

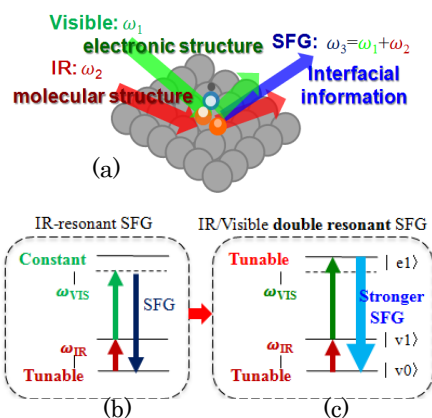
## Potential-Dependent Double Resonance Sum Frequency Generation Spectroscopy as In Situ Probe of Electronic Structure at Electrode/Electrolyte Interface

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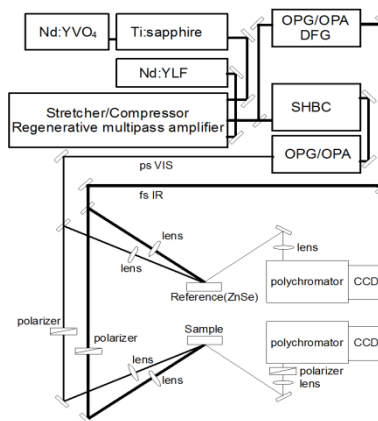
In order to understand the mechanism and improve the efficiency of interfacial processes in electrochemical reactions, it is essential to obtain in situ information on the geometric structure of the electrode surface, molecular structures of reactant, product, intermediate and solvent at electrode/electrolyte interface, and electronic structure of the interface.

Although many useful techniques applicable to electrode/electrolyte interfaces have been developed in last thirty years, in situ techniques to probe the electronic structure at electrochemical interface are still limited because of the presence of electrolyte solution, in which it is impossible to use techniques with electron probes, which are most powerful for determining electronic structure in ultrahigh vacuum (UHV).

Recently, Somorjai et al. reported an interesting technique, IR/visible double resonance sum frequency generation (DR-SFG) spectroscopy, which is developed based on traditional SFG spectroscopy.<sup>[1]</sup> SFG is particular noted for its high surface-sensitivity, in which sum frequency signal at  $\omega_3 = \omega_1 + \omega_2$  is generated by overlapping IR and visible beams with frequencies of  $\omega_1$  and  $\omega_2$  on the surface, as shown in Figure 1(a). A vibrational SFG spectrum is obtained by tuning only IR wavelength over vibrational transition energies at the interface (Figure 1(b)), which reveals the molecular structures of surface chemicals. With tuning both IR and visible wavelengths, when IR is resonant with the vibrational state and SFG is resonant with the electronic state of surface species, doubly resonant enhancement of SFG signal, i.e. DR-SFG effect, takes place, as shown in Figure 1(c). Thus, DR-SFG spectroscopy allows a simultaneous probing for vibrational and electronic transitions at the interface. This technique has been successfully used to elucidate interfacial electronic structure in UHV condition.<sup>[1]</sup> It should be a promising technique to probe the electronic structure of electrochemical interface, because it is a photon input-photon output technique. Figure 2 shows a broadband femtosecond SFG laser system employed for our DR-SFG measurements,



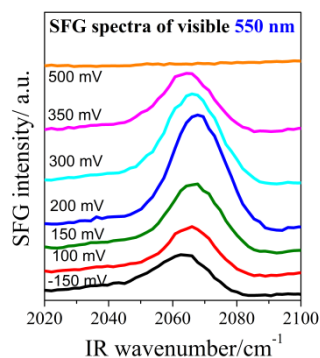
**Figure 1.** (a) Experimental schematic of SFG spectroscopy. Energetic excitation diagram for (b) SFG and (c) DR-SFG process.



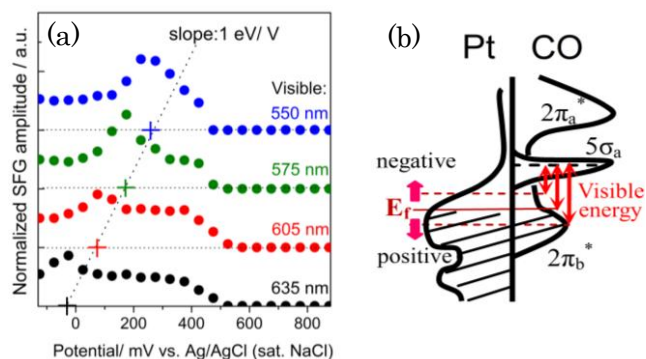
**Figure 2.** Block diagram of the broadband femtosecond SFG laser system used for DR-SFG measurements.

in which the fluctuation of SFG intensity due to laser intensity fluctuation was removed by introducing a reference CCD detector.

In the present study, the DR-SFG technique combined with electrochemical method was applied to probe the electronic structure of CO adsorbed on various Pt electrode surfaces, including Pt(111), polycrystalline Pt and Pt thin layers modified Au substrates, in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution by using visible light of different energies, since CO/Pt interface is the simplest and most studied model system for fundamental studies of many important electrochemical reactions.<sup>[2,3]</sup> Figure 3 shows potential-dependent SFG spectra of Pt(111) electrode with pre-adsorbed CO in a CO free Ar saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution using 550 nm as a visible light. In Figure 3, a SFG peak due to C-O stretching of CO adsorbed on Pt atop site is observed at around 2060 cm<sup>-1</sup>. Both wavenumber and intensity of the SFG peak depend on potential. Anomalous intensity increase of the SFG peak is observed prior to anodic CO oxidation. The SFG peak intensity is also dependent on the energy of visible light. The potential, at which the anomalous SFG peak is observed, is found to be shifted negatively as the energy of the incident visible light decreases, as shown in Figure 4(a). The peak potential and visible light energy are linearly related with the slope of 1 eV/V, showing that the origin of the anomalous increase of SFG intensity at CO/Pt(111) electrode interface is due to a surface electronic resonance, in which the energy of visible and/or SF light becomes equal to the energy of interfacial electronic transition from the Fermi level of Pt(111), which is tuned by the electrode potential, to the 5σ<sub>a</sub> antibonding state of adsorbed CO, as shown in Figure 4(b). Furthermore, in order to well understand the relationship between interfacial electronic structure and catalytic activity of the electrode, the effect of substrate on the electronic structure of CO/Pt was also discussed.



**Figure 3.** Potential-dependent SFG spectra of CO/Pt(111) in a CO free Ar saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> using 560 nm visible light.



**Figure 4.** (a) The normalized SFG peak amplitude of atop CO band as a function of potential obtained using various visible energy. (b) A model of electronic structure of CO/Pt(111) interface.

The present work demonstrates a new possibility of the potential-dependent DR-SFG spectroscopy to probe the interfacial electronic structure, which is difficult to be determined in electrochemical environment.

## References

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