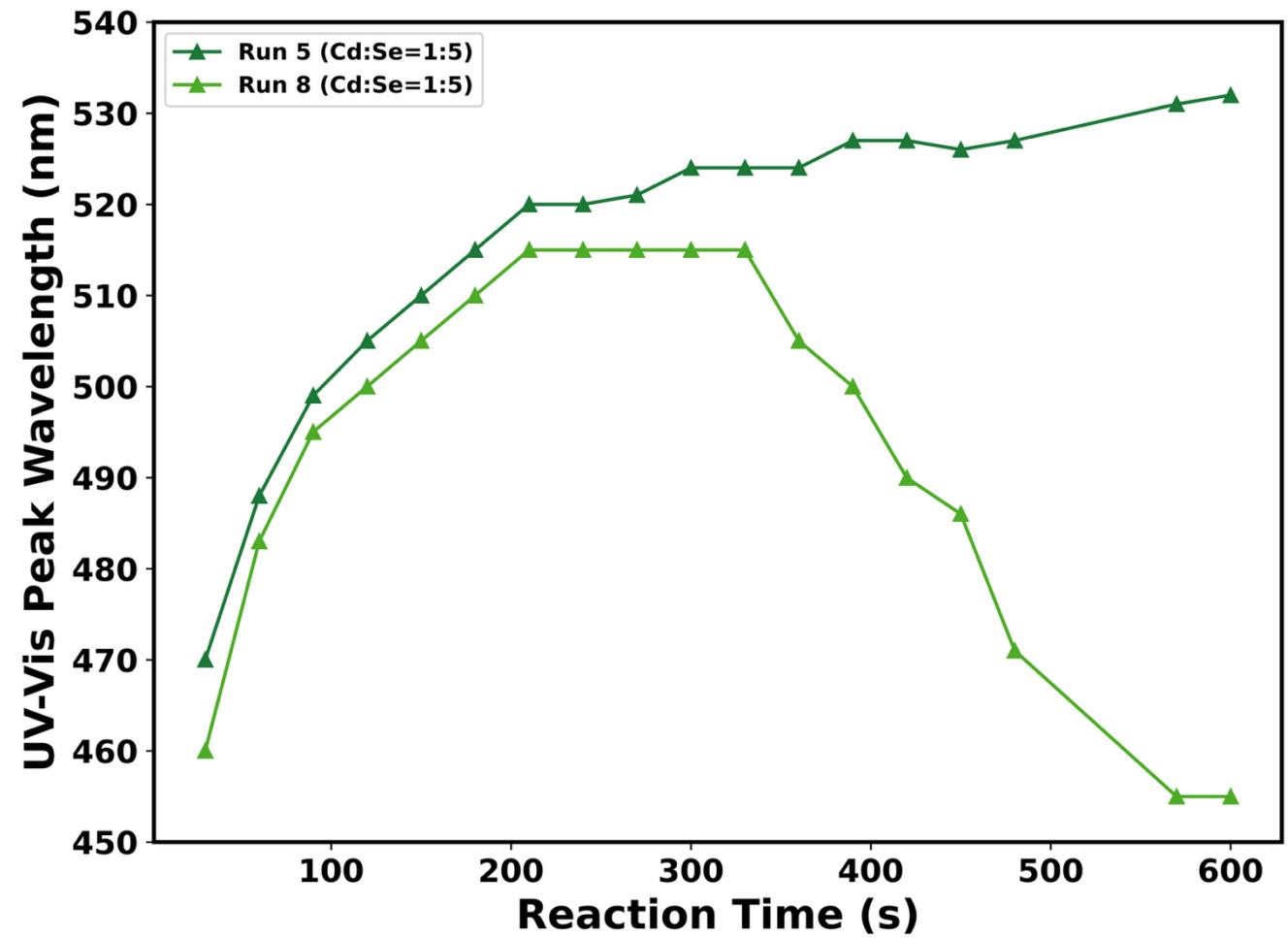
Emission  
peak wavelength  
vs.  
Reaction time

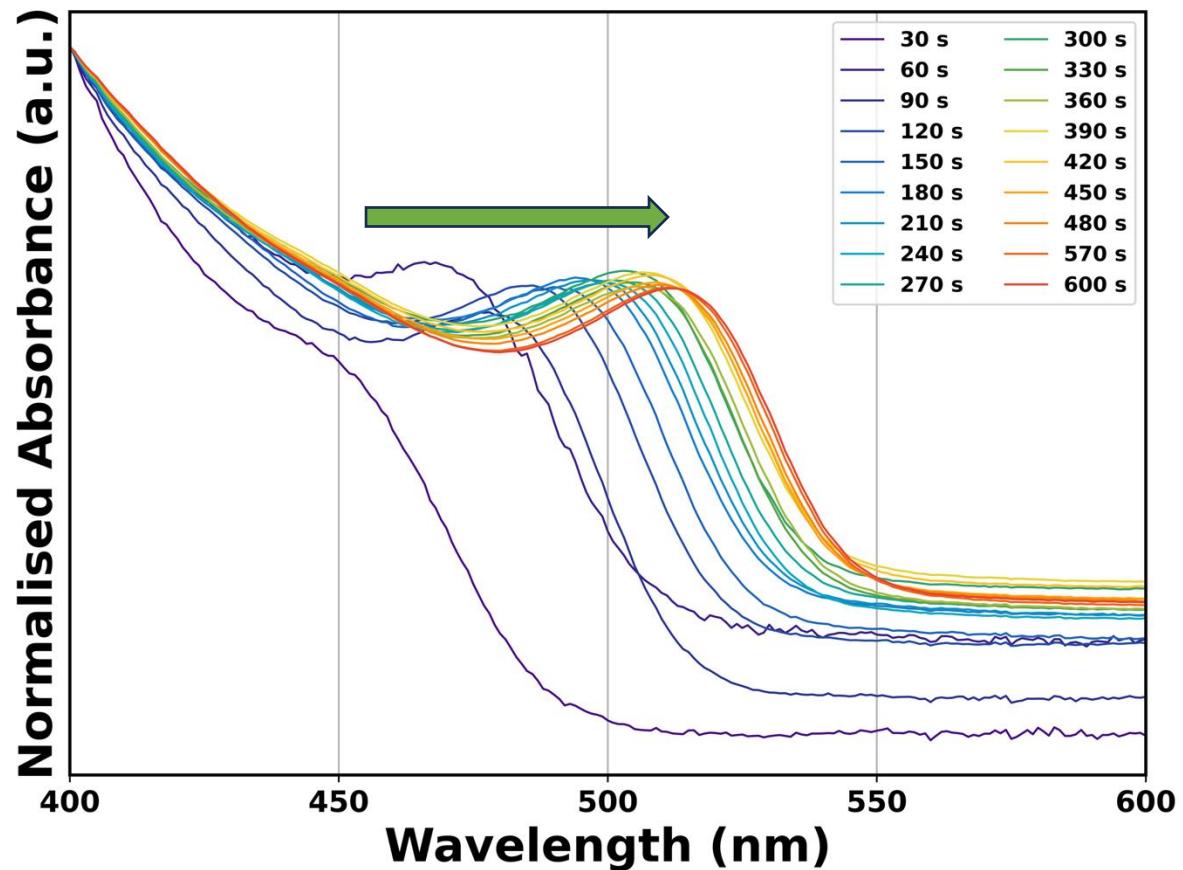


Excitation  
peak wavelength  
vs.  
Reaction time

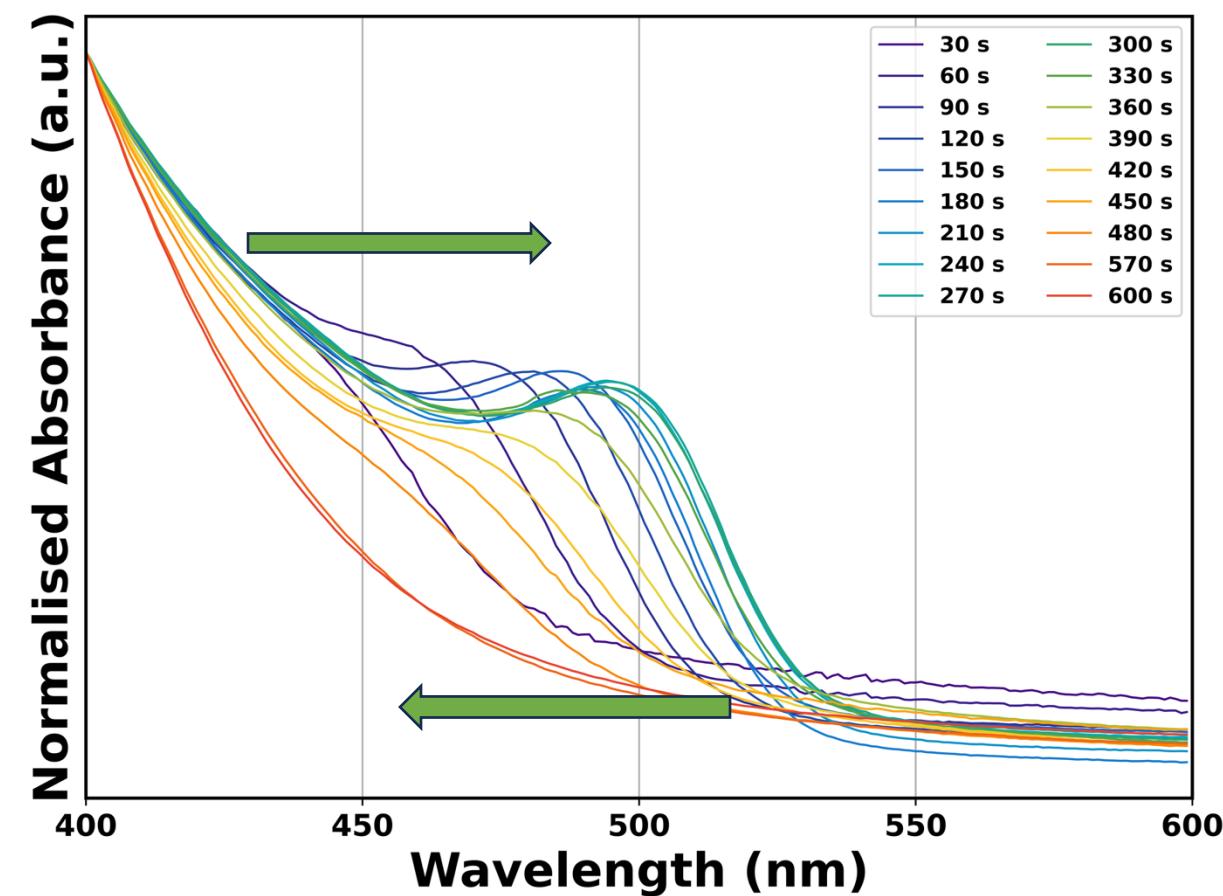


UV-Vis  
absorption  
peak wavelength  
vs.  
Reaction time



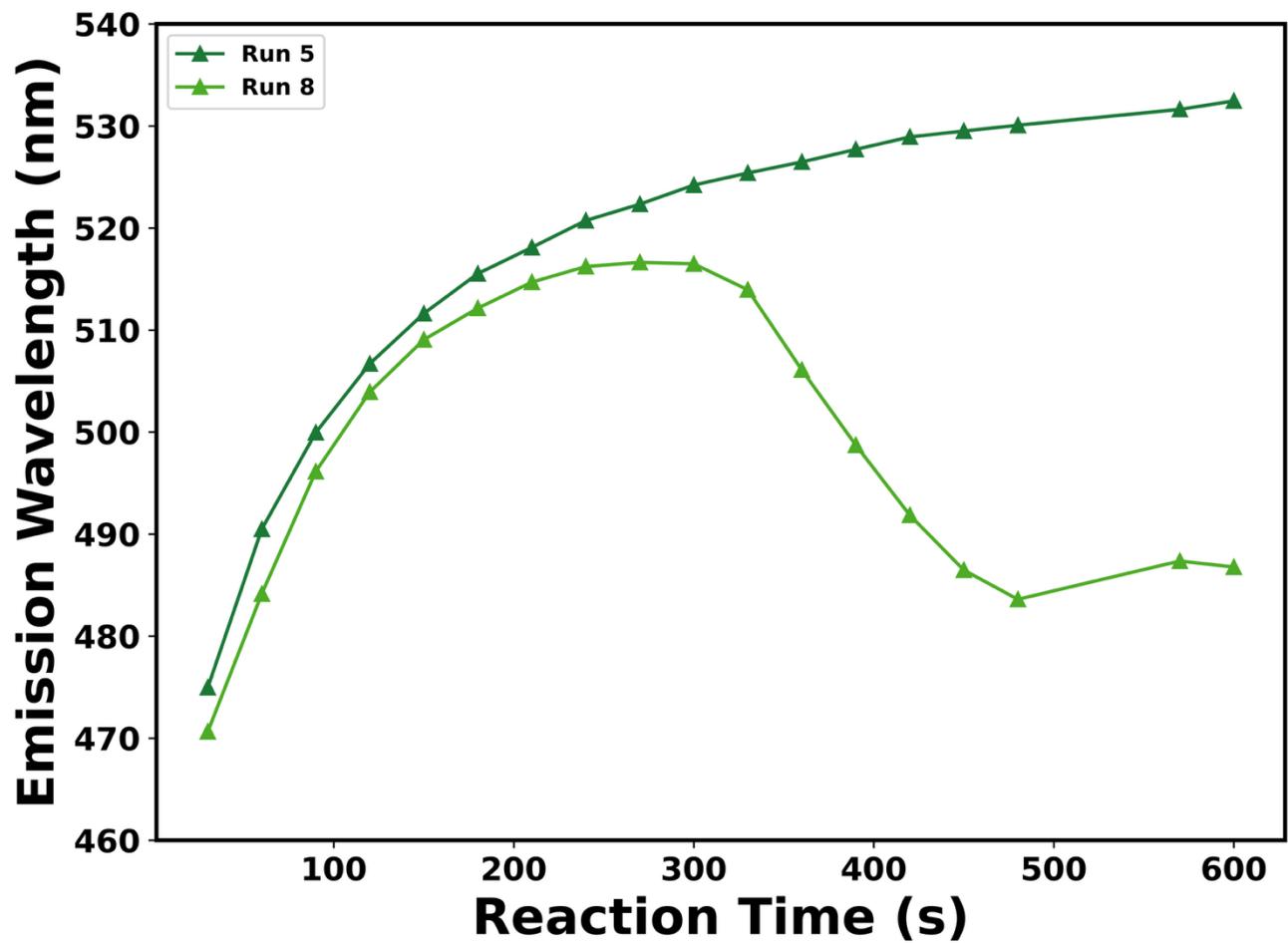


Run 5

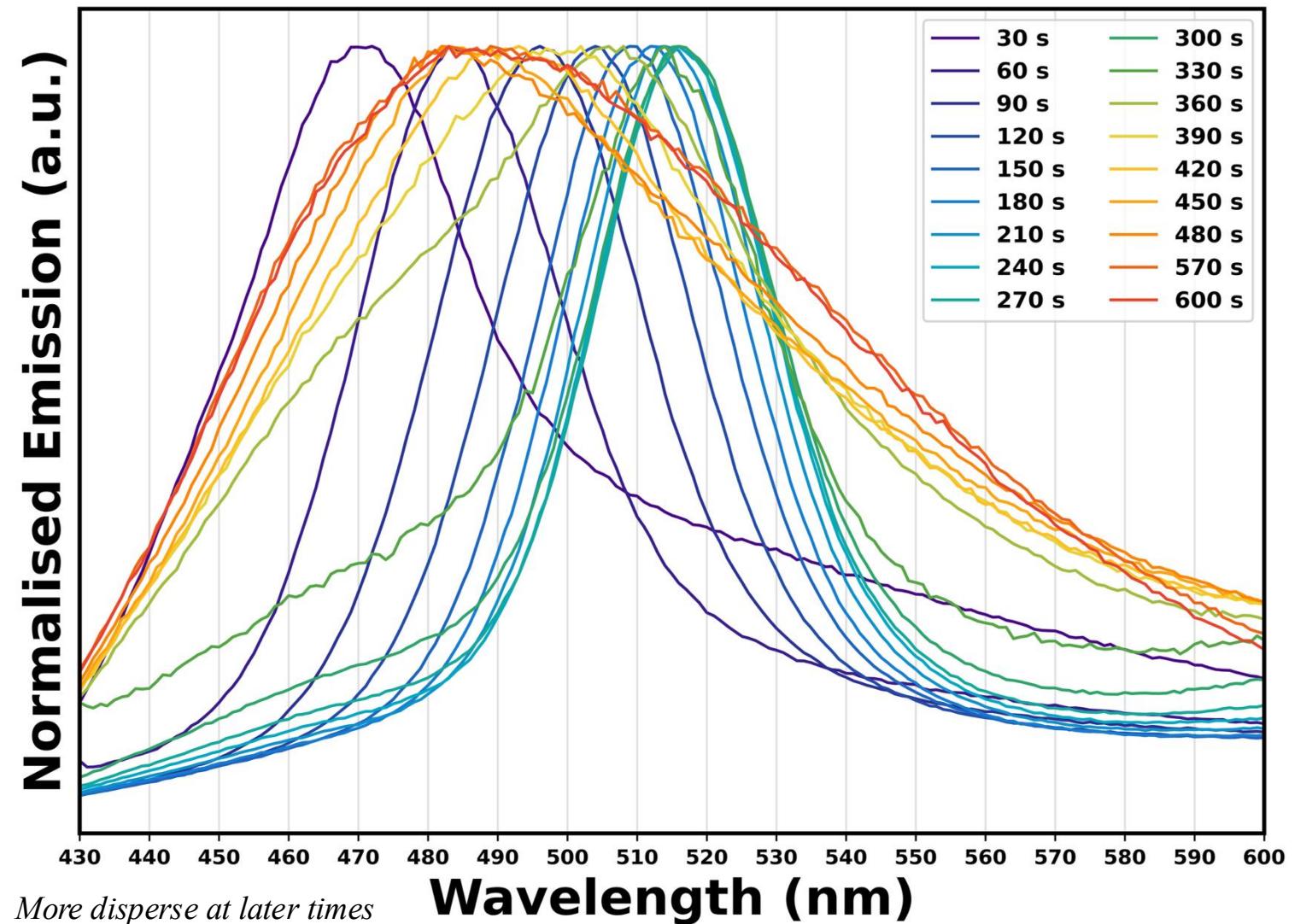


Run 8

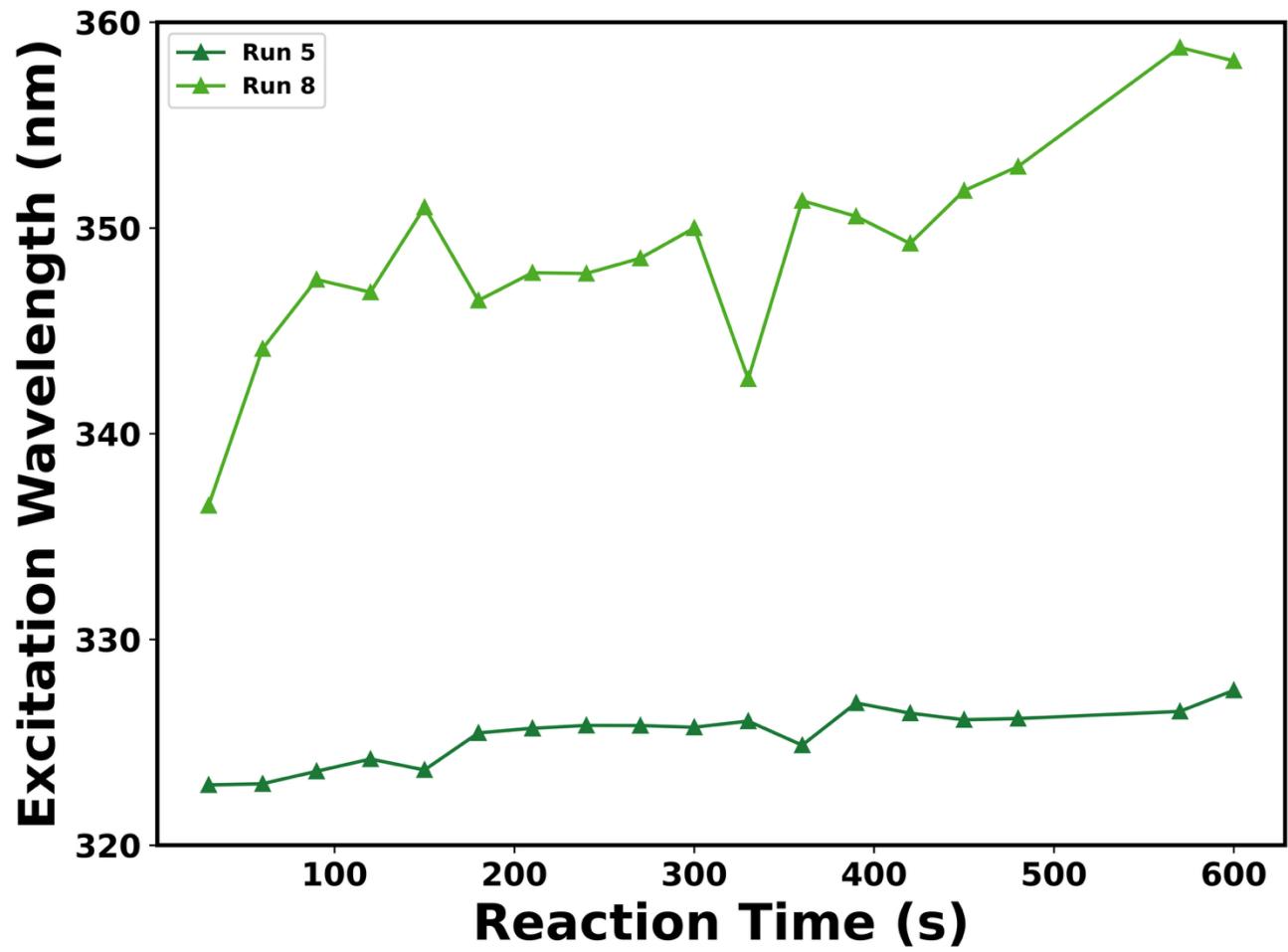
Emission  
peak wavelength  
vs.  
Reaction time



# Run 8 Emission Spectra

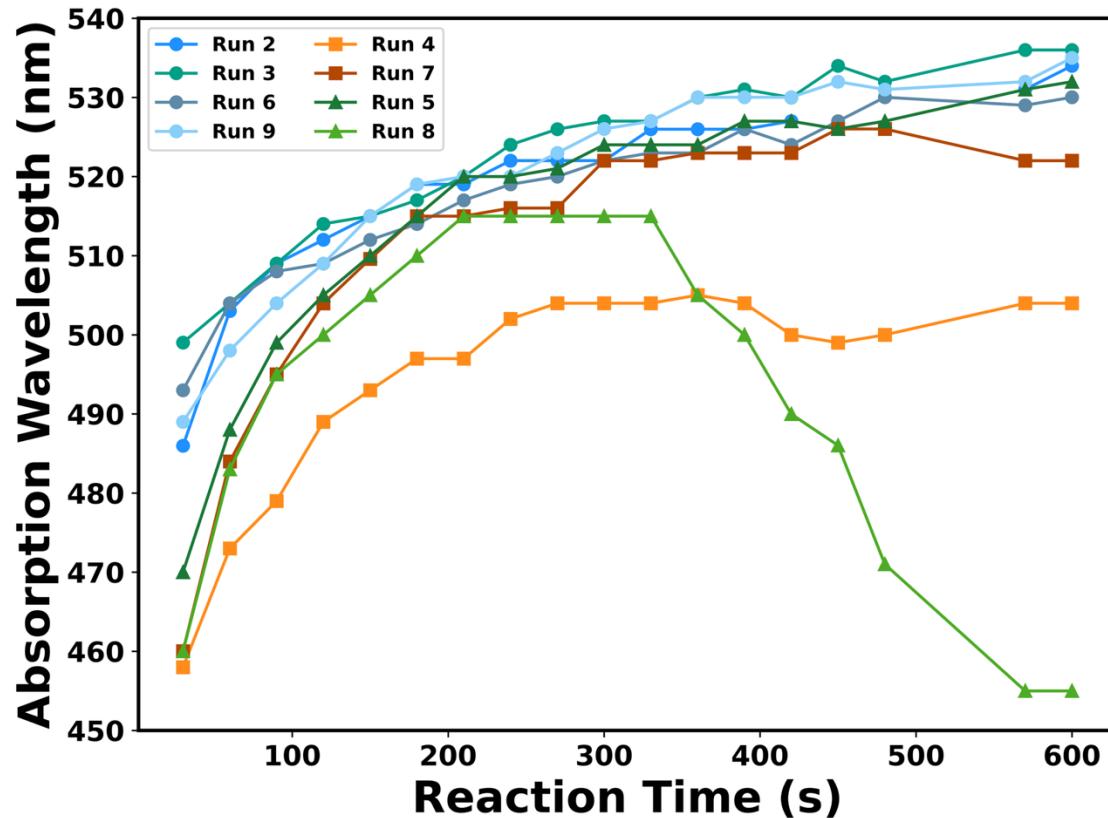


# Excitation peak wavelength vs. Reaction time

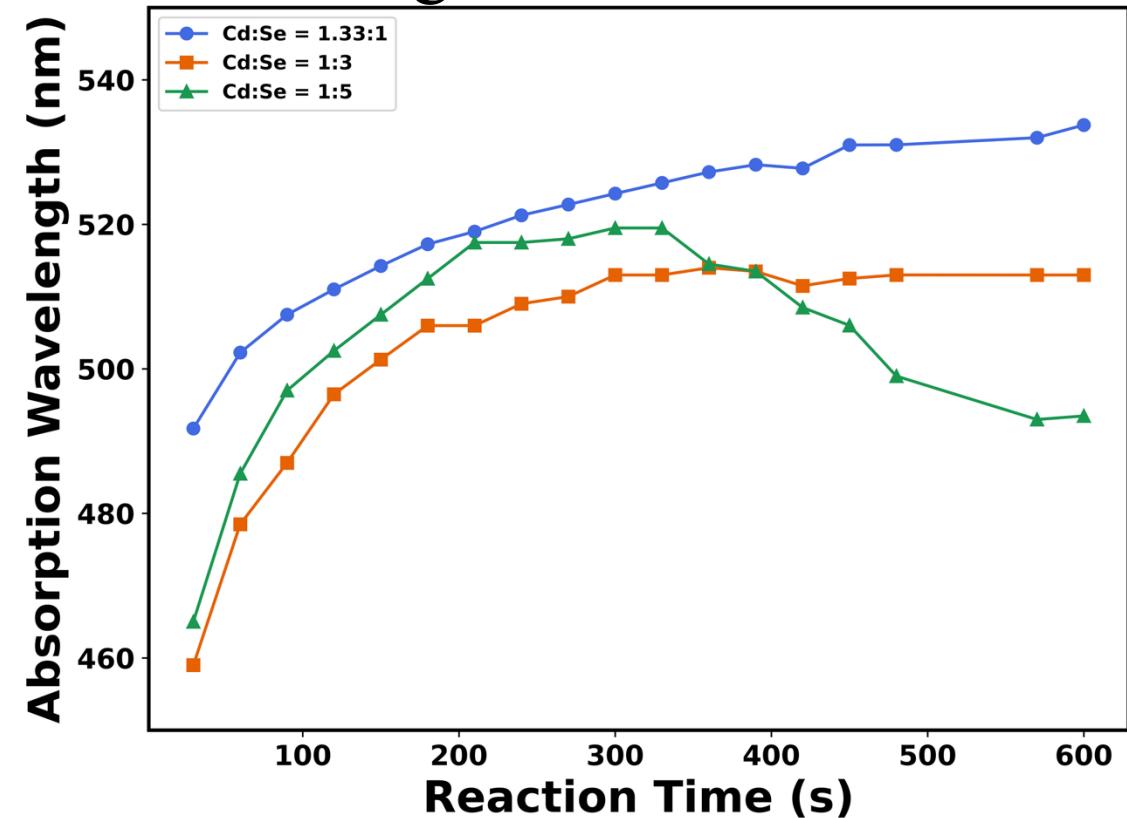


# UV-Vis Comparison I

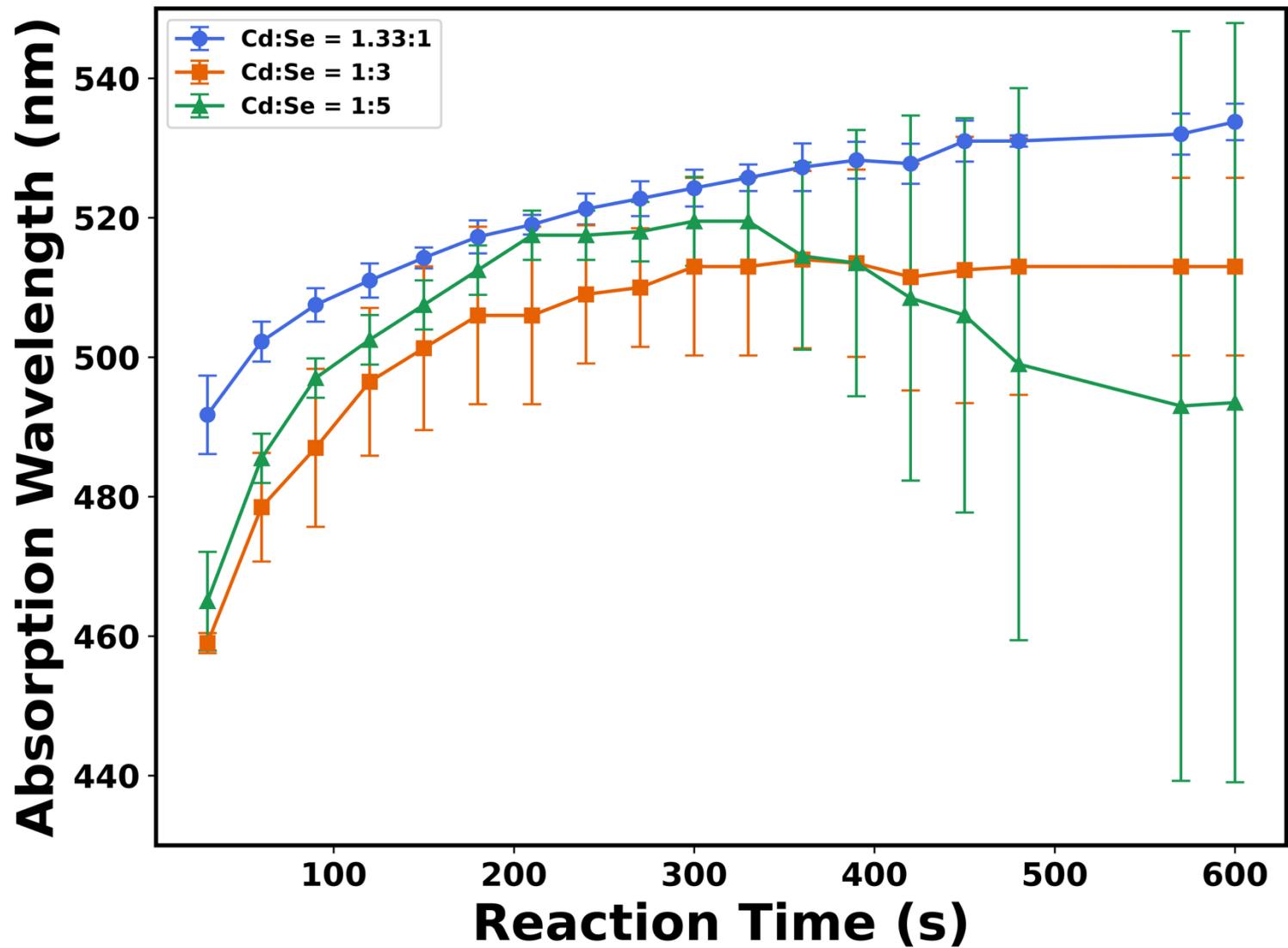
Absorption peak wavelength vs. Reaction time all runs



Averaged absorption peak wavelength vs. Reaction time

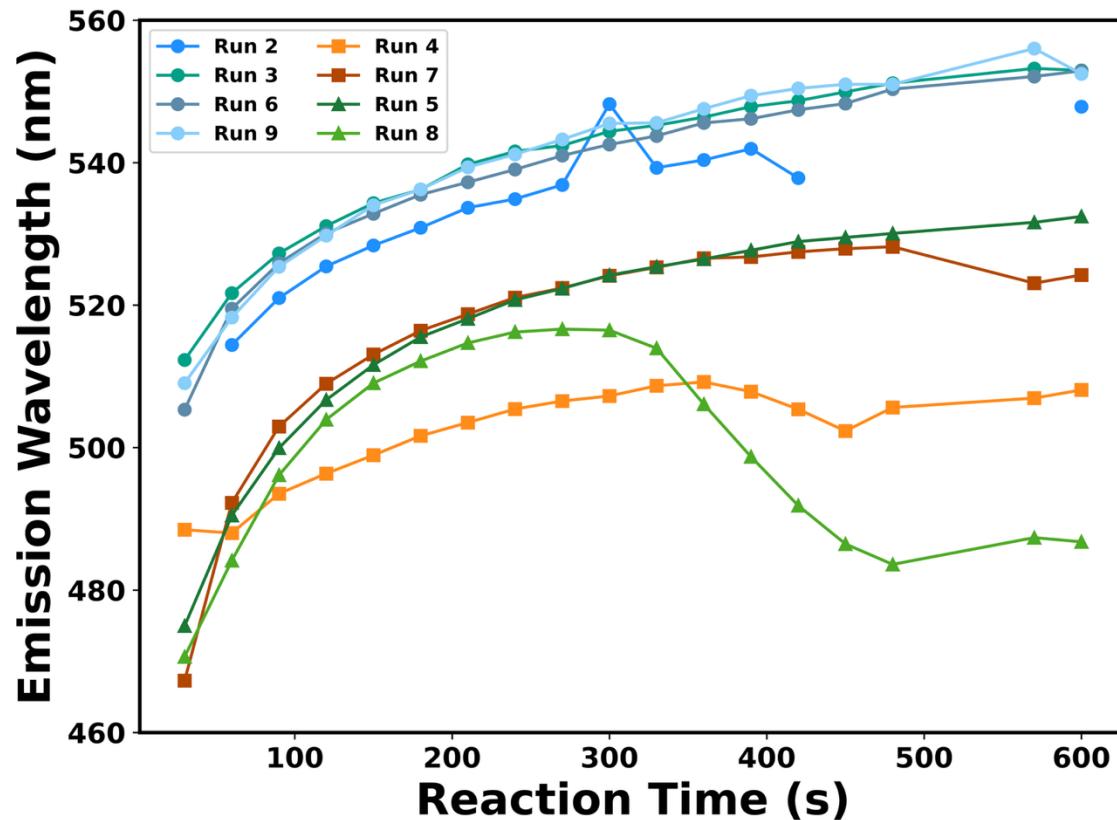


# UV-Vis Comparison II



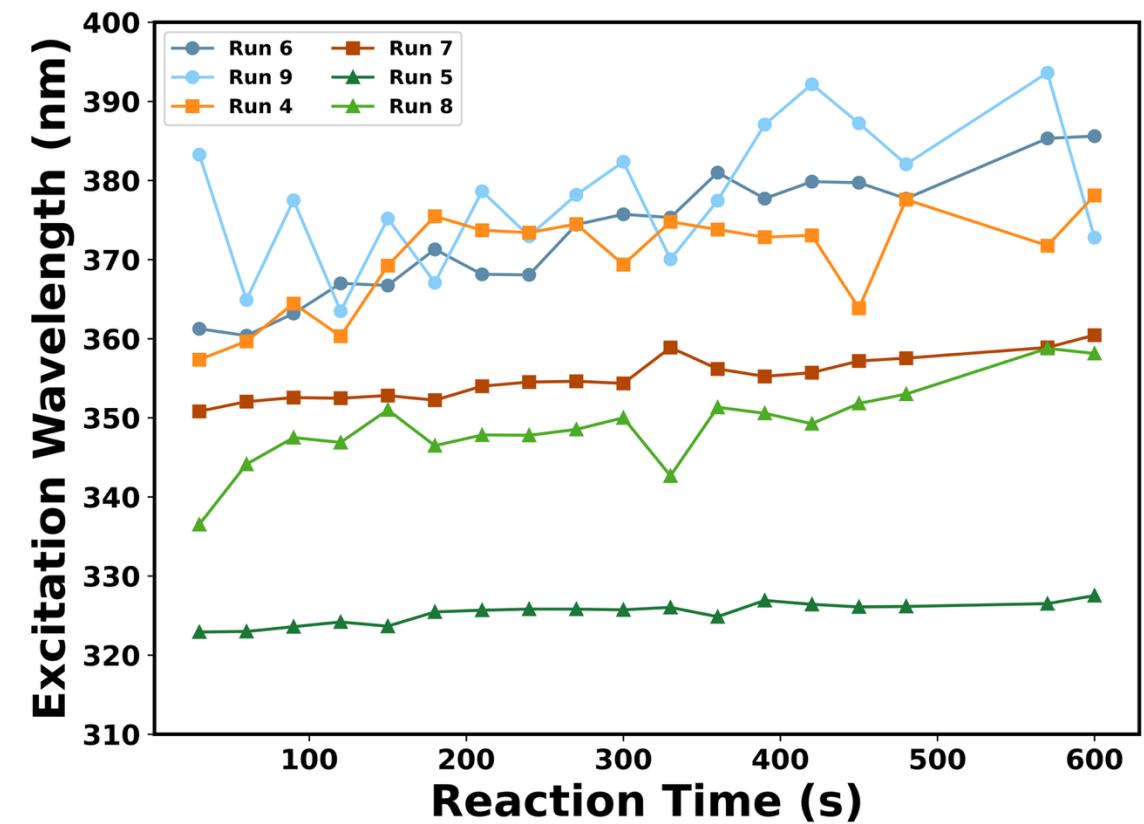
# Fluorescence Comparison

Emission peak wavelength vs.  
Reaction time all runs



Note: some of the data are not recorded in run 2.

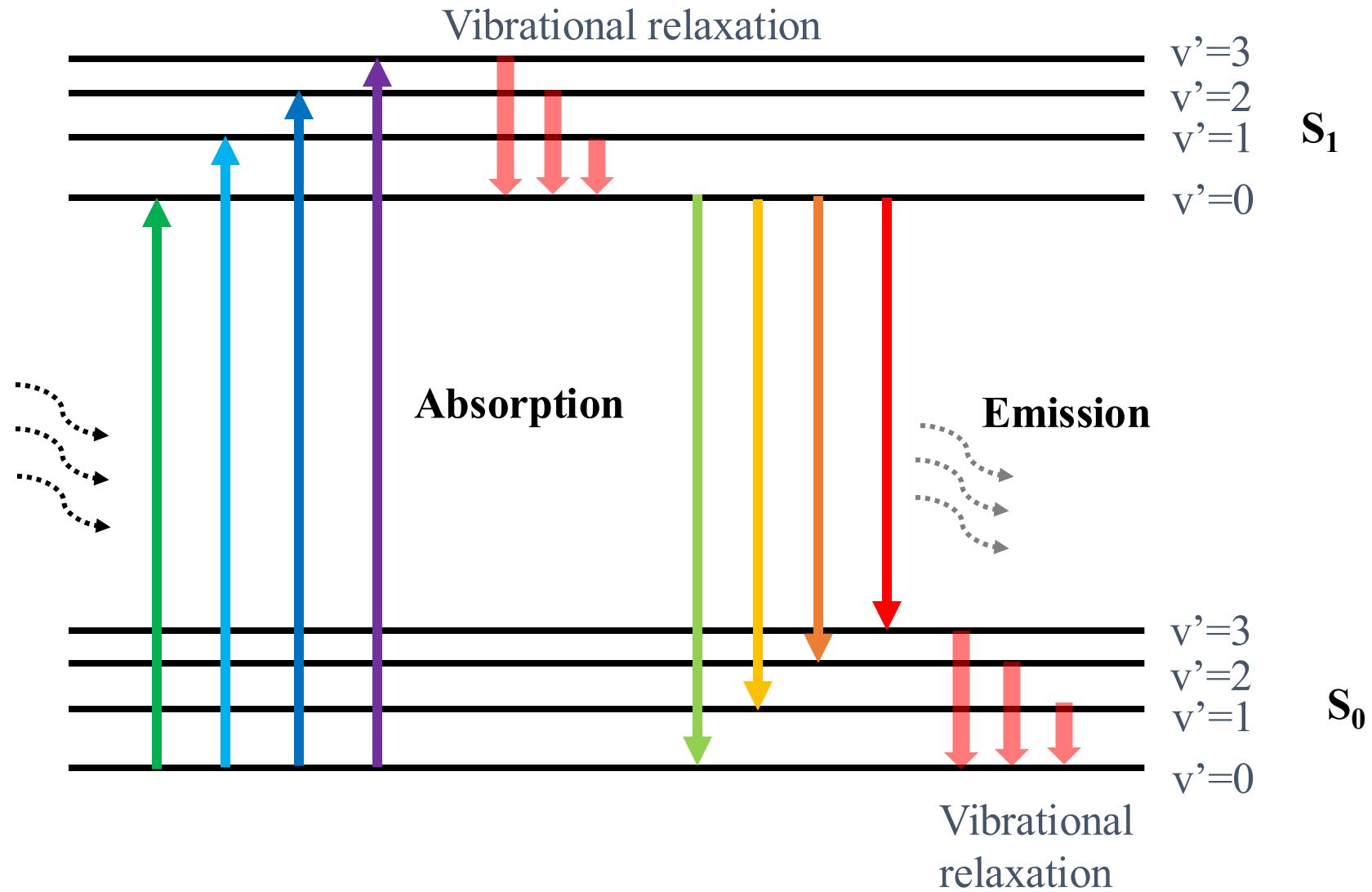
Excitation peak wavelength vs.  
Reaction time all runs



Note: the excitation spectra are not recorded for run 2 and 3.

# Jablonski Diagram

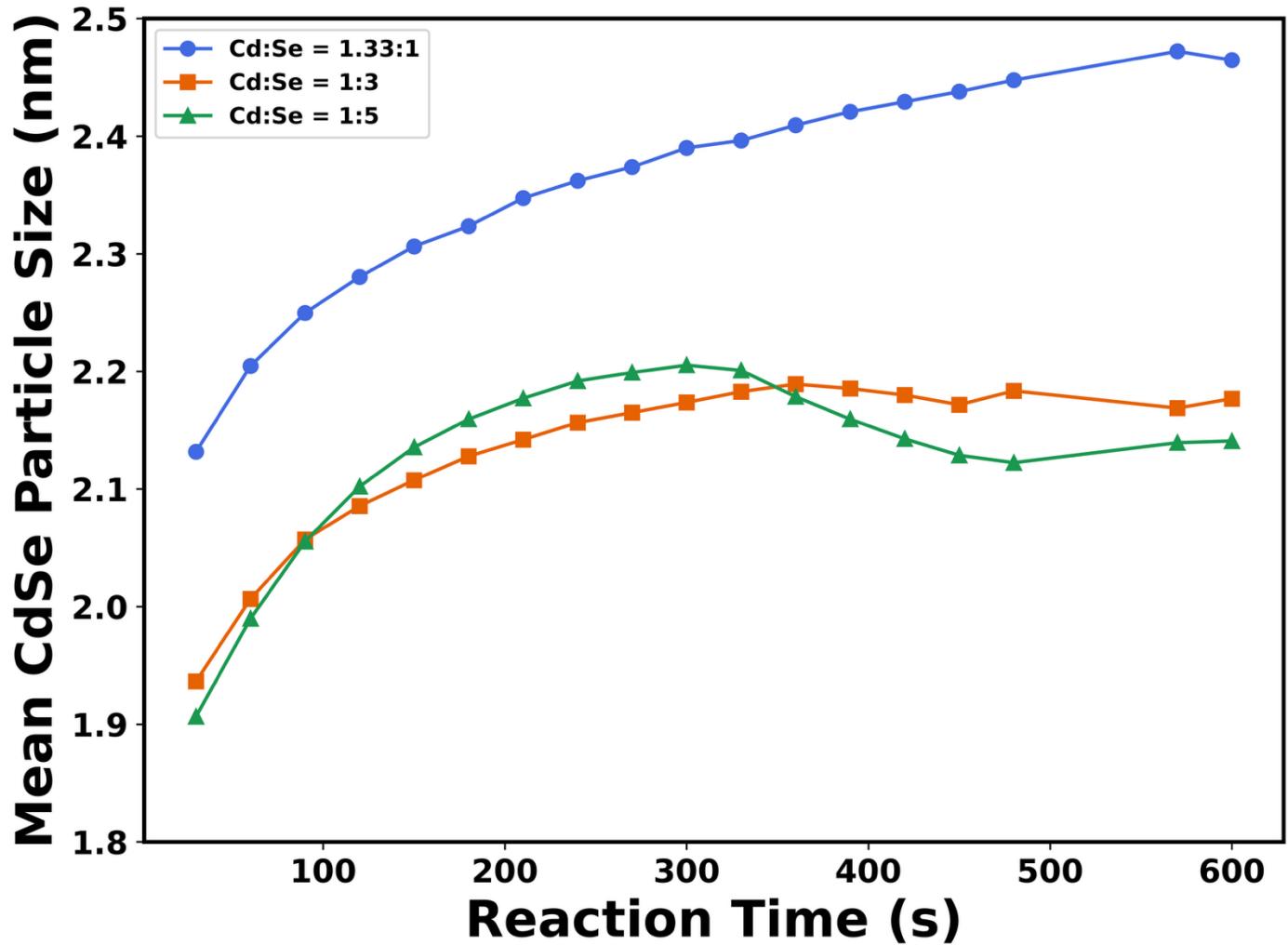
Absorption and emission spectra can be used to find band gap of nanocrystals



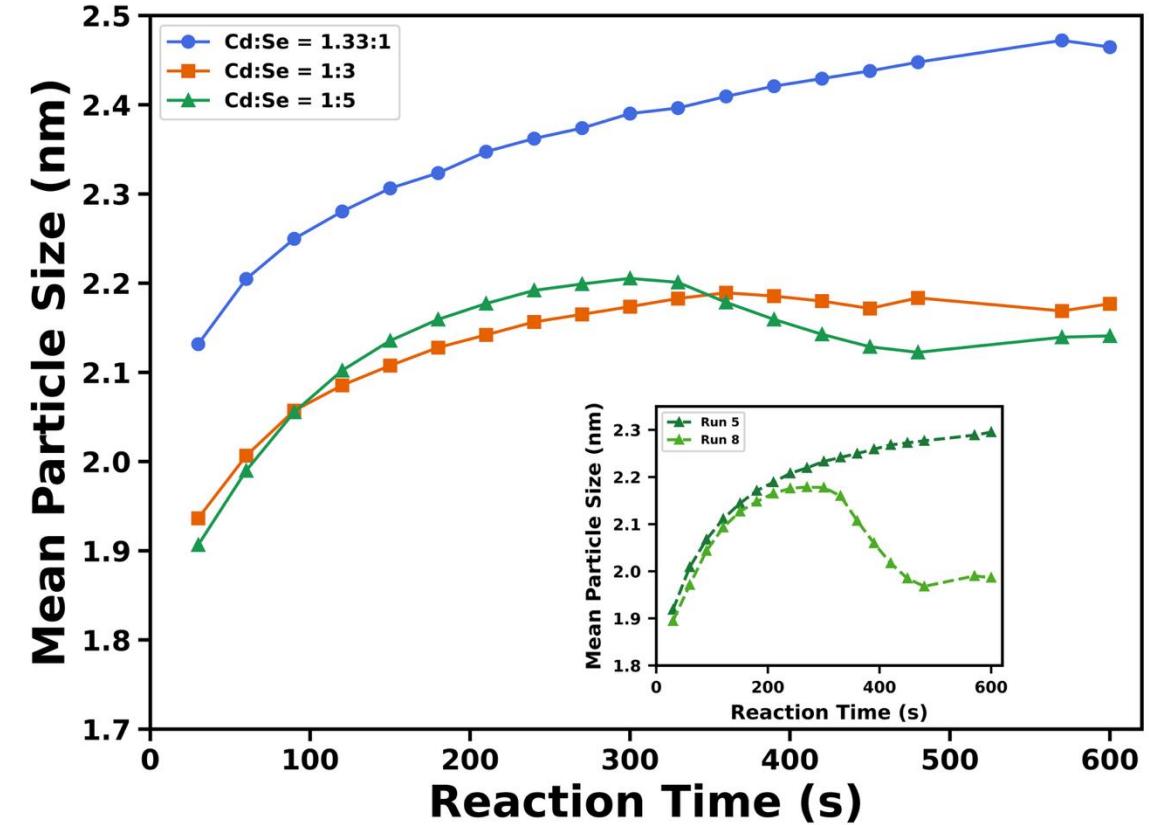
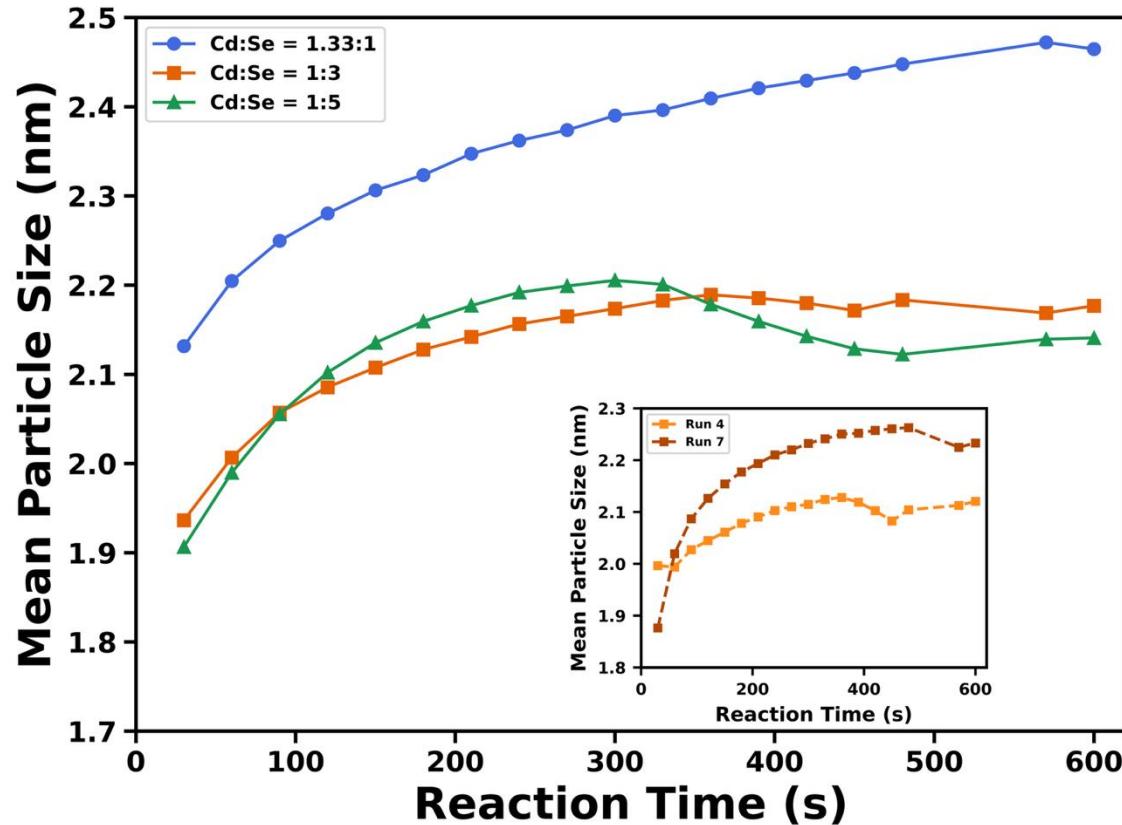
# Mean Particle Size I

Brus Equation

$$E'_g = E_g + \frac{h^2}{8a^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon a}$$



# Mean Particle Size II

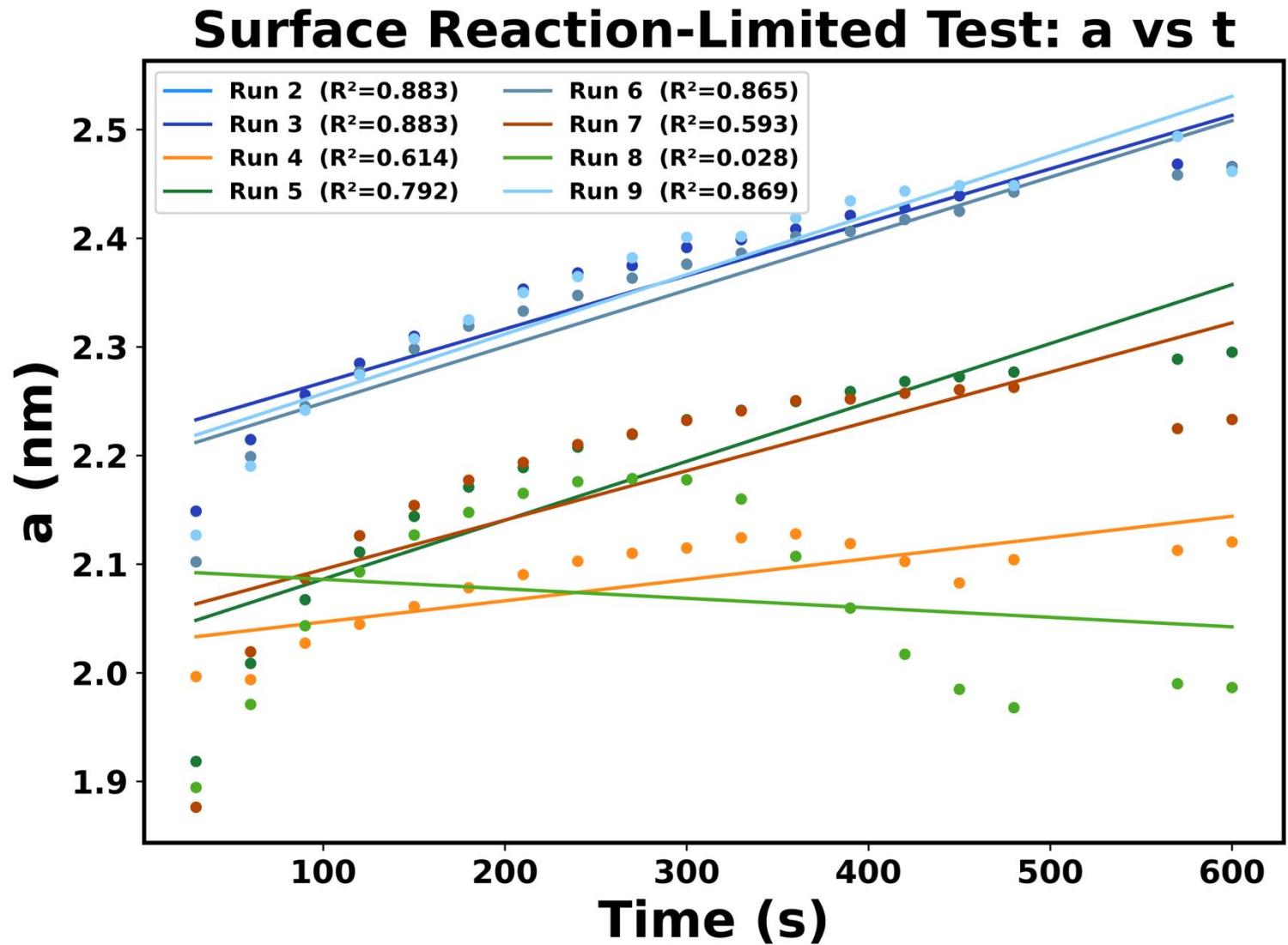


Note: Run 8 has a very different trend!

# Proposed Growth Mechanism I

Mathematical Formula

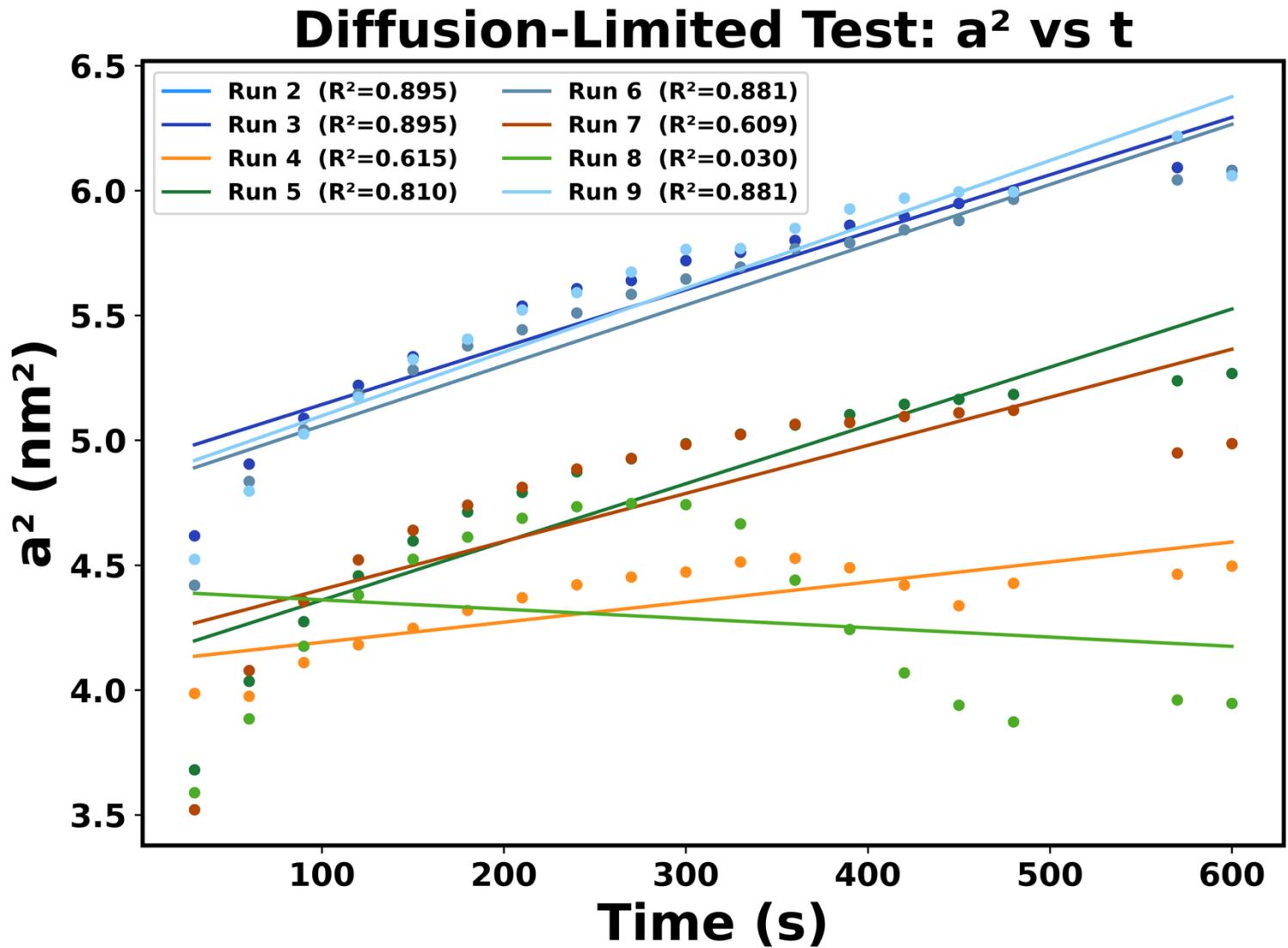
$$\frac{da}{dt} = k$$
$$a = a_0 + kt$$



# Proposed Growth Mechanism II

Mathematical Formula

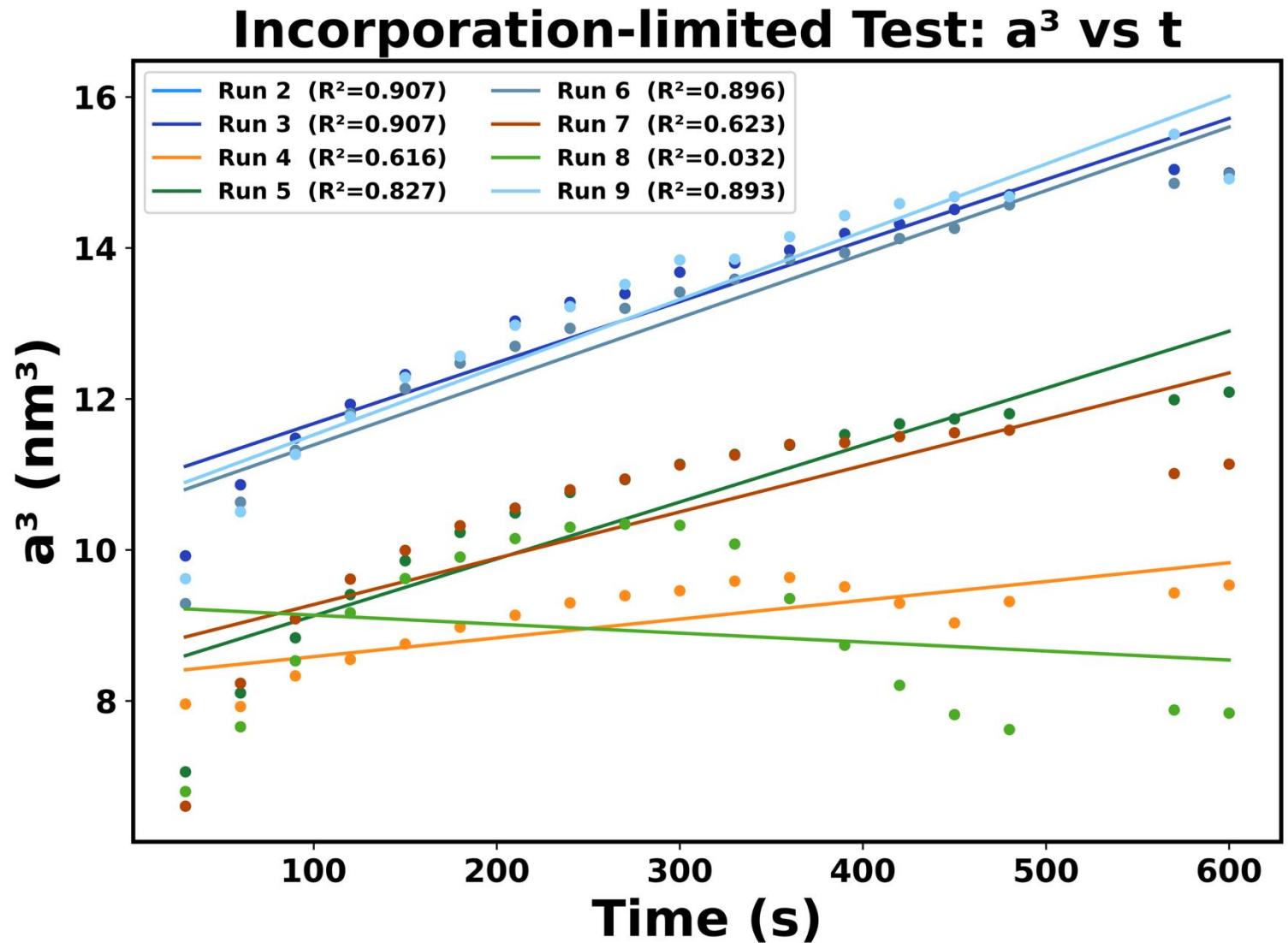
$$\frac{da}{dt} = ka^{-1}$$
$$a^2 = a_0^2 + kt$$



# Proposed Growth Mechanism III

Mathematical Formula

$$\frac{da}{dt} = ka^{-2}$$
$$a^3 = a_0^3 + kt$$

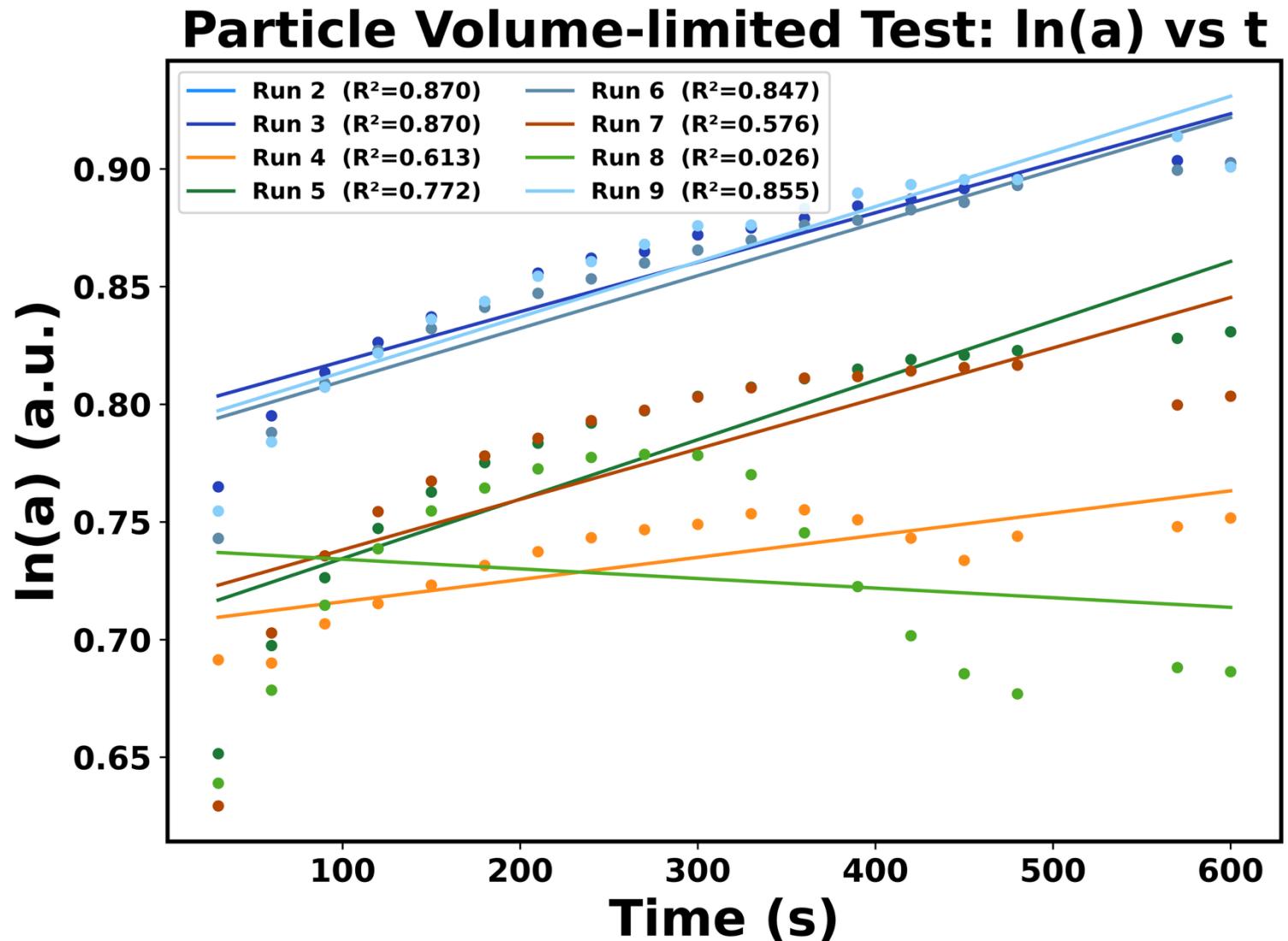


# Proposed Growth Mechanism IV

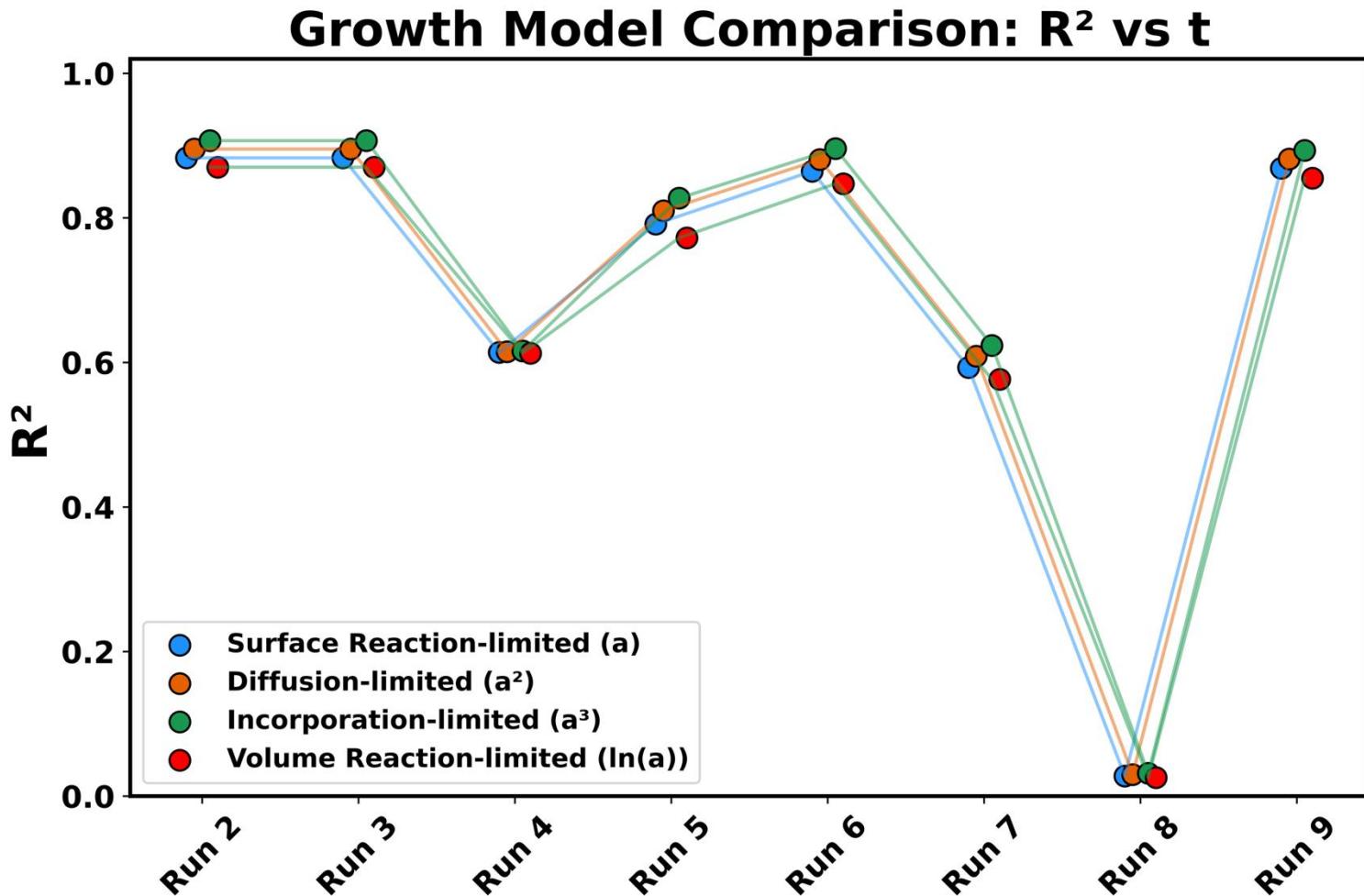
Mathematical Formula

$$\frac{da}{dt} = ka$$

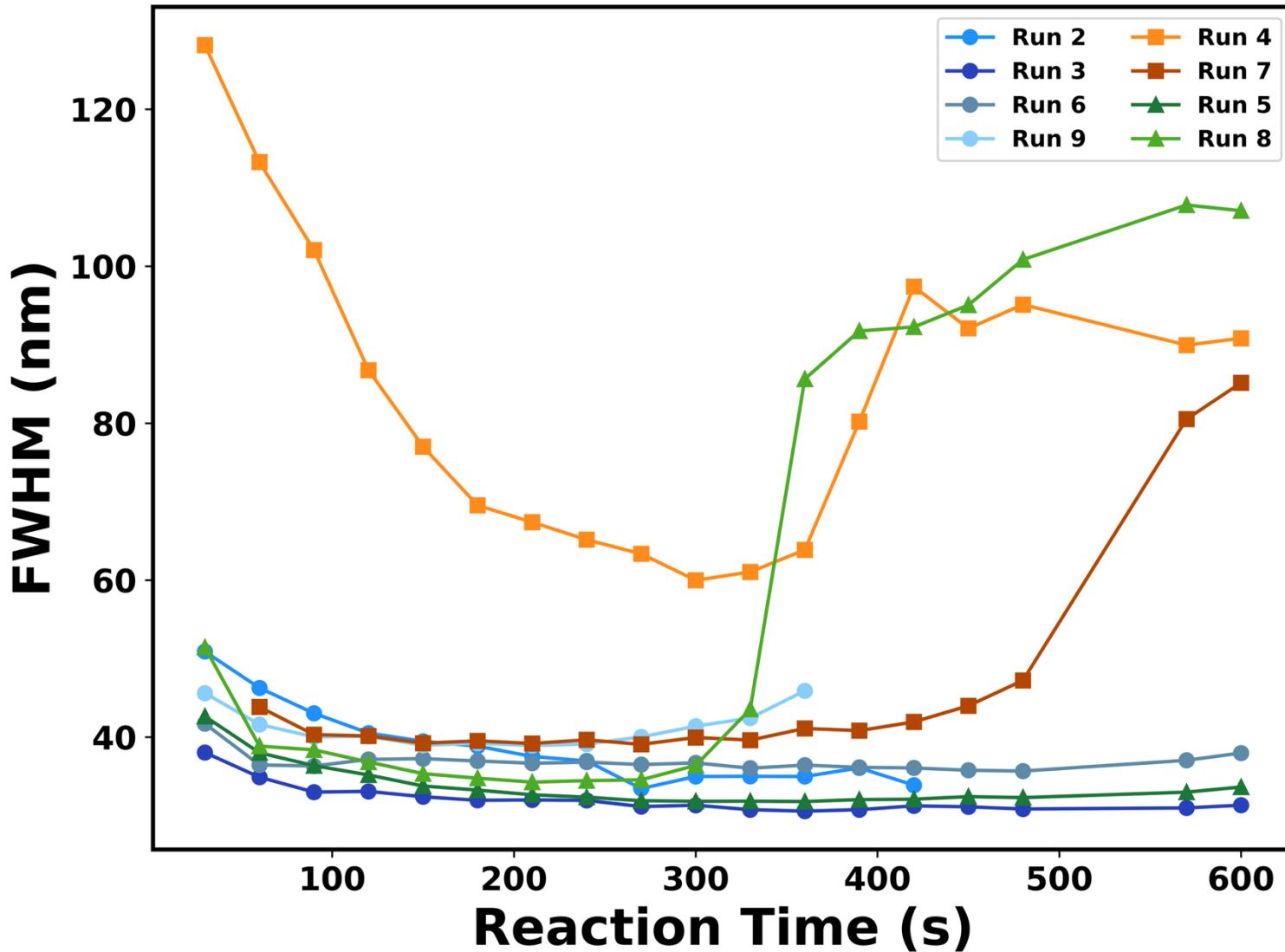
$$\ln a = \ln a_0 + kt$$



# Proposed Growth Mechanism V



# Proposed Growth Mechanism VI



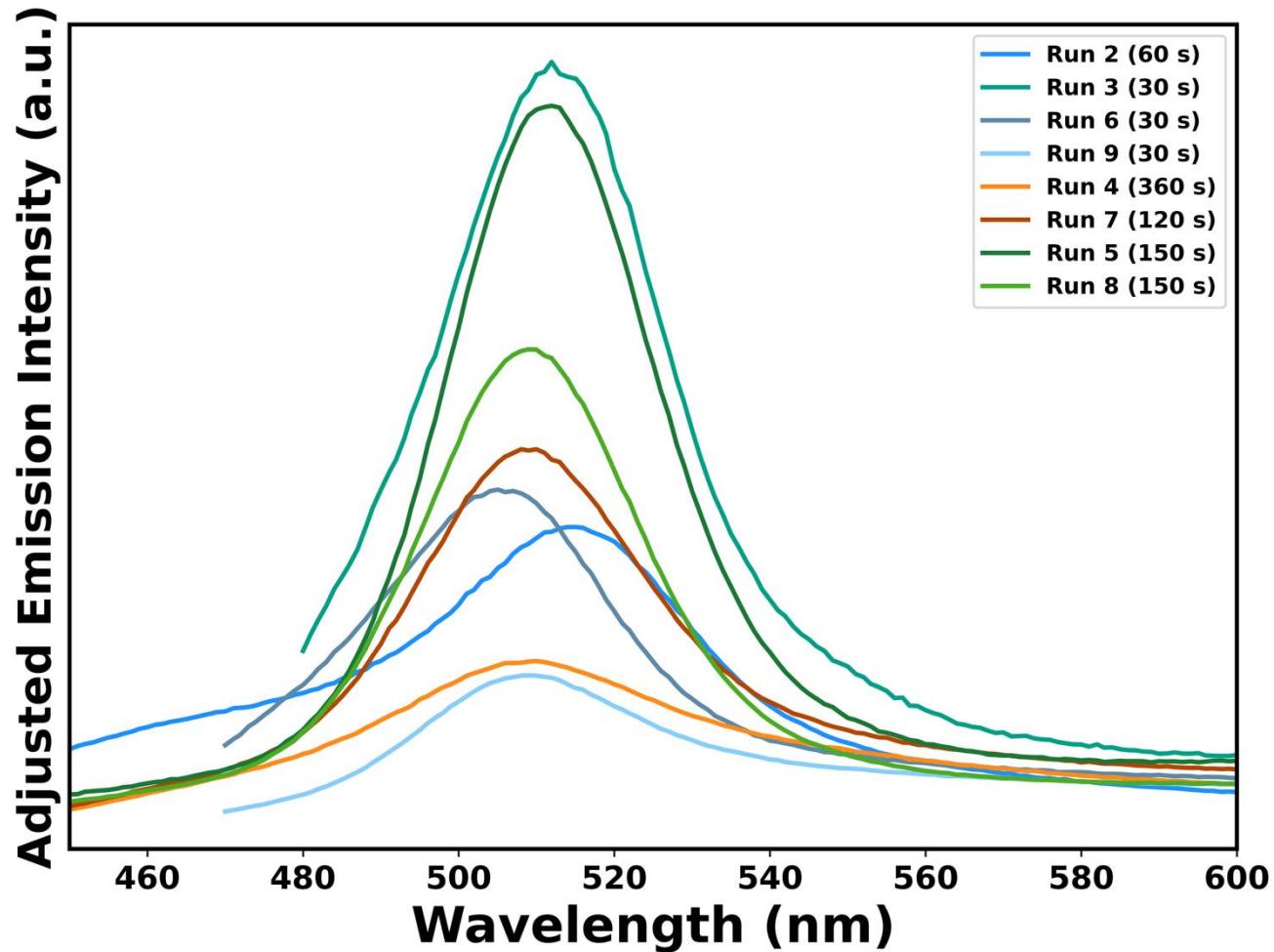
# Optimum reaction conditions I

- All reaction conditions measured have similar growth rates

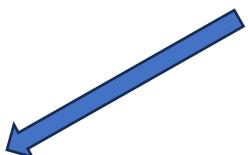
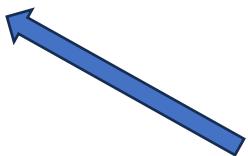
For determining which conditions yield most highly fluorescent particles:

- 1) Only compare particles with the same emission wavelength (510 nm)
- 2) Determine the fraction of photons contributing to emission (control for concentration differences by accounting for absorbance)
- 3) Compare adjusted emission intensities

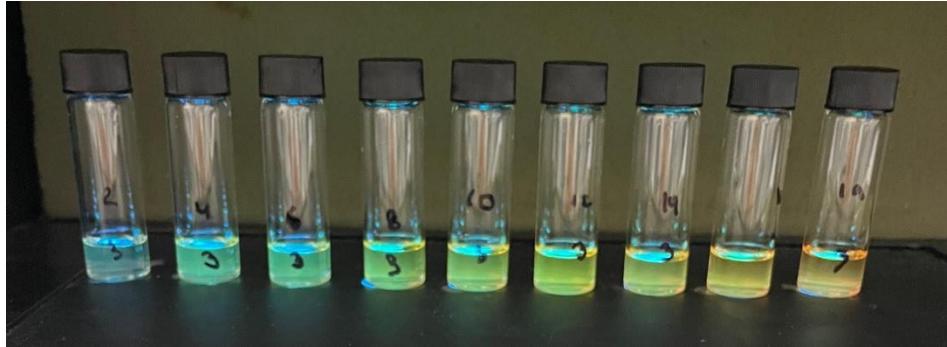
# Optimum reaction conditions II



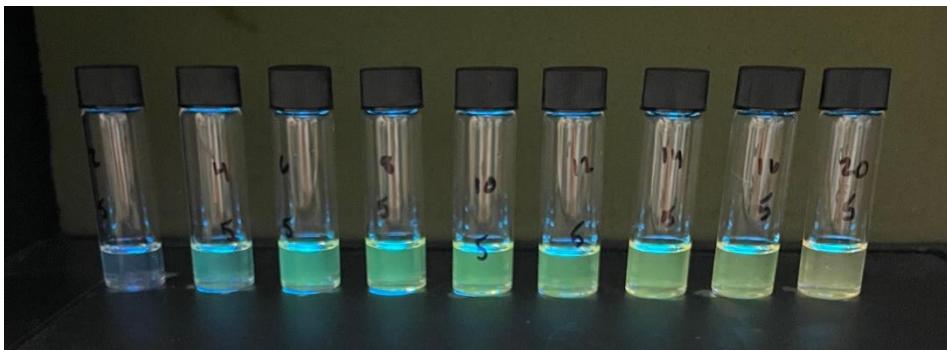
# Best-performing CdSe Quantum Dots



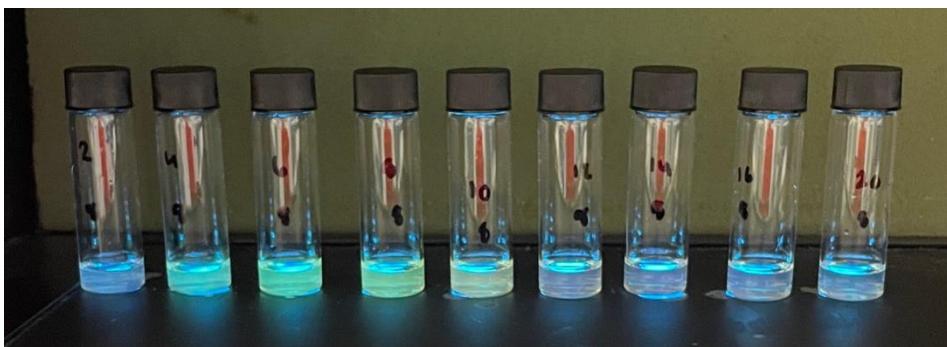
Best  
performing  
dots at 510  
nm



Run 3

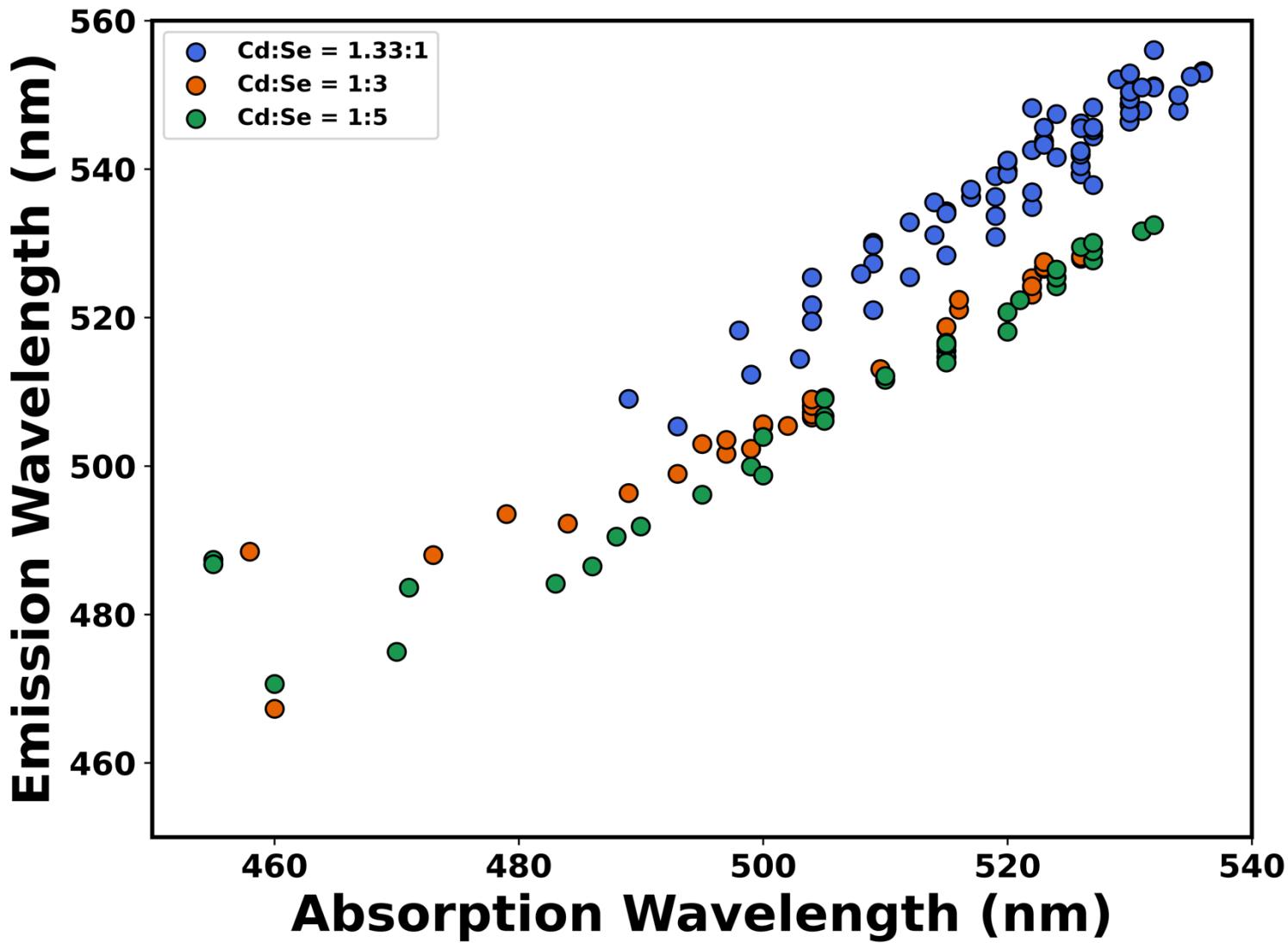


Run 5

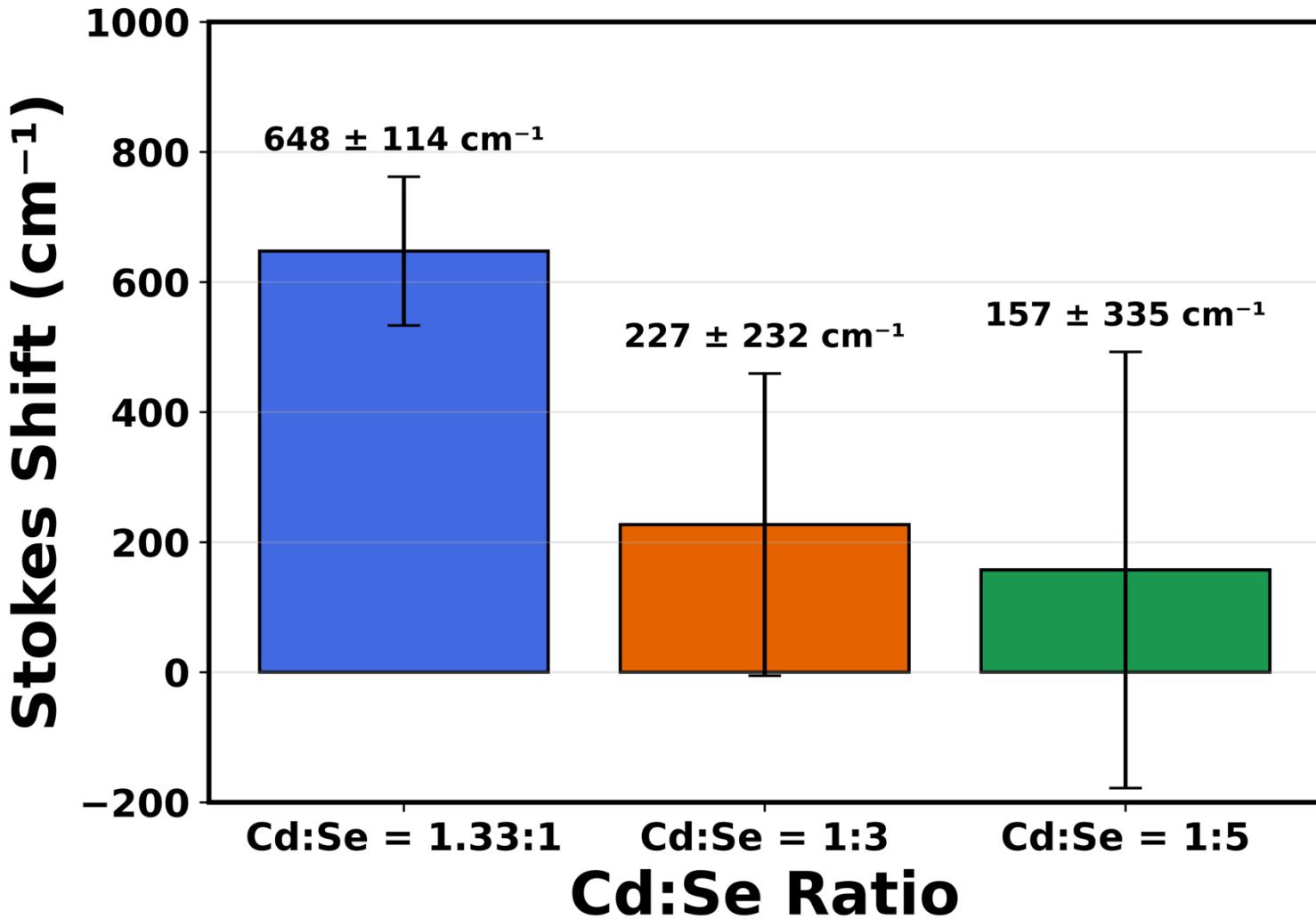


Run 8

# Emission vs. Absorption Peak wavelength

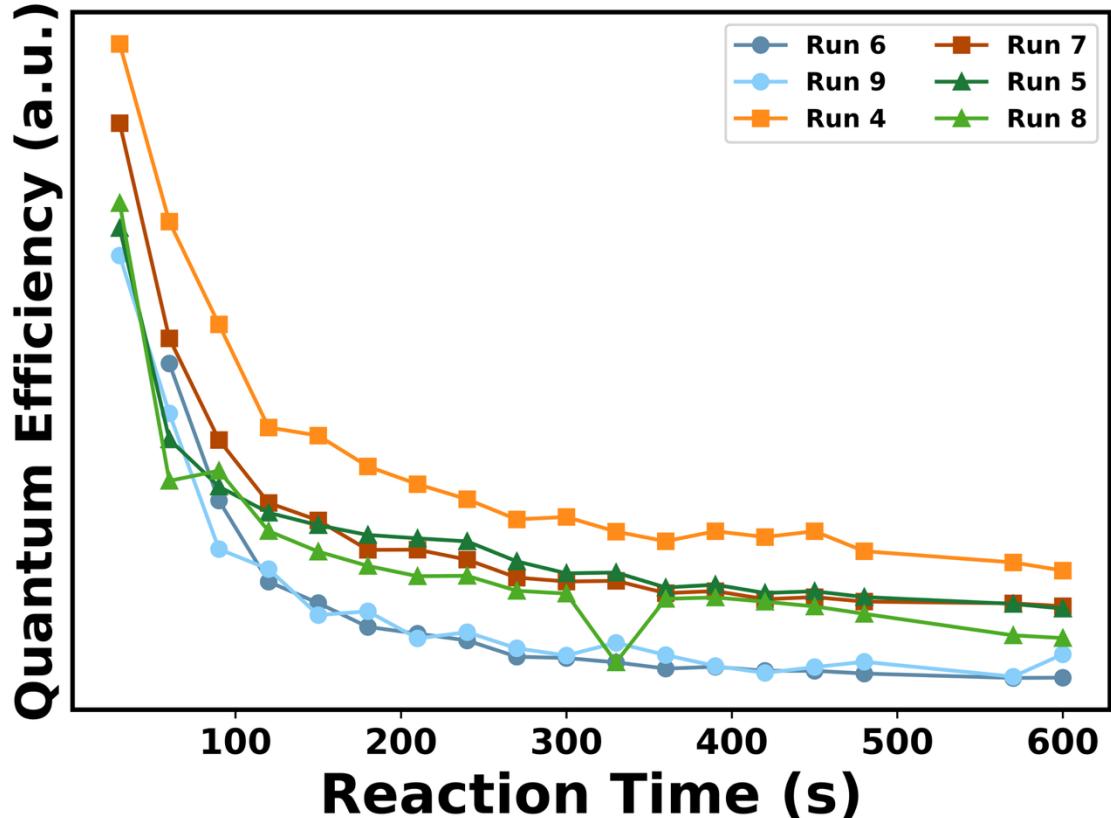


# Stokes Shift



The greater the stokes shift, the more energy lost from absorption to emission via vibrational relaxation.

# Quantum Efficiency



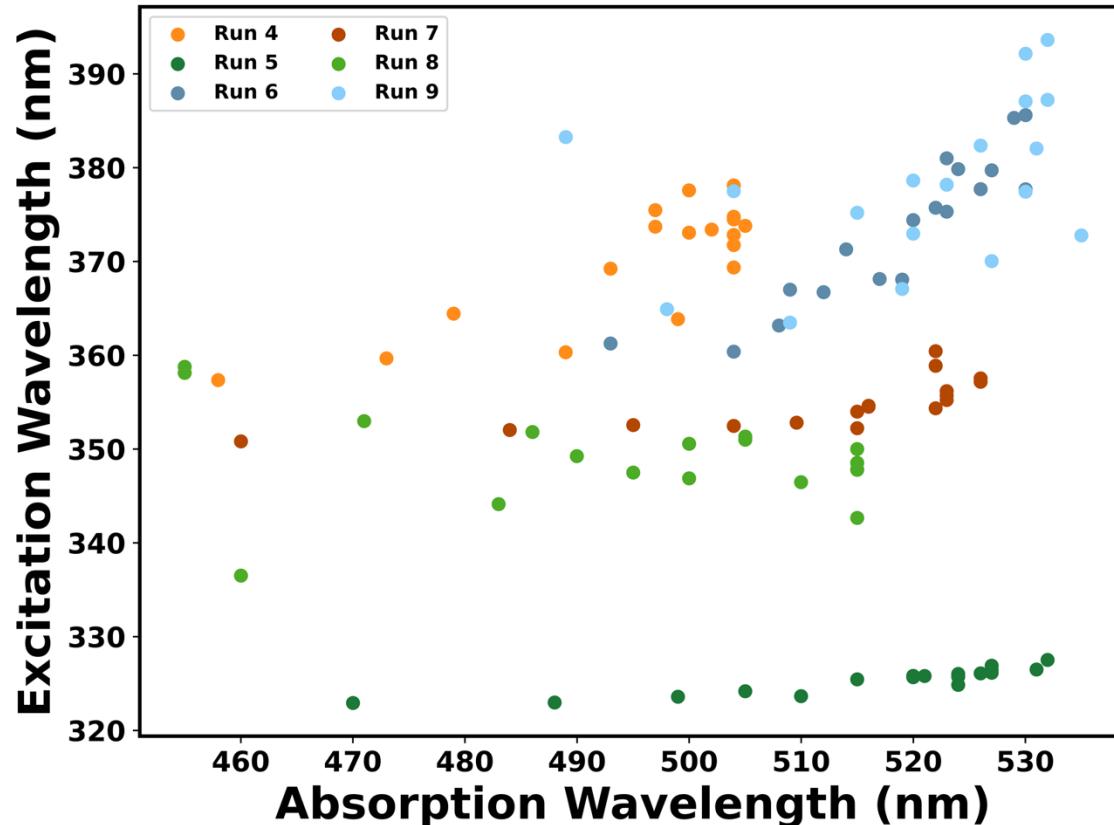
**Absorption spectra:** scan across wavelengths and measure change in intensity to get absorbance

$$A = \varepsilon cd = \log(I/I_0)$$

**Excitation spectra:** set emission wavelength, scan across excitation wavelengths, and measure intensity

$$\text{QE} \propto I_{\text{excitation}}/I_{\text{absorption}}$$

# Relation between excitation and absorption



**Expect:** for highly efficient fluorophores, similar excitation wavelength and absorption wavelength

**Results:** No particular trend, potentially due to emission wavelength selection (too high in energy)

# Potential Impurities

## 1. Cadmium hydroxide formation

If heated and exposed to water, Cd(OH)<sub>2</sub> (insoluble white solid) formation possible.

## 2. Potential underreaction in CdO to Cd(oleate) conversion

CdO is crystalline with band gap 2.2-2.7 eV<sup>6,7</sup>

Broad emission: 600 - 650 nm (orange emission)

- Deep trap emission<sup>6</sup>

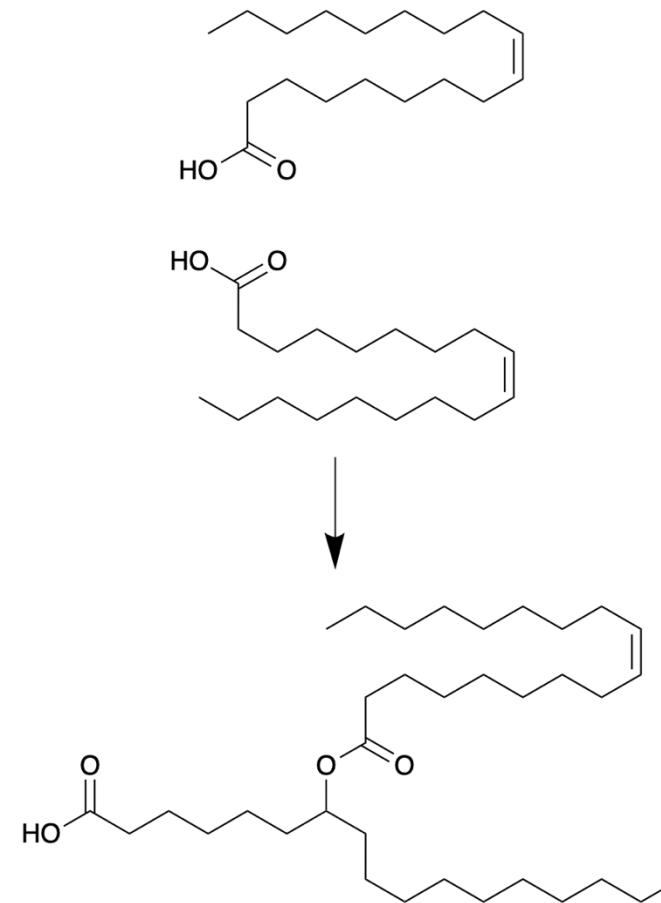
Sharp emission: 700 and 720 nm (red emission)

- Surface state emission

Excitation wavelength: 480 nm<sup>6</sup>

## 3. Polymerisation of Oleic acid at high temperature (via thermal oxidation)<sup>5</sup>

Allylic H abstraction generating unstable alkyl radical hydroperoxide / hydroxide formation.



*Cd(oleate) solution used from runs 7, 8, and 9. Small white insoluble particles observed*

## 4. Octadecene potentially polymerises

*but should not result in observed little crystals*

# Further Work

- More repetition to reduce random errors
- Set the emission wavelength to higher nm in the excitation spectra
- Use a reference for fluorescence data, so quantum yield can be quantitatively determined
- Test different Cd:Se concentrations (5:1, 3:1, and 1:1.33)<sup>9</sup> and different reaction temperatures
- Greener synthesis: using paraffin oil instead of TOP<sup>4</sup>

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## Synthesis with Different Se Concentrations and Optical Studies of CdSe Quantum Dots via Inverse Micelle Technique

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In this work, Cadmium selenide quantum dots (CdSe QDs) are synthesized successfully without the use of trioctylphosphine (TOP) at various concentrations of selenium (Se) precursor. UV-vis, PL and FTIR spectroscopy, as well as TEM and XRD are used for characterization studies of the CdSe QDs. The XRD pattern shows zinc-blend phase of the CdSe QDs. The absorption and PL spectra exhibit a strong blue-shift with decreasing QDs size, which is attributed to the quantum confinement effect. TEM image reveal that the CdSe QDs are spherical, compact and dense in structure with a maximum particles size of ~8nm. The results of this research also indicate the increasing the Cd and Se molar ratios affect the size of CdSe QDs. The FTIR results also show the bonding on the surface of QDs. The results are likely to be useful towards the understanding on the formation mechanism of CdSe QDs.

**Keywords:** Semiconductors; nanostructures; chemical synthesis; optical properties.  
PACS numbers: 78.66.Bz, 81.07.Nb

### 1. INTRODUCTION

Semiconductor nanoparticles are notable for their wide fundamental research and industrial applications [1-2]. Their defining characteristics are their size, which is within the range of 1-100 nm, and excellent chemical processibility. The strong confinement of excited electrons and holes leads to dramatically different optical and electronic properties compared to the bulk semiconductor [3]. Many studies have been devoted on III-V and II-VI semiconductor quantum dots (QDs) throughout the world. For II-VI QDs, CdSe QDs prepared by chemical methods are the most popular [4]. Many studies were focused on CdSe QDs because of their high luminescence quantum yield, narrow band gap and variety of optoelectronic conversion properties compared to bulk CdSe [5]. Considerable progress has been made in the synthesis of CdSe QDs [6, 7]. Most of the techniques employed

*From reference 4*

# References

- [1] Singh, D., Thapa, S., Singh, K. R., Verma, R., Singh, R. P. & Singh, J. (2023) Cadmium selenide quantum dots and its biomedical applications. *Materials Letters: X.* 18 100200. 10.1016/j.mlblux.2023.100200.
- [2] "Nobel Prize in Chemistry 2023." NobelPrize.Org, The Nobel Prize Organisation. Accessed 7 Nov. 2025.
- [3] J. Th. G. Overbeek, *Adv. Colloid Interface Sci.*, 1982, 15, 251–277. DOI: 10.1016/0001-8686(82)80003-1
- [4] Hamizi, N. A., Ying, C. S. & Johan, M. R. (2012) Synthesis with Different Se Concentrations and Optical Studies of CdSe Quantum Dots via Inverse Micelle Technique. *International Journal of Electrochemical Science.* 7 (5), 4727–4734.10.1016/S1452-3981(23)19577-0.
- [5] Bonetti R, Parker WO Jr. Insights into polymerization of vegetable oil: oligomerization of oleic acid. *J Am Oil Chem Soc.* 2019; 96: 1181–4.
- [6] Köhler, H. (1972) Optical properties and energy-band structure of CdO. *Solid State Communications.* 11 (12), 1687–1690. 10.1016/0038-1098(72)90772-7.
- [7] Baykul MC, Orhan N (2014) Effect of seed layer on surface morphological, structural and optical properties of CdO thin films fabricated by an electrochemical deposition technique. *Solid State Electron* 101:29–32. doi:10.1016/j.sse.2014.06.033
- [8] Dhaene E, Billet J, Bennett E, Van Driessche I, De Roo J. The Trouble with 1-Octadecene; Polymerization During Nanocrystal Synthesis. *ChemRxiv.* 2019; doi:10.26434/chemrxiv.8832320.v1
- [9] Aydin, Hakan & Karim, MR & Balaban, Mesut & Ünlü, Hilmi. (2016). Colloidal Synthesis And Characterization Of Cdse Quantum Dots: Role Of Cd: Se Molar Ratio And Temperature. *International Journal of Scientific & Technology Research.* 5. 66-70.