In situ layered double hydroxide (LDH) catalyst study using Sum-frequency generation spectroscopy

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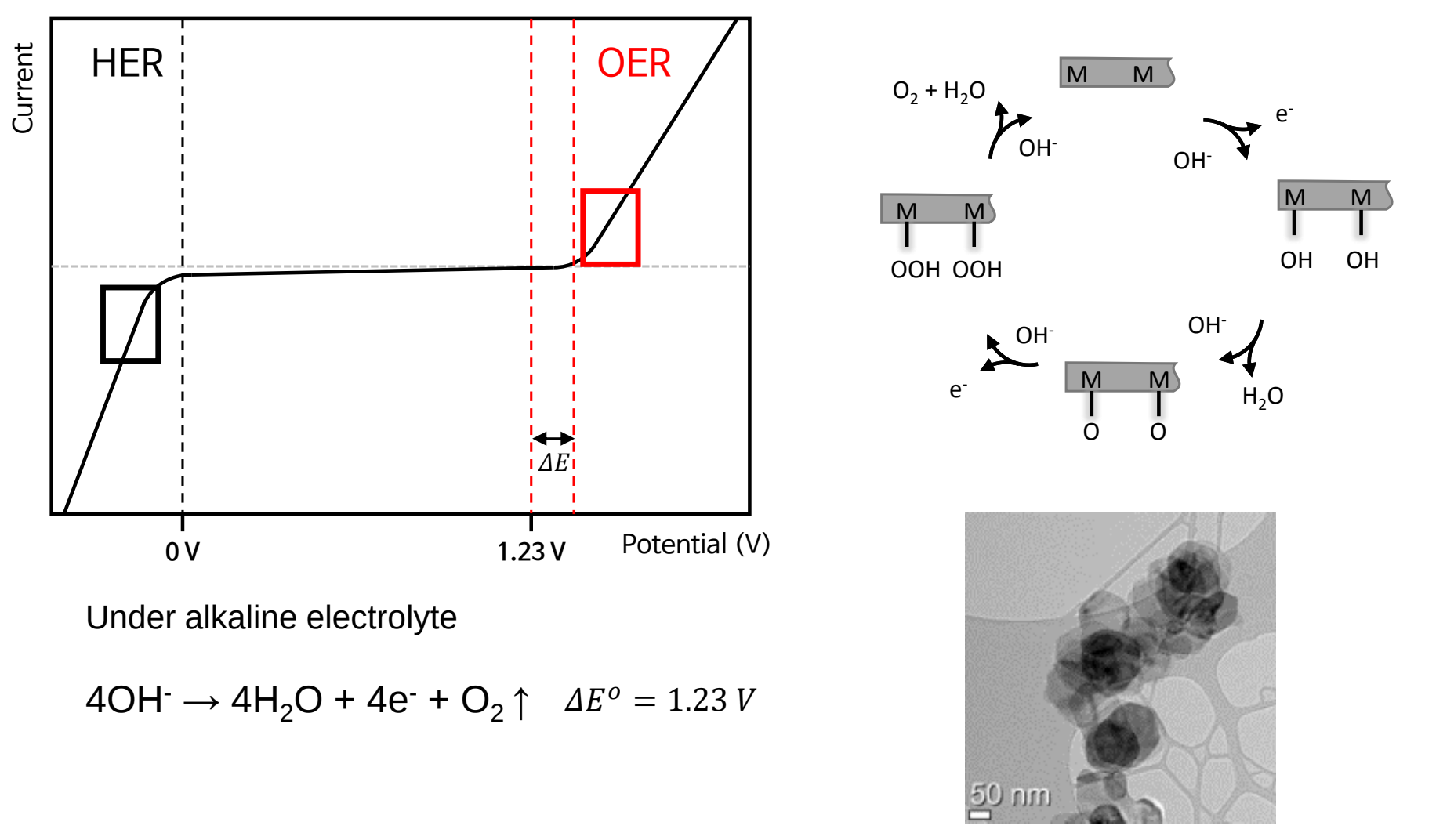
Abstract

Water oxidation is an essential reaction for energy storage such as forming of hydrogen or hydrocarbons without accumulation of by-product. Unfortunately, This reaction is consist of a complex multistep, which adds a considerably large overpotential to the actual process. Although many studies have been conducted on OER catalysts with low overpotential and high stability, the specific catalytic reaction mechanism has not yet been elucidated. Among them, NiFe catalysts, which form layered double hydroxide (LDH) structures by potential, show excellent performance in alkaline conditions. The performance of the catalyst varies depending on the distance between the layers and the ratio of Ni and Fe. To understand this catalytic tendency and mechanism, it is important to use surface/interface selective spectroscopic method. Here, using vibrational sum-frequency generation (VSFG) spectroscopy, we selectively identified graphene electrode-electrolyte interfacial molecules. we designed spectro-electrochemical (SEC) cell for in situ SFG experiment. In this work, using nonlinear spectroscopic method, we observed that the hydrogen bonding network of the interfacial water molecules changes at each potential. Our results show that the SFG signal from the interface is originated from the confined water of LDH catalyst and water molecules of electrolyte.

Water splitting reaction



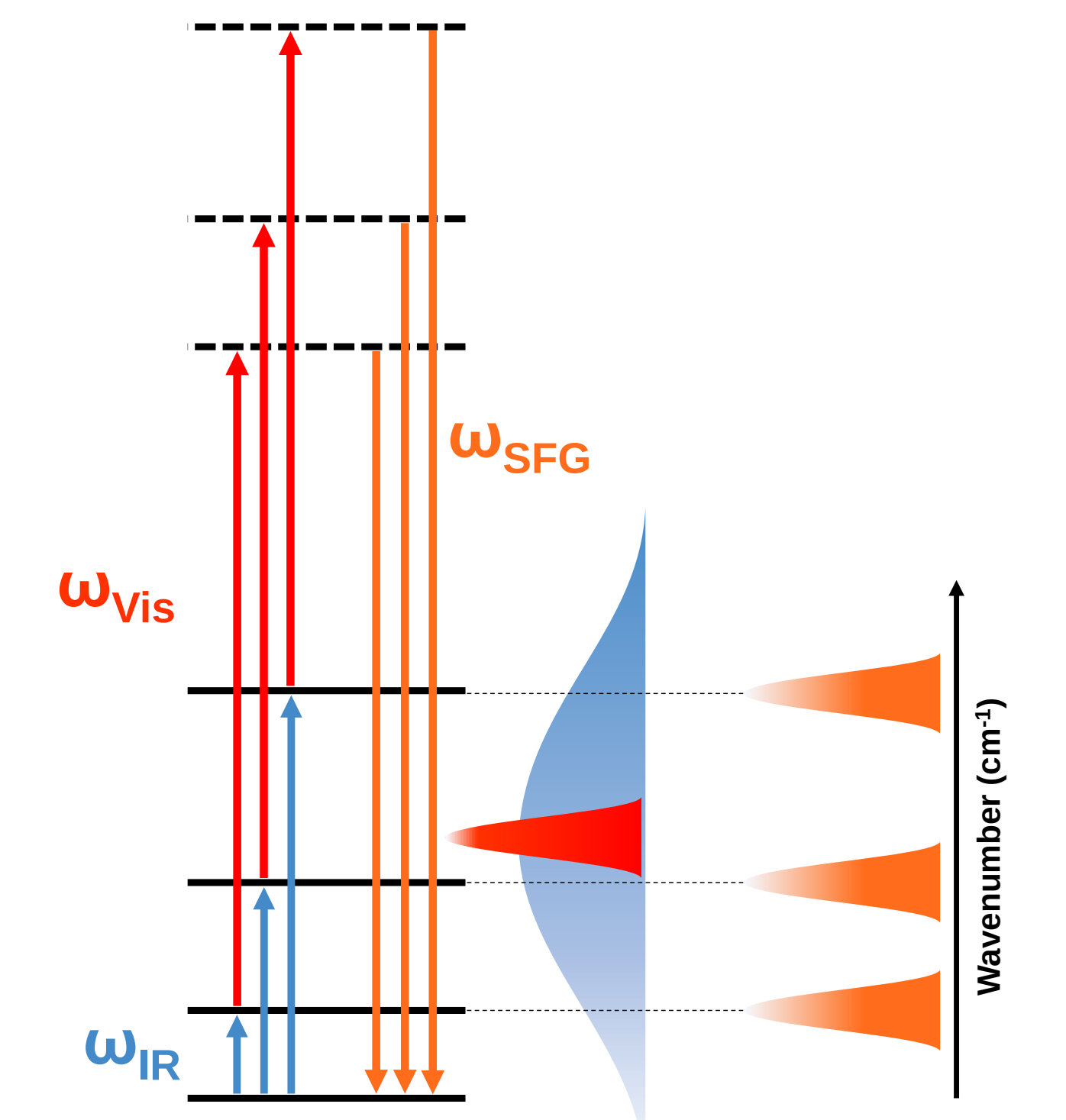
Under alkaline electrolyte

$4OH^- \rightarrow 4H_2O + 4e^- + O_2\uparrow \quad \Delta E^o = 1.23\ V$

Ni based layered double hydroxide catalyst

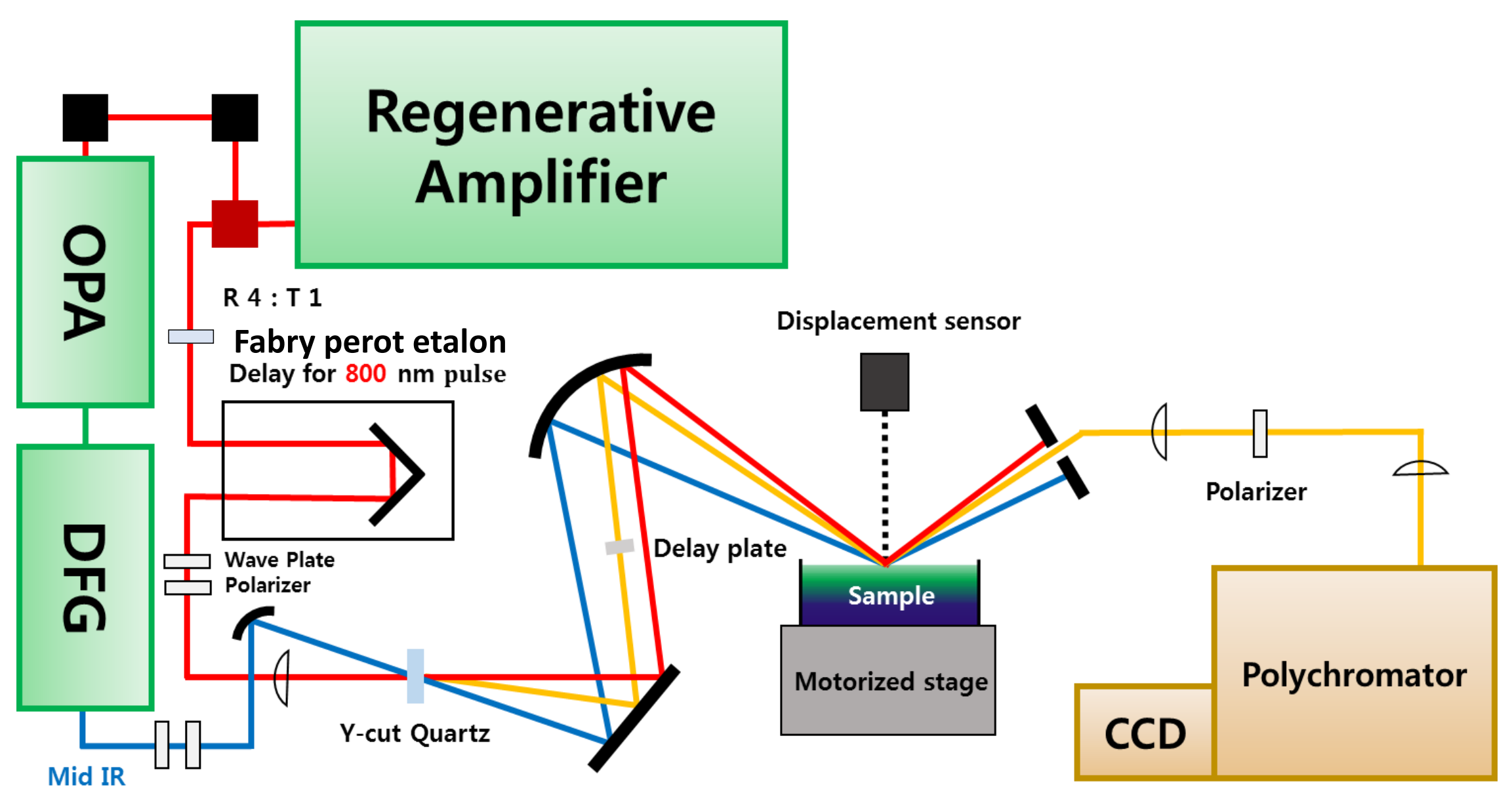
Experimental background

Concept of SFG



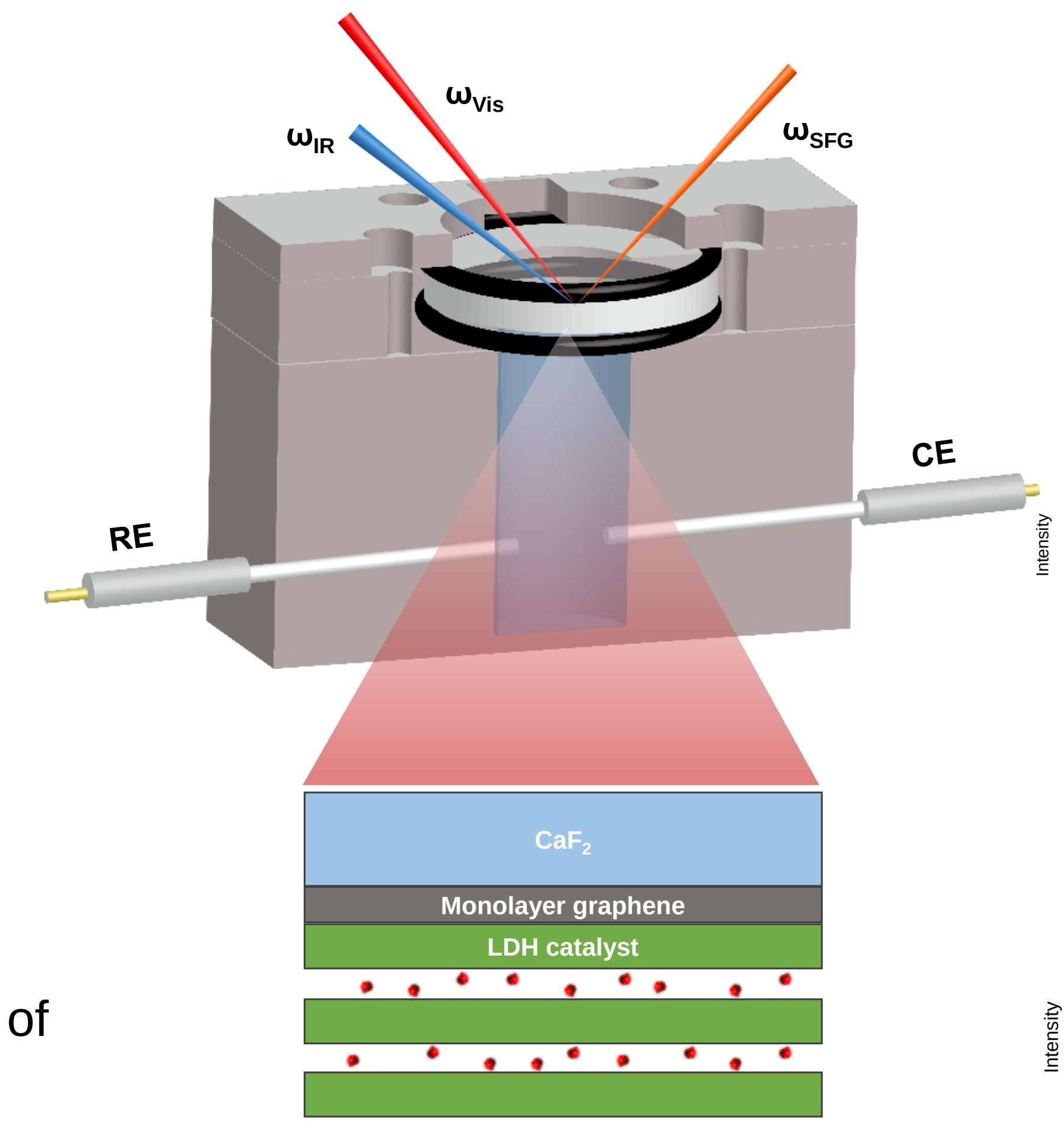
- ✓ The narrow band vis beam (800 nm) is just prerequisite for the second order nonlinear process.
- ✓ The broadband IR resonates with the vibrational mode of the sample.

Experimental setup

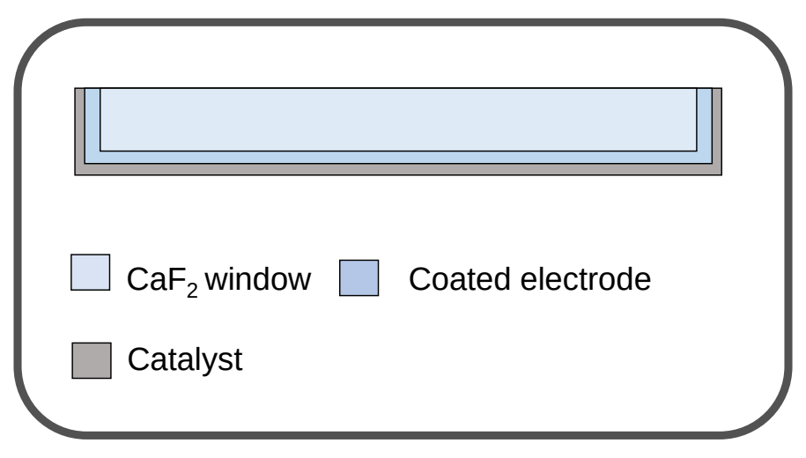


- ✓ 800 nm vis, tunable mid IR focused on sample stage and generate sum frequency signal.
- ✓ Using a displacement sensor, accurately measure the height of the sample stage to control the overlap between vis and IR.

In situ electrochemical cell



Requirements for electrode coated on CaF_2 window

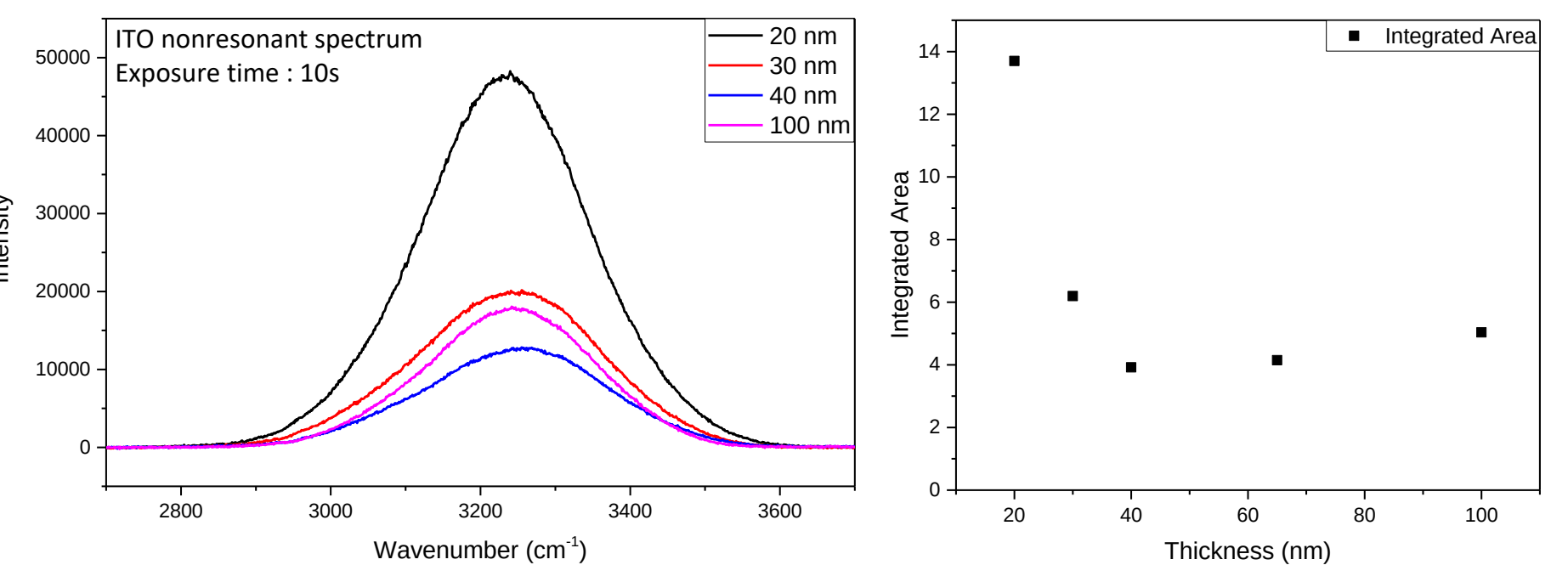


- ✓ There is non-resonant signal enhancement when using semiconductor material such as iTO.

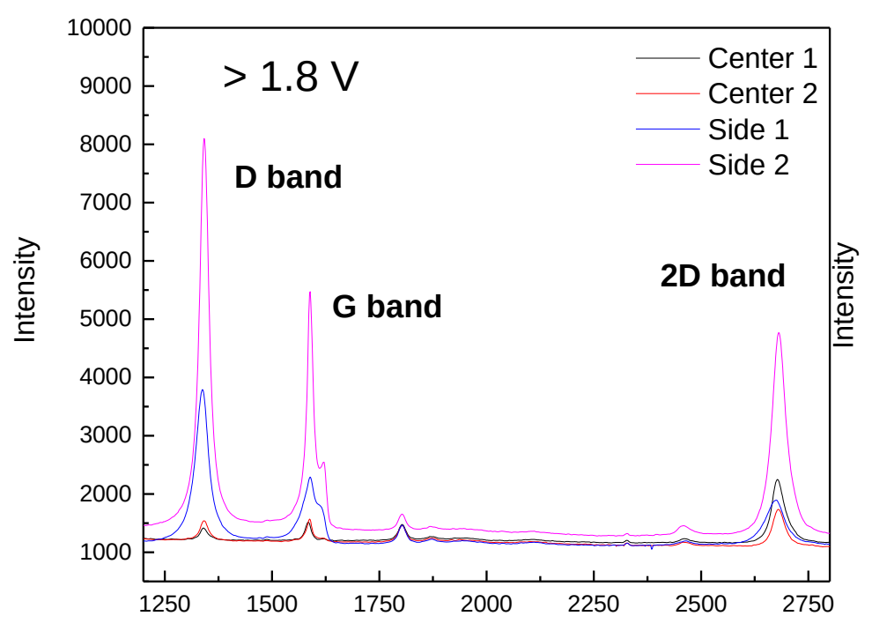
$$I_{SFG} \propto \left|\chi_{NR}^{(2)} + \sum_{v=1}^{n} \chi_{res,v}^{(2)} e^{i\gamma_v}\right|^2$$

- ✓ Raising above a certain potential causes graphene to oxidize to form graphene oxide.

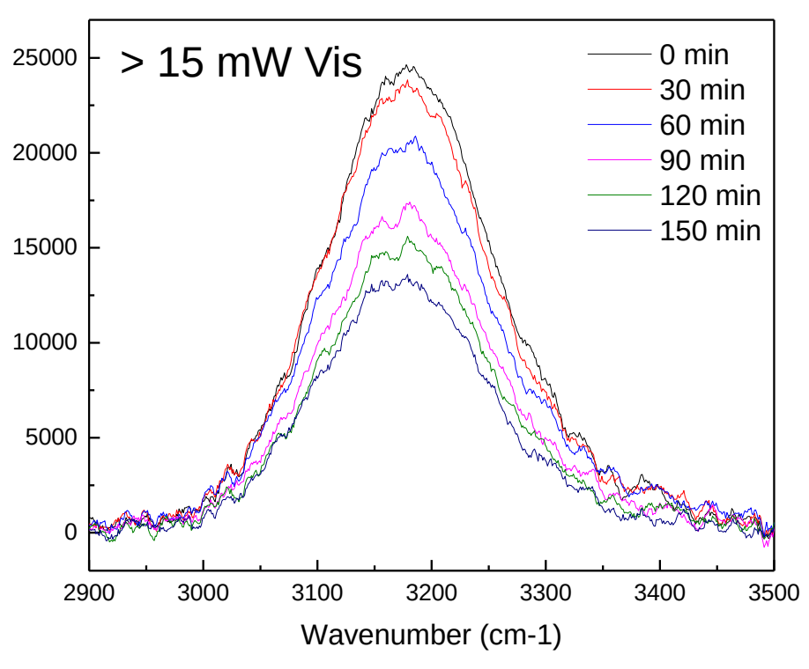
Non-resonant signal of iTO



Raman spectra of oxidized graphene



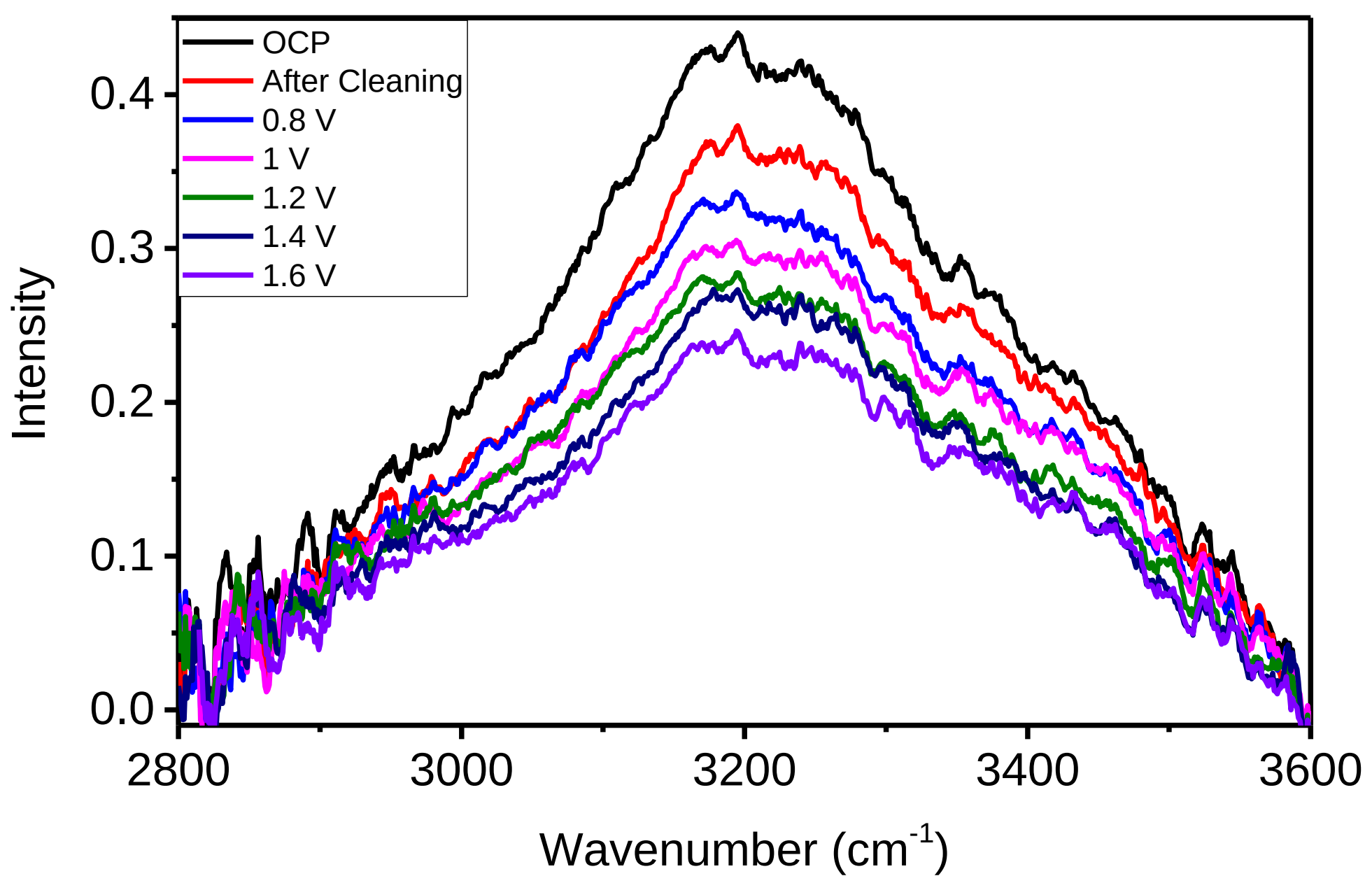
Laser degradation of graphene



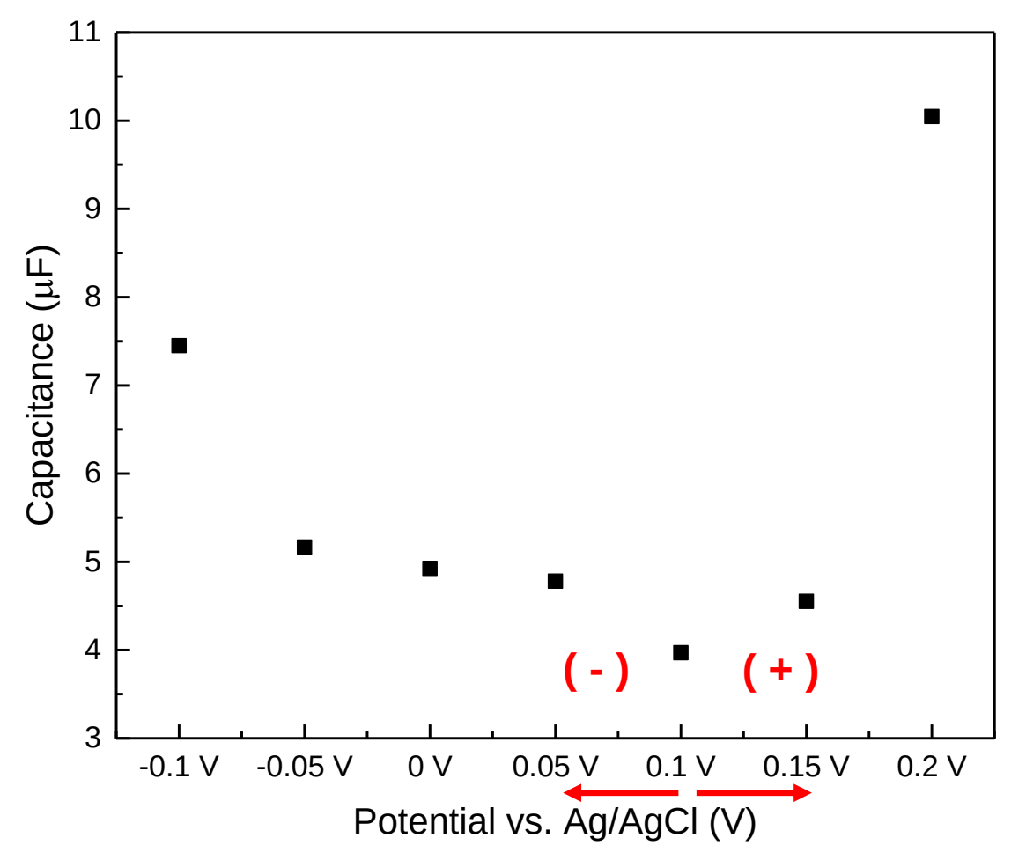
Experimental results

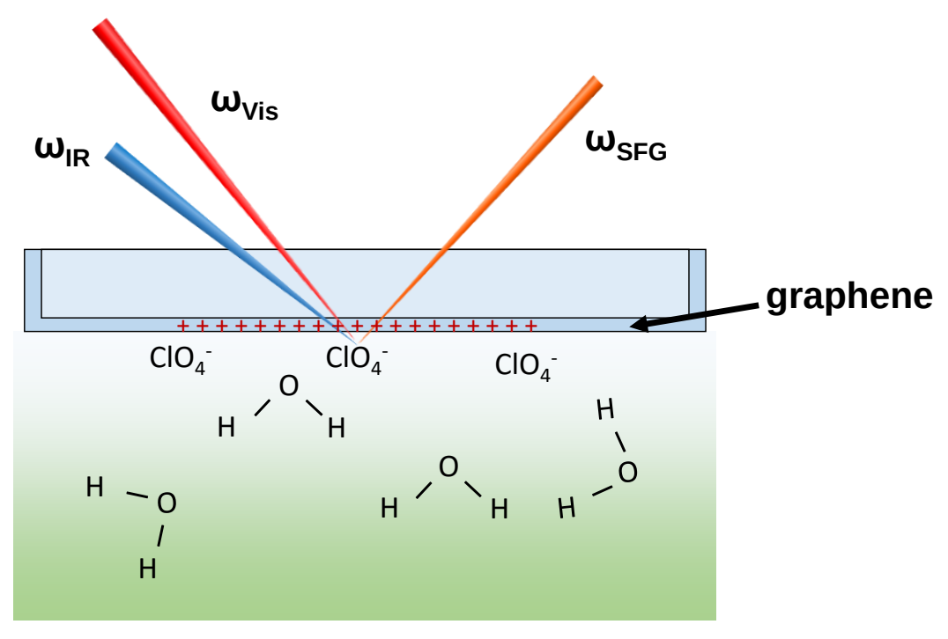
In situ graphene/electrolyte interface study

Potential dependent spectra at interface

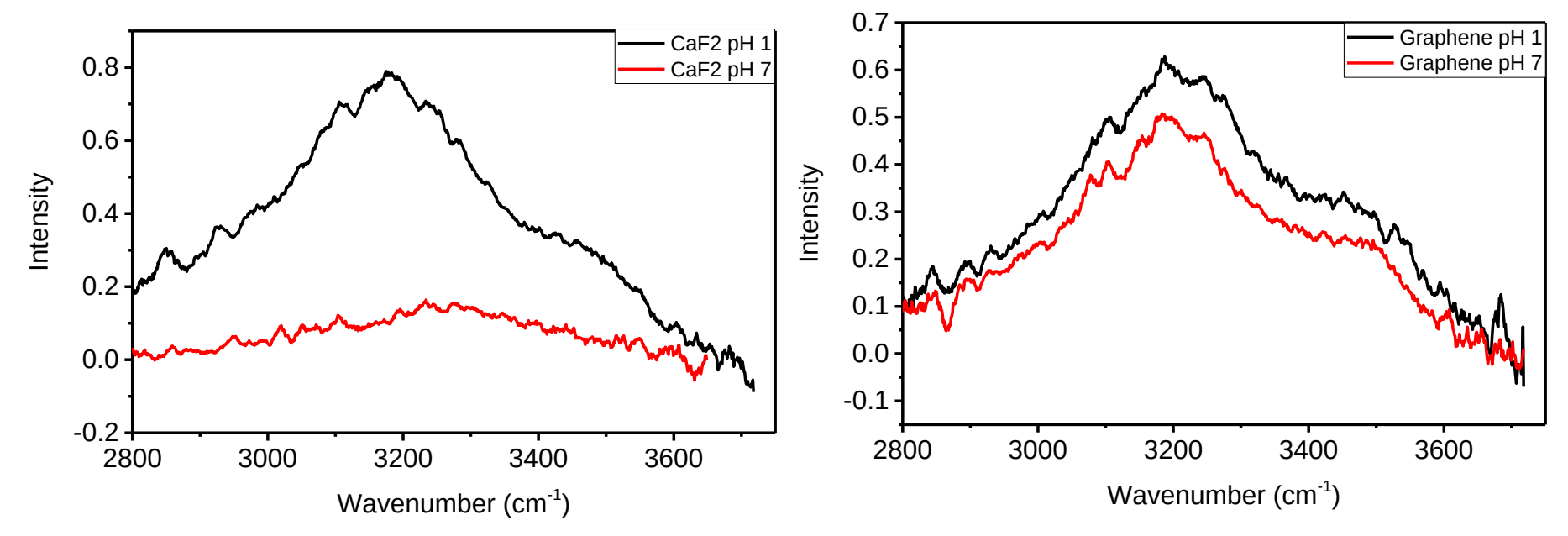


Measurement of PZC using EIS

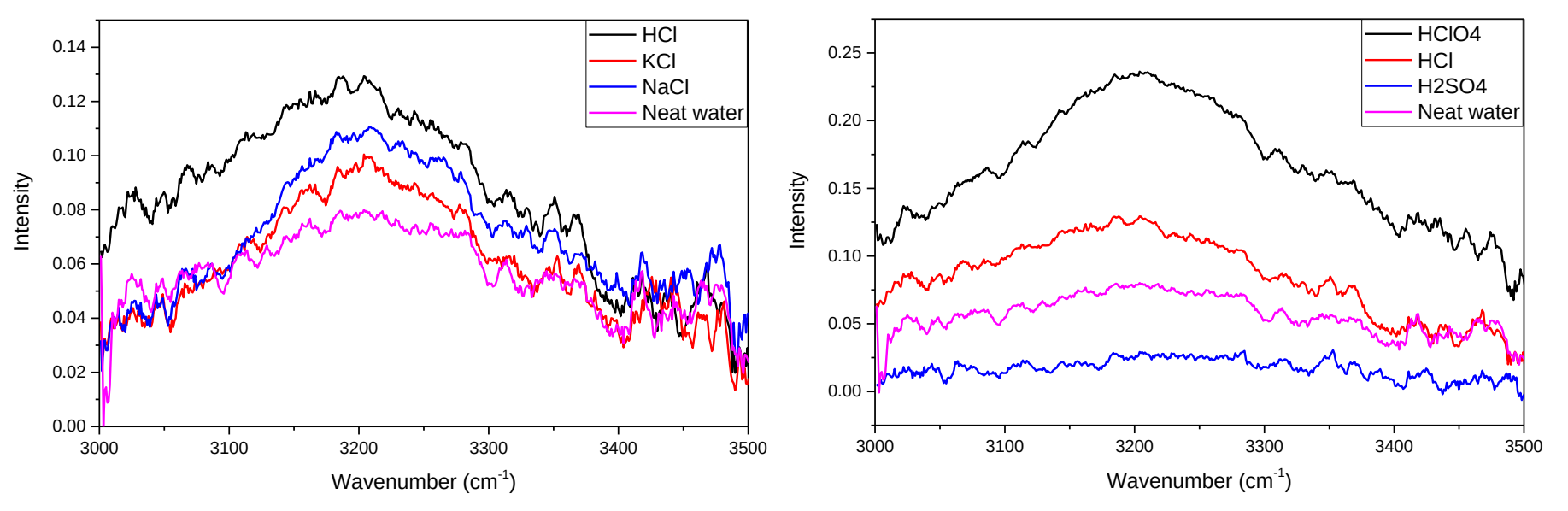




Spectra of CaF_2, graphene at different pH

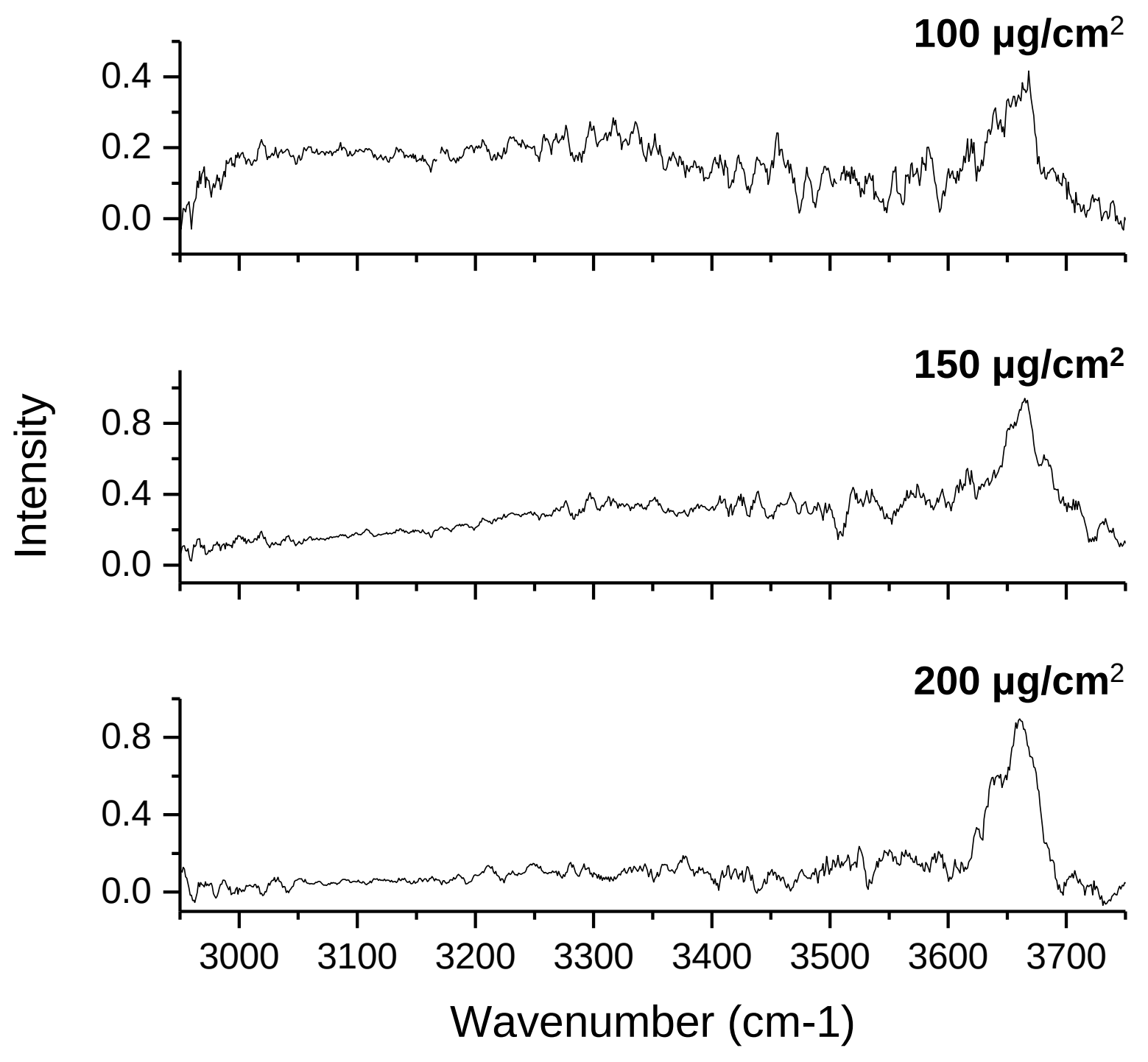


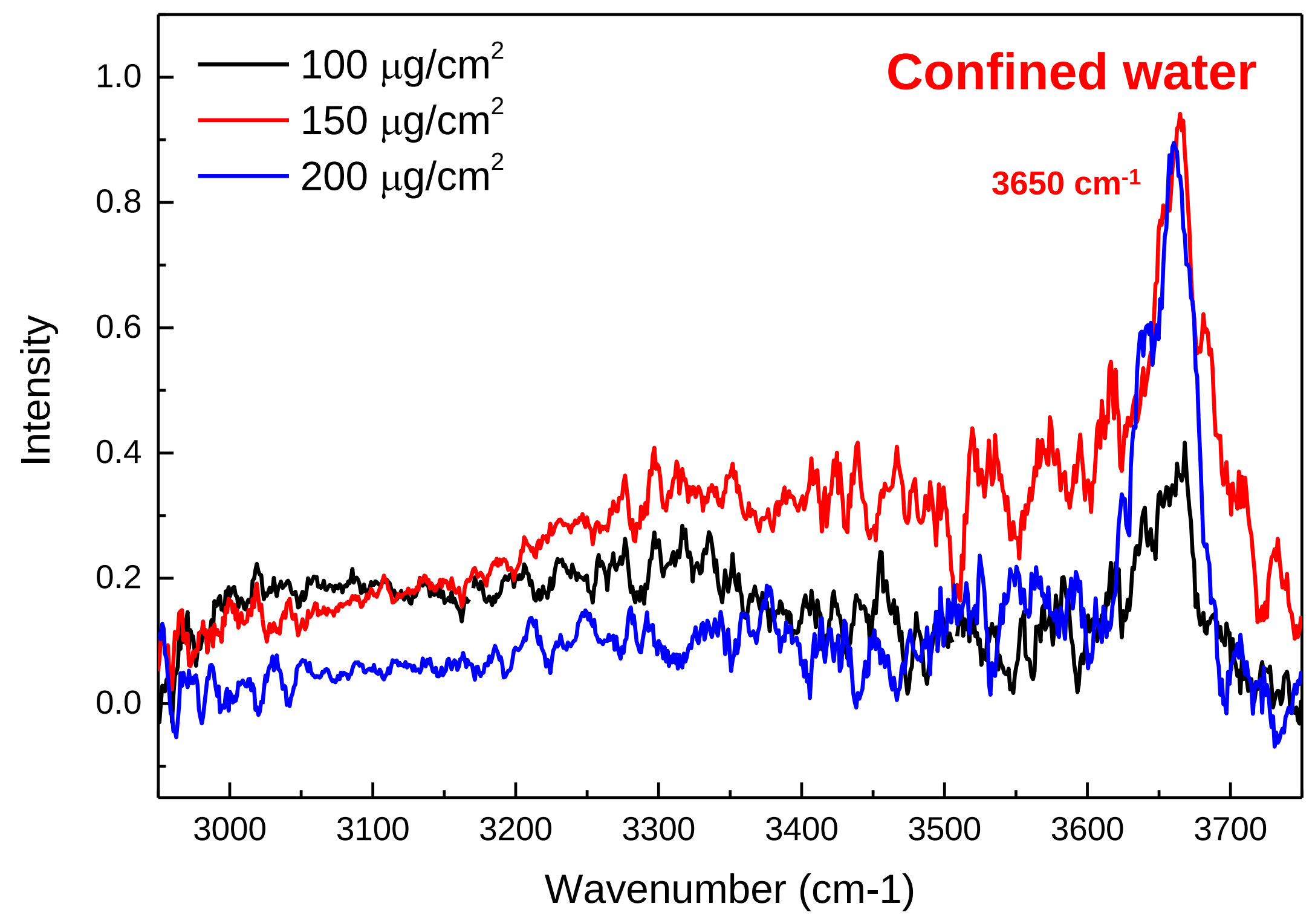
Spectra of graphene at different electrolyte



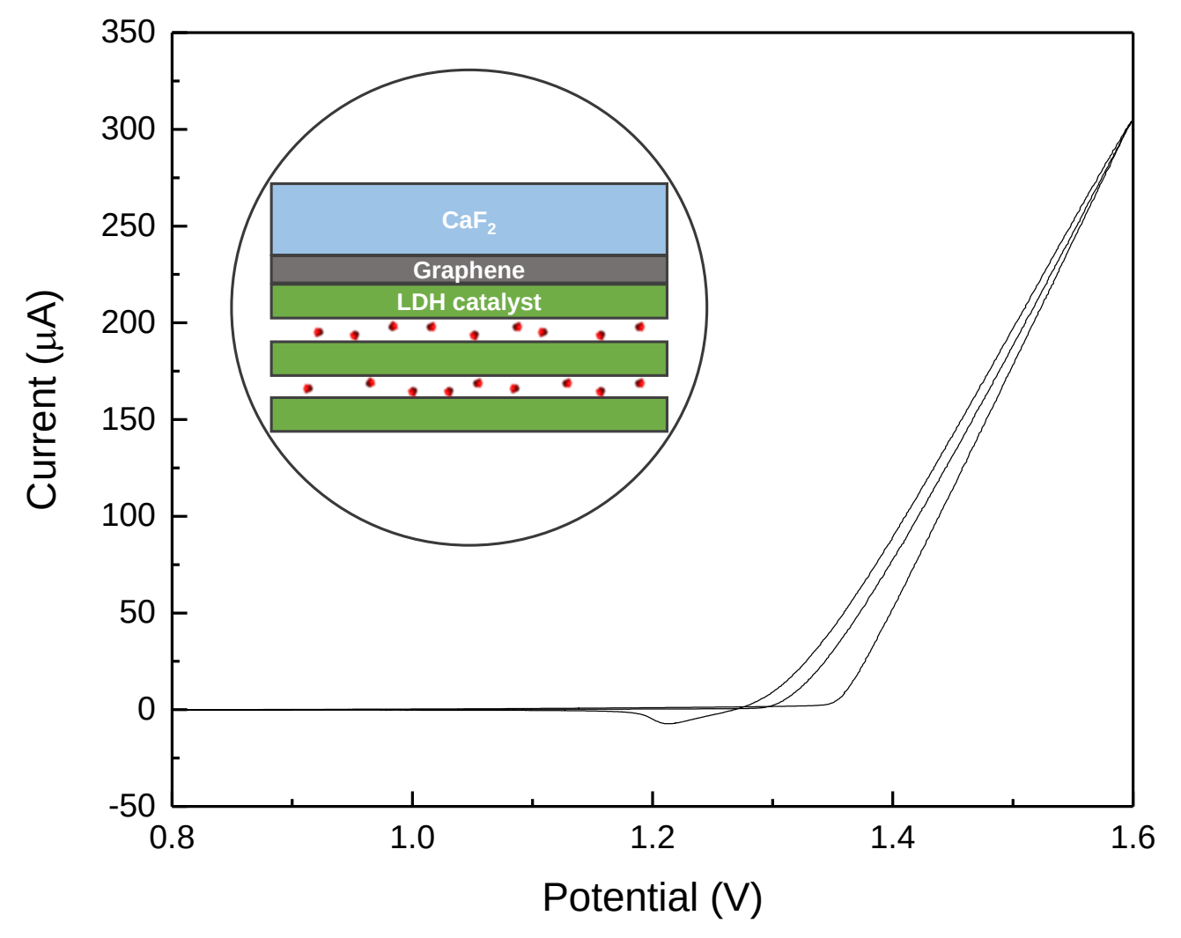
- ✓ Using the Electrochemical impedance spectroscopy, we confirmed that the point of zero charge of the graphene / acid interface was 0.1 V.
- ✓ As the potential increased, the signal intensity gradually decreased, which is expected to be an *anion screening effect* with increasing surface charge.
- ✓ Interfacial signal intensity is also different depending on the electrolyte.

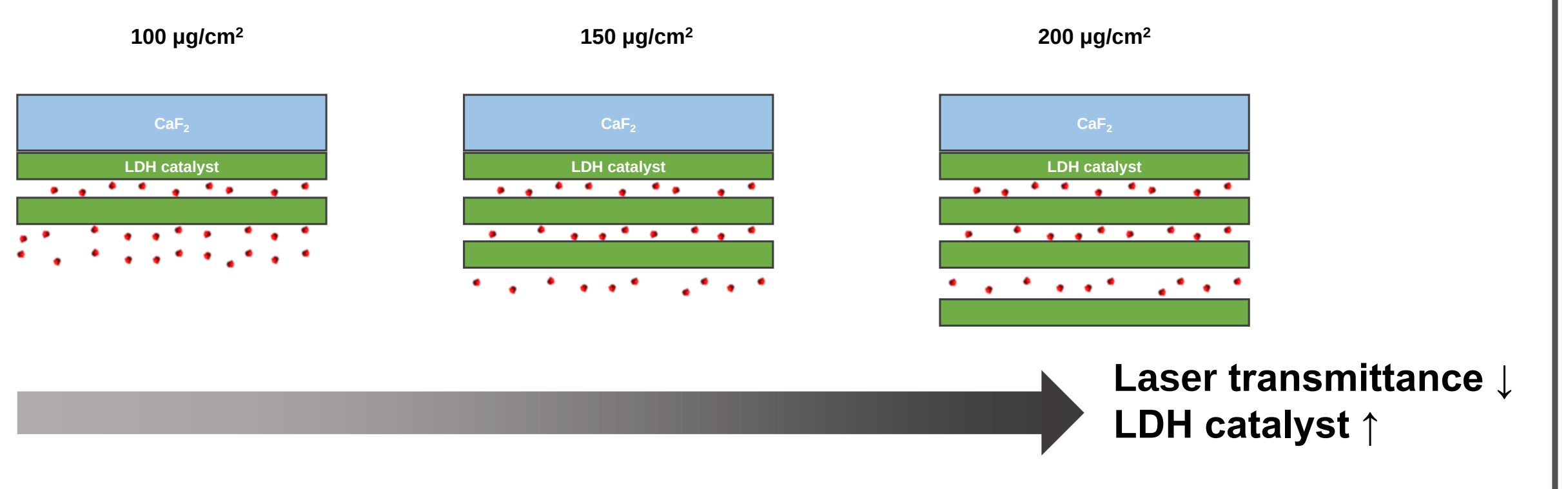
In situ confined water of LDH catalyst study





Electrochemical test (CV)





- ✓ As measured by varying the amount of catalyst, the 3650 cm⁻¹ peak tended to increase and the intensity of the 3000 to 3400 cm⁻¹ (hydrogen bonded region) increased and then decreased.
- ✓ As the amount of catalyst increases, laser transmittance decreases, so it can be seen that the OH intensity of electrolyte decreases and the intensity of the confined OH between layers of catalyst increases.

Summary

- ✓ The spectro-electrochemical cell work successfully using graphene monolayer electrode without using semiconductor material that is origin of strong non-resonant background.
- ✓ At the graphene/water interface, the increase of potential results in an increase of surface charge, which results in increase of anion. As a result, the number of water molecules present at the interface decreases, thereby reducing the signal intensity. These effects vary depending on the type of electrolyte and are dramatic depending on the anion rather than cation.
- ✓ As the catalyst thickness increased, the electrolyte signal decreased and the catalyst signal increased. At this time, since 3650 cm^{-1} is an OH peak with little hydrogen bonding, it can be seen that it is OH of confined water existing between catalyst layers.