

Mini Review

The *In-Situ* Spectroscopy to Investigate the Electrochemical Reduction of CO₂

Meng Y^{1,2*}, Feng X^{3,4}, Hao C⁵, Sun Q⁶ and Javey A⁷¹State Key Laboratory of Advanced Optical Communications System and Networks, School of Electronics Engineering and Computer Science, Peking University, Beijing, China²Center for Flexible Electronics Technology, Tsinghua University, Beijing, China³Department of Engineering Mechanics, Tsinghua University, Beijing, China⁴Interdisciplinary Research Center for Flexible Electronics Technology, Tsinghua University, Zhongguancun North First Street 2, Beijing, China⁵State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, P.R. China⁶Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, No.8 Yangyan West One Road, Huairou District, Yanxi Economic Development Zone, Beijing, China⁷Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan, USA

*Corresponding author: Yanfang Meng, State Key Laboratory of Advanced Optical Communications System and Networks, School of Electronics Engineering and Computer Science, Peking University, Beijing 100871, China; Center for Flexible Electronics Technology, Tsinghua University, Beijing, 100084, China

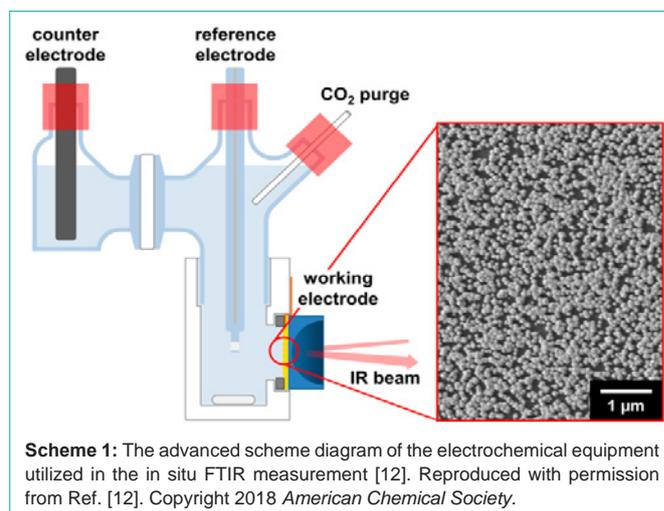
Received: January 28, 2022; Accepted: February 26, 2022; Published: March 05, 2022

Background

The *in situ* attenuated total reflection Fourier transform infrared spectroscopic (FTIR) [1-3], dating back to the 90s' of last decades, is the most powerful approach to real time character the oxygen-containing group on the catalyst during the electrochemical reduction CO₂ reaction. The FTIR offers platform for tackle the greenhouse effect stemming form continuous increase of CO₂ emissions. Though the monitoring real time the attenuated total reflection Fourier transform infrared spectroscopy of the catalyst and intermediate products separately, we can acquire the information of the intermediate products and variation condition of the reaction system and gain strong evident for further analysis. Therefore, the FTIR possesses the advantages of comprehensive, real-time and high sensitivity [4,5].

Research Gap

First, the interpretation of principle of relationship between the microstructure of the corresponding catalysts and the reaction product properties is not accessible by *in situ* attenuated total reflection Fourier transform infrared spectroscopy. Second, the optimum of synergistic interactions among the multiple factors is supposed to be unambiguities by *in situ* attenuated total reflection Fourier transform infrared spectroscopy. Third, to meet the new demands of area of high efficiency, the comprehensive properties of



Scheme 1: The advanced scheme diagram of the electrochemical equipment utilized in the *in situ* FTIR measurement [12]. Reproduced with permission from Ref. [12]. Copyright 2018 American Chemical Society.

the measurement are supposed to be explored urgently.

Research Question

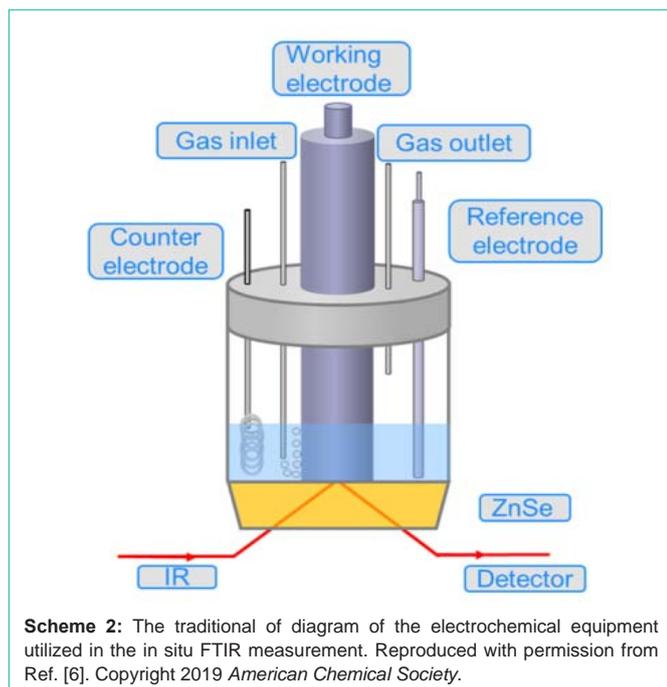
The evaluating the setup of the *in situ* attenuated total reflection Fourier transform infrared spectroscopy (FTIR)

Scheme 1 illustrates the traditional of diagram of the electrochemical equipment utilized in the *in situ* FTIR measurement [6].

The reaction tank equipped with counter electrode, reference electrode, gas inlet and gas outlet. The infrared laser is fixed in the bottom of the device and accompanied with a detector. The real time *in situ* attenuated total reflection Fourier transform infrared spectroscopy measurement is conducted using each Cu film, which is plated on a hemispherical Si ATR prism. Spectra can be read out *via* the Kretschmann attenuated total reflection (ATR) configuration using a JASCO FT/IR4200 Fourier transform IR spectrometer equipped with the HgCdTe (MCT) detector with a resolution of 4 cm⁻¹. However the traditional setup of the *in situ* FTIR had the drawbacks of unsatisfying sensitivity and stability.

The mechanism of the *in situ* attenuated total reflection Fourier transforms infrared spectroscopy (FTIR)

To describe the mechanism of the *in situ* ATR- FTIR, the experiments are carried out in two custom spectroelectro-chemical instruments. Spectroscopic measurements are collected in a cell described in their previous work. Experiments were performed in a newly designed spectroelectrochemical cell, which allows for stirring of the electrolyte using a magnetic stir bar. Practically, both cells are the same when not stirred to guarantee that we can directly make comparison between the data from experiments at each concentration from these two cells. The ability to monitor reactions under convection represents a significant step forward in the operando investigation of



electrochemical processes.

The IR spectra were calculated using the following equation [7]:

$$\Delta R/R = [R(E_a) - R(E_b)] / R(E) \dots \dots \text{Equation 1}$$

Where, the parameters of $R(E_a)$ and $R(E_b)$ are the reflectivities from the electrode surface recorded at the applied electrode potential E_1 (+0.1V vs. RHE) and E_2 , respectively.

The analysis procedure of the *in situ* ATR- FTIR

The *in situ* ATR-FTIR displays the real time IR spectra of the catalyst and intermediate products respectively. In the process of electrochemical reduction, the *in situ* attenuated total reflection Fourier transform infrared spectroscopy monitor the real time variation of the spectroscopy of the catalyst and intermediate products of during the potential stepwise sweeping from 0 to -0.8 V in a CO_2 -saturated 0.5M KHCO_3 solution. Figure 1 show the real-time ATR-IR spectra recorded during stepping the Pd/C loaded on an Au-coated Si prism from 0 to -0.8V in a CO_2 -saturated 0.5M KHCO_3 solution. It is can be observed several absorbance bands between 2400 and 1600 cm^{-1} for all the samples. Among these bands, the reversed band centered at 2343 cm^{-1} should be ascribed to the consumption of CO_2 in the solution [8]. The band with positive orientation between 2010 and 1960 cm^{-1} can be assigned to the linear-bonded CO (COL). The most evident band sit between 1890 and 1830 cm^{-1} is ascribed to the vibration feature of bridgebonded CO (COB) [9,10]. Another weak band around 1800 and 1780 cm^{-1} locates at the high potential region involved triple-bonded (COT) or multibonded CO (COM) [11]. However, the efficiency of above analysis procedure of the *in situ* ATR- FTIR is not desired.

Methods

The evaluating the setup of ATR-FTIR

To overcome the unsatisfying sensitivity and stability of

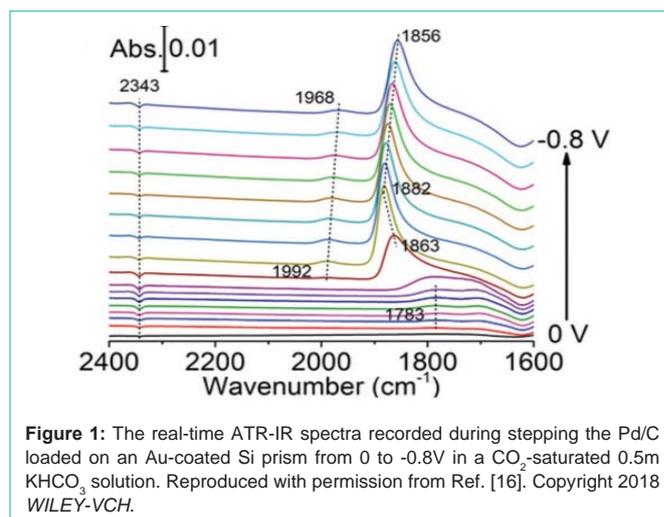
traditional setup of the *in situ* attenuated total reflection Fourier transform infrared spectroscopy (FTIR), the evaluating the setup of the *in situ* attenuated total reflection Fourier transform infrared spectroscopy (FTIR) is proposed.

Scheme 2 illustrates the advanced scheme diagram of the electrochemical equipment utilized in the *in situ* FTIR investigation.

Marco Dunwell et al. [12] proposed an advanced scheme diagram of the electrochemical equipment utilized in the *in situ* FTIR measurement with Au film working electrode, Ag/AgCl reference electrode, and graphite rod counter electrode. The spectroscopic measurement during the whole process is under stirred to guarantee the stability in 0.5 M NaHCO_3 . The scanning electron microscope image of the Au film on Si is inserted in Scheme 2. The *in-situ* measurement experiments were conducted in two custom spectroelectrochemical cells. In 0.25 and 1.0 M NaHCO_3 solution, the Spectroscopic measurements were carried out in a cell described in their previous work [13]. Experiments in 0.5M NaHCO_3 aqueous solution were performed in a newly designed spectroelectrochemical cell with the Si ATR crystal is mounted on the side of the cell, enables for stirring of the electrolyte using a magnetic stir bar (Scheme 2). Practically, the measurements are adopted the identical cells when not stirred, such that data from experiments at each concentration from these two cells can be directly compared. The capacity to monitor reactions under convection demonstrates a significant step forward in the operando investigation of electrochemical processes. In traditional interfacial Fourier Transform infrared spectroscopy, transport is severely hindered by the thin-layer electrolyte configuration. Although the use of ATR-SEIRAS enhances transport significantly, transport was still determined solely by diffusion in all previous spectroelectrochemical studies [14].

The mechanism of the *in situ* ATR-FTIR

To further clarify the mechanism of the ATR-FTIR, blank experiments are supposed to be conducted. The catalyst species and intermediates can also be labeled by isotope and can be real-time detect by luminance from isotope. As an example, Song Jin et al. [15] have dramatically elevated the efficient of the electrochemical reduction carbon dioxide by incorporating the oxygen-containing



species onto the copper electrode. They carried out the *in situ* spectroscopy combining with the isotope exchanging strategy to verify that the new peak was ascribed to the a kind of intermediates-surface hydroxyl group.

The analysis procedure of the *in situ* ATR-FTIR

Apart from the basis experiment, control experiments were also carried out using FTIR in an Ar-saturated 0.5M KHCO₃ solution. For example, Shangqian Zhu et al. conducted FTIR by control experiments were also carried out using FTIR. They found that CO bands could still be observed even no external CO₂ source was provided. Nevertheless, the CO band intensities were drastically decreased and the onset potentials for the observation of CO were more negative as compared with the spectra recorded in the CO₂-saturated solution. They anticipated that this phenomenon could be explained by CO₂ molecules in equilibrium with bicarbonate anions could still promote the reaction, and was consistent with their previous surface enhanced IR spectroscopic investigation on Cu surfaces [16]. Besides, they also detected that all the CO bands were absent in the spectra recorded in the saturated phosphate buffered saline solution, suggesting they were generated from CO₂ reduction in the Ar-saturated KHCO₃ solution.

The *in-situ* spectroscopy to investigate the electrochemical reduction of CO₂ provides the information of the intermediate products and variation condition of the reaction system and gain the evidence for further analysis. Koga Osamu et al. employed *in situ* attenuated total reflection Fourier transform infrared spectroscopy to studies the adsorbed species on Ni and Fe electrode in electrochemical reduction of CO₂. They detected that the two species, ascribe to linear and bridged CO molecule were also formed on Ni electrode [5]. The ATR-IR analysis provided deep insight for them to processing optimization to promote the conversion efficiency of CO₂.

Significance

With the growing awareness towards environmental protection, the electrochemical reduction of CO₂ have been given considerable attention to fulfill the demands of essential environmental protection and utilization of source. The great progresses have been made to improve the efficient of electrochemical reduction of CO₂. Through systematically introducing the fundamental knowledge of mechanism of the electrochemical reduction of CO₂ *in situ* attenuated total reflection Fourier transform infrared spectroscopy, our review offer systematical information for the corresponding scientists and researchers to exploit he electrochemical reduction CO₂ by the *in situ* attenuated total reflection Fourier transform infrared spectroscopy (FTIR). However, there are still many challenges for the development of exploitation he electrochemical reduction CO₂ by the *in situ* attenuated total reflection Fourier transform infrared spectroscopy (FTIR).

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