

Supplementary Materials for

## **A Spectroscopic Study on the Nitrogen Electrochemical Reduction Reaction on Gold and Platinum Surfaces**

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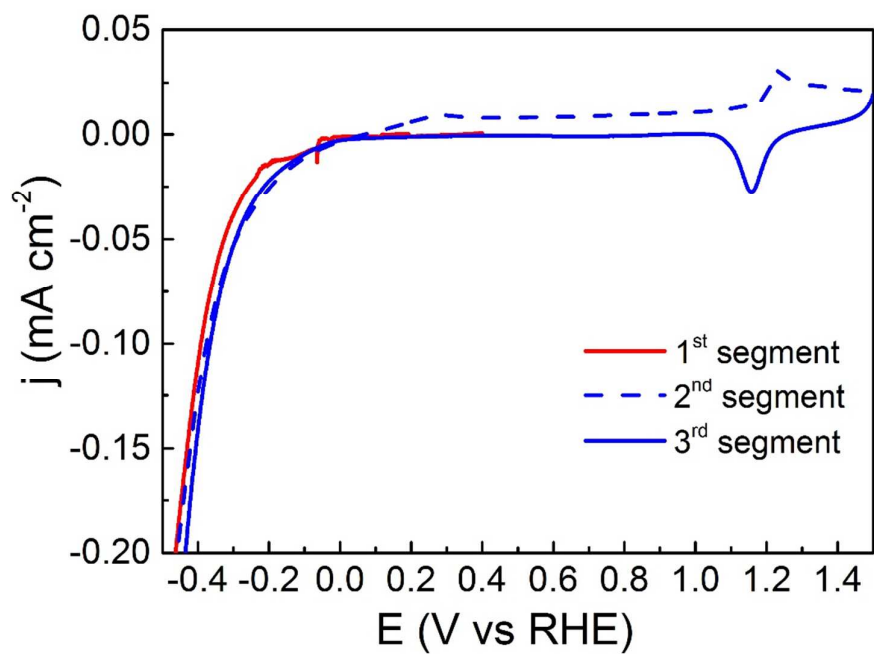
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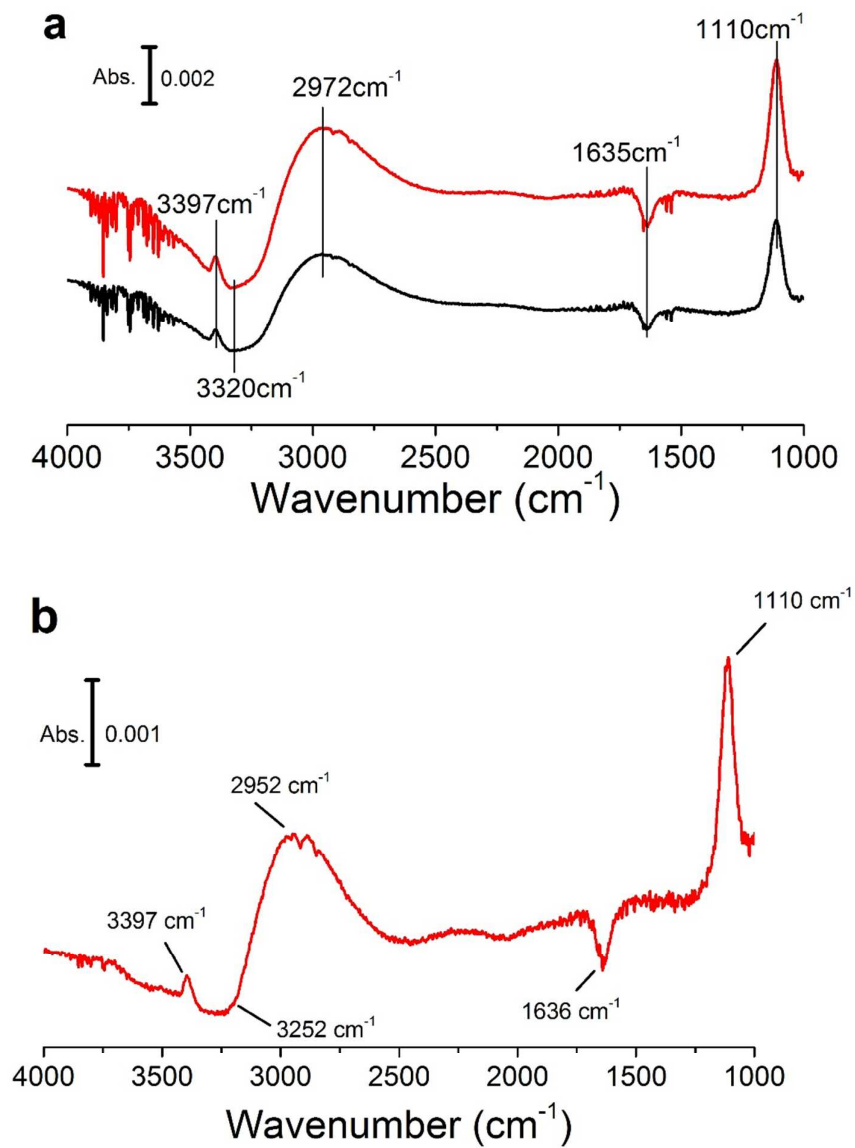
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### CV of Au thin-film in an Ar-saturated KOH electrolyte



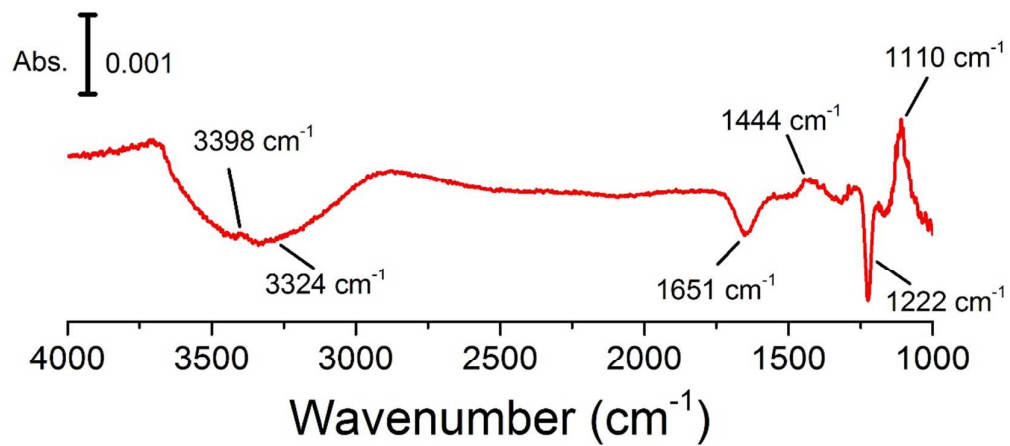
**Figure S1.** The cyclic voltammograms of Au thin-film supported on a Si prism in Ar-saturated 0.1M KOH aqueous solution; potential scan rate:  $2.5\text{mV s}^{-1}$ .

**Infrared spectroscopy of ammonia water in a KOH solution using ZnSe prism as window**



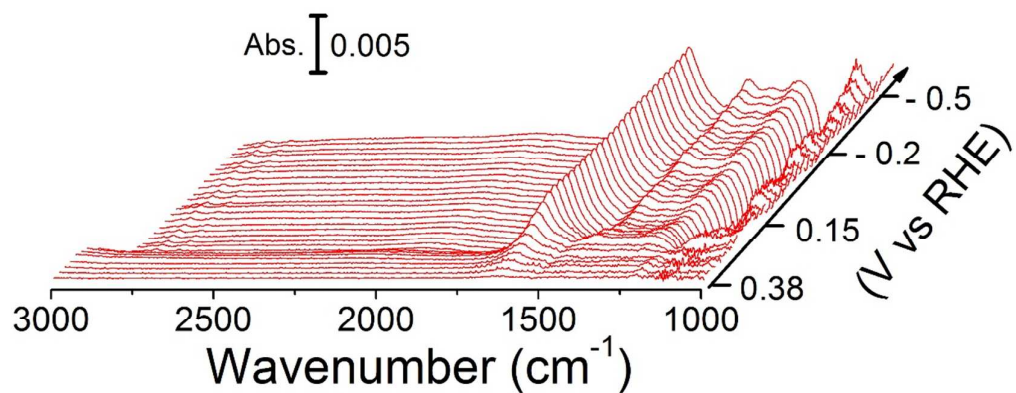
**Figure S2.** a) IR spectrum of 0.7M  $\text{NH}_3\cdot\text{H}_2\text{O}$  (black line) and 1M  $\text{NH}_3\cdot\text{H}_2\text{O}$  (red line) in a 0.1M KOH solution when using ZnSe prism as window. The reference spectrum was taken in a 0.1M KOH solution. b) Subtractive IR spectrum between 1M  $\text{NH}_3\cdot\text{H}_2\text{O}$  and 0.7M  $\text{NH}_3\cdot\text{H}_2\text{O}$  in a 0.1M KOH solution when using ZnSe prism as window.

**Subtractive infrared spectroscopy of ammonia water in a KOH solution  
using Au film - Si prism as window**



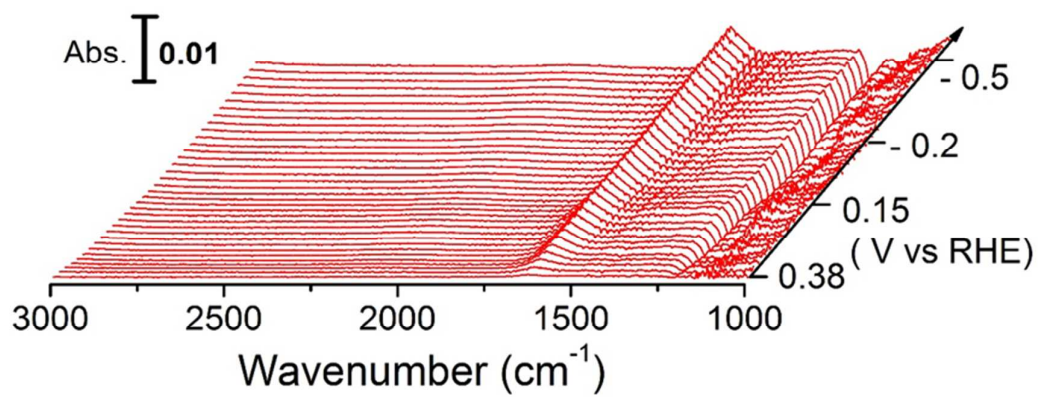
**Figure S3.** Subtractive IR spectrum between 1M NH<sub>3</sub>·H<sub>2</sub>O and 0.7M NH<sub>3</sub>·H<sub>2</sub>O in a 0.1M KOH solution when using Au film- Si prism as window.

**The repeated FTIR spectra of Au film in N<sub>2</sub>-saturated 0.1M KOH**



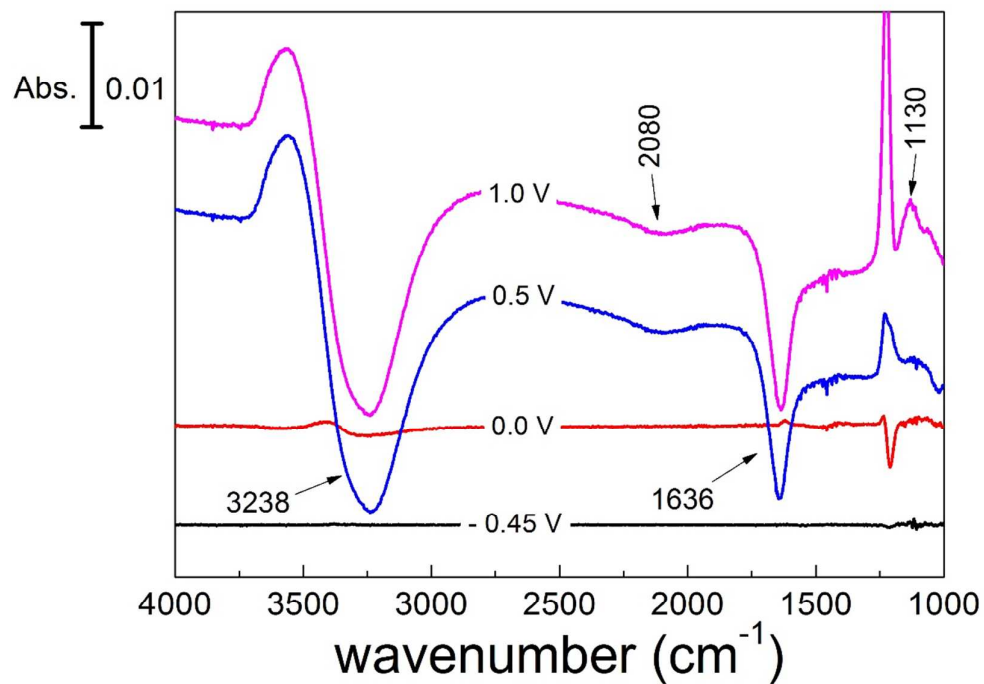
**Figure S4.** FTIR spectra during the 1<sup>st</sup> segment from 0.4 V to -0.5 V on the Au film electrode in a N<sub>2</sub>-saturated 0.1 M KOH solution. The reference spectrum was taken at 0.4 V.

### The repeated FTIR spectra of Au film in Ar-saturated 0.1M KOH



**Figure S5.** FTIR spectra during the 1<sup>st</sup> segment from 0.4 V to -0.5 V on the Au film electrode in a Ar-saturated 0.1 M KOH solution. The reference spectrum was taken at 0.4 V.

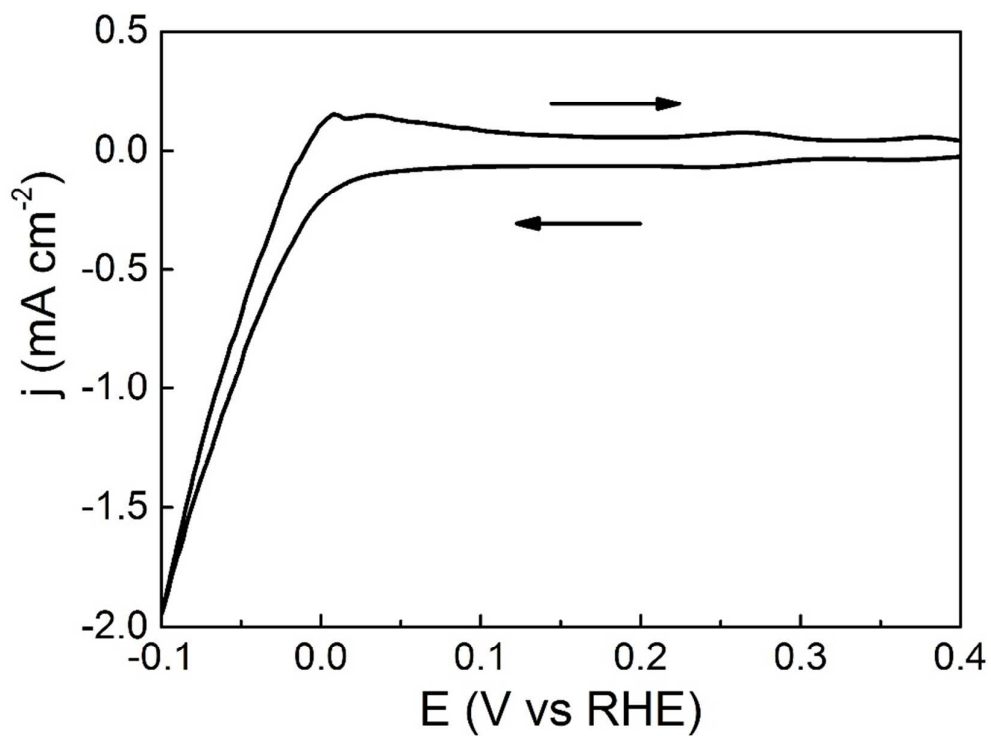
**FTIR spectrum of Au film in an Ar-saturated KOH electrolyte at the 2<sup>nd</sup> segment**



**Figure S6.** The FTIR spectra recorded in the 2<sup>nd</sup> segment from -0.5 V to 1.0 V on the Au film electrode in Ar-saturated 0.1M KOH aqueous solution. The background spectrum was taken at -0.5 V.

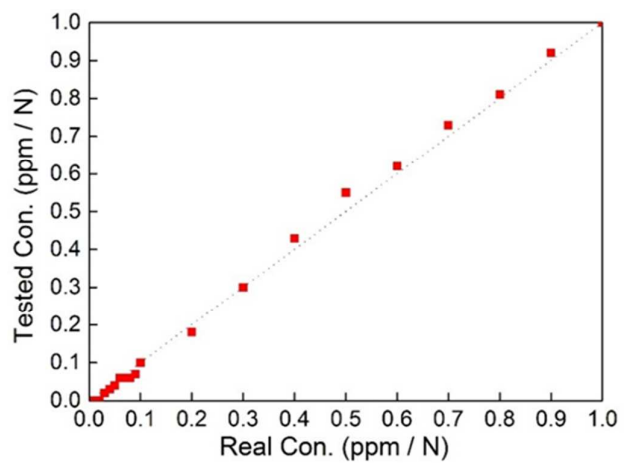


**The CV of Pt film in a N<sub>2</sub>-saturated KOH electrolyte**



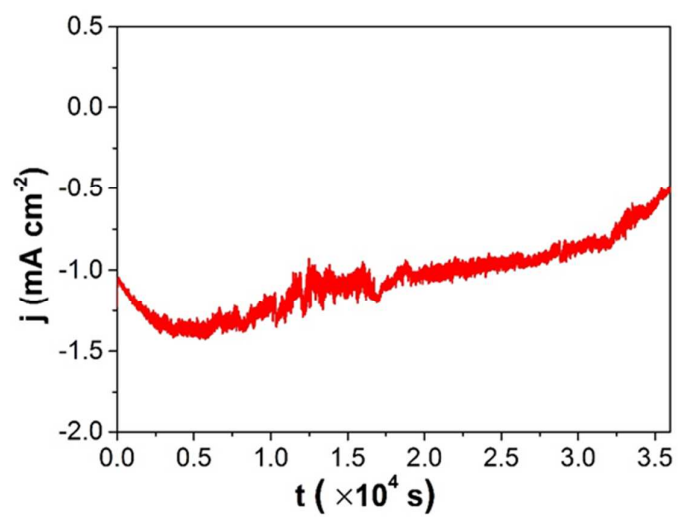
**Figure S7.** The cyclic voltammograms of Pt film electrode supported on a Si prism in N<sub>2</sub>-saturated 1M KOH aqueous solution. The potential scan rate: 2.5mV s<sup>-1</sup>.

## The calibration curve of the ammonia meter



**Figure S8.** Calibration of ammonia meter for  $\text{NH}_4^+$  measurement in a 1mM  $\text{H}_2\text{SO}_4$  solution.

### Current-time plot of the Au foil



**Figure S9.** Current-time plot of the Au foil at -0.5 V in a  $\text{N}_2$ -saturated 0.1M KOH solution.