Supporting Information

Ionic Liquid–Engineered Core–Shell Polymer Nanospheres for Photocatalytic Nitrogen Reduction

Ning ZHANG,[a] Dorian PRIANO,[a] Catherine SANTINI,[a] Jinlong ZHANG [b] and Stephane DANIELE*[a]

a. Universite Lyon 1, CP2M-ESCPE Lyon, CNRS-UMR 5128, 69616 Villeurbanne cedex, France. E-mail address: stephane.daniele@univ-lyon1.fr.

b. Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China. E-mail address: jlzhang@ecust.edu.cn.

Ammonia detection procedures:

The identification of synthesized ammonia in the photocatalytic nitrogen fixation process utilizes UV spectrophotometry. In photocatalytic reactions, supplementary ions in the liquid phase reaction system may interact with the color developer, so distorting the experimental outcomes and inflating the apparent yield of ammonia beyond the actual yield. Consequently, selecting a suitable color developer for detection in the photocatalytic nitrogen fixation reaction is essential. The Nessler reagent method utilizes ammonia nitrogen as free ammonia or ammonium ions, which react with Nessler's reagent to form a light reddish-brown complex. The absorbance of the complex correlates with its ammonia nitrogen content and is quantified at 420 nm. The standard curve is constructed using ammonium chloride.

Given the intricate laboratory environment, the presence of various impurities during material synthesis may lead to inaccuracies in experimental outcomes. Additionally, the low sensitivity of the detection method necessitates the employment of multiple techniques to accurately measure the ammonia produced in the photocatalytic nitrogen fixation reaction. Subsequently, we employ the iodophenol blue method to identify and measure the generated ammonia. Ammonia in deionized water, together with sodium nitrite, iron oxide, and sodium hypochlorite, interacts with salicylic acid to produce a blue-green phenol blue color. Absorbance is quantified at a wavelength of 697.5 nm based on color depth using ultraviolet spectrophotometry. The standard curve is constructed from aqueous solutions of ammonium chloride.

Nessler’s reagent spectrophotometry

The procedure for the spectrophometric study using the Nessler reactant is as follows:

1- **Nessler's reagent** = mercuric iodide, potassium iodide, and sodium hydroxide solution (HgI_2-KI-NaOH): Weighing 16.0 g of sodium hydroxide (NaOH), dissolving it in 50mL of water, and cooling to room temperature. Weighing 7.0 g of potassium iodide (KI) and 10.0g of mercuric iodide (HgI_2) and dissolving them in water. Slowly adding this solution to the aforementioned 50mL sodium hydroxide solution while stirring. Diluting to 100mL with water. Storing in a plastic bottle, seal with a rubber stopper or polyethylene cap and in a dark area. The shelf life is one year.

2- **Potassium sodium tartrate solution**, ρ=500 g/L: Weighing 50.0 g of potassium sodium tartrate ($KNaC_4H_6O_6 \cdot 4H_2O$) and dissolving it in 100mL water, heating and boiling to drive off ammonia, then cooling thoroughly and diluting to 100mL.

3- **Ammonium standard solution** (ρNH_4^+ = 2.00 mg/L): Weighing 5.9304 g of high-grade pure ammonium chloride (NH_4Cl, dried at 100℃-105℃ for 2 hours), dissolving it in water and transferring it to a 1000 mL volumetric flask, and storing it at 2℃-5℃ for 1 month. Preparing different ammonia solutions trough dilution of the standard one ($C_{standard}$ = 2.00 mg/L) just before use.

4- **Calibration curve**:In 5 colorimetric tubes, adding 0.00 mL, 1.00 mL, 2.00 mL, 3.00 mL, 3.75 mL, and 5.00 mL of ammonium standard solution, with corresponding ammonium concentrations solution of 0.00 mg/L, 0.40 mg/L, 0.80 mg/L, 1.20 mg/L, 1.50 mg/L, and 2.00 mg/L, respectively, and adding water until 5 mL solution, as shown in table 2.3. Adding 1.0 mL potassium sodium tartrate solution in the 5.0 mL different concentration of NH_4Cl standard solution, followed by 1.5 mL Nessler's reagent, and shaking thoroughly. After 10 minutes, measuring the absorbance at 420 nm using a 10 mm cuvette and water as a reference. Plotting a calibration curve using the absorbance after blank correction as the ordinate and the ammonia nitrogen concentration (mg/L) as the abscissa.

Note: A 10 mm cuvette should be used, based on the concentration of the material to be examined.

Table 1. NH_4Cl Standard solutions and absorbance data

$C_{standard}$ (mg/L)	V_A (mL)	V_{water} (mL)	Abs (420 nm)
0.00	0.00	5.00	0.138
0.40	1.00	4.00	0.203
0.80	2.00	3.00	0.261
1.20	3.00	2.00	0.325
1.50	3.75	1.75	0.385
2.00	5.00	0.00	0.458

Iodophenol blue spectrophotometry

The procedure for the spectrophometric study using the iodophenol reactant is as follows:

1- Salicylic acid solution, 50 g/L: Weighing 10.0 g of salicylic acid and 10.0 g of sodium citrate, then add approximately 50 mL of water, followed by 55 mL of sodium hydroxide solution [c (NaOH) = 2 mol/L], then dilute to 200 mL with water. This reagent is somewhat yellow and will remain stable at room temperature for one month.

2- Sodium nitroso ferricyanide solution (10g/L): Weighing and dissolving 1.0 g of sodium nitrosoferricyanide in 100 mL of water. It can be kept in the fridge for one month.

3- Sodium hypochlorite solution: NaClO (10%).

4- Ammonium standard solution (ρNH_4^+ = 2.00 mg/L): Weighing 5.9304 g of high-grade pure ammonium chloride (NH_4Cl, dried at 100℃-105℃ for 2 hours), dissolving it in water and transferring it to a 1000 mL volumetric flask, and storing it at 2℃-5℃ for 1 month. Preparing different ammonia solutions trough dilution of the standard one ($C_{standard}$ = 2.00 mg/L) just before use.

5- Calibration curve : In 5 colorimetric tubes, adding 0.00 mL, 1.00 mL, 2.00 mL, 3.00 mL, 3.75 mL, and 5.00 mL of ammonia standard solution, with corresponding ammonium concentrations of 0.00 mg/L, 0.40 mg/L, 0.80 mg/L, 1.20 mg/L, 1.50 mg/L, and 2.00 mg/L, respectively, and adding water until 5 mL solution, as shown in table 2.4. Adding 0.5 mL salicylic acid solution in the 5.0 mL different concentration of NH_4Cl standard solution, followed by 0.1 mL sodium nitrosoferricyanide solution and 0.1 ml sodium hypochlorite solution, and shaking thoroughly. After 10 minutes, measuring the absorbance at 697.5 nm using a 10 mm cuvette and water as a reference. Plotting a calibration curve using the absorbance after blank correction as the ordinate and the ammonia nitrogen concentration (mg/L) as the abscissa.

Note: A 10 mm cuvette should be used based on the concentration of the material to be examined.

Table 2. NH_4Cl Standard solutions and absorbance data

$C_{standard}$ (mg/L)	V_A (mL)	V_{water} (mL)	Abs (697.5 nm)
0.00	0.00	5.00	0.0049
0.40	1.00	4.00	0.5070
0.80	2.00	3.00	1.1129
1.20	3.00	2.00	1.7854
1.50	3.75	1.75	2.3574
2.00	5.00	0.00	3.1117

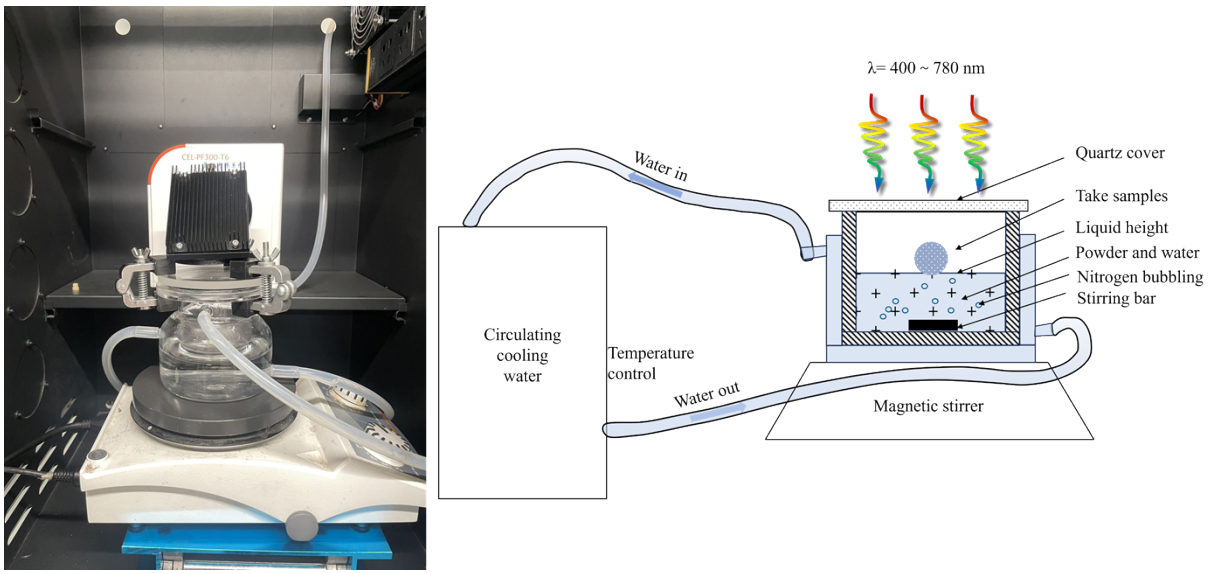

Figure. 1 Photocatalytic N_2 fixation system.

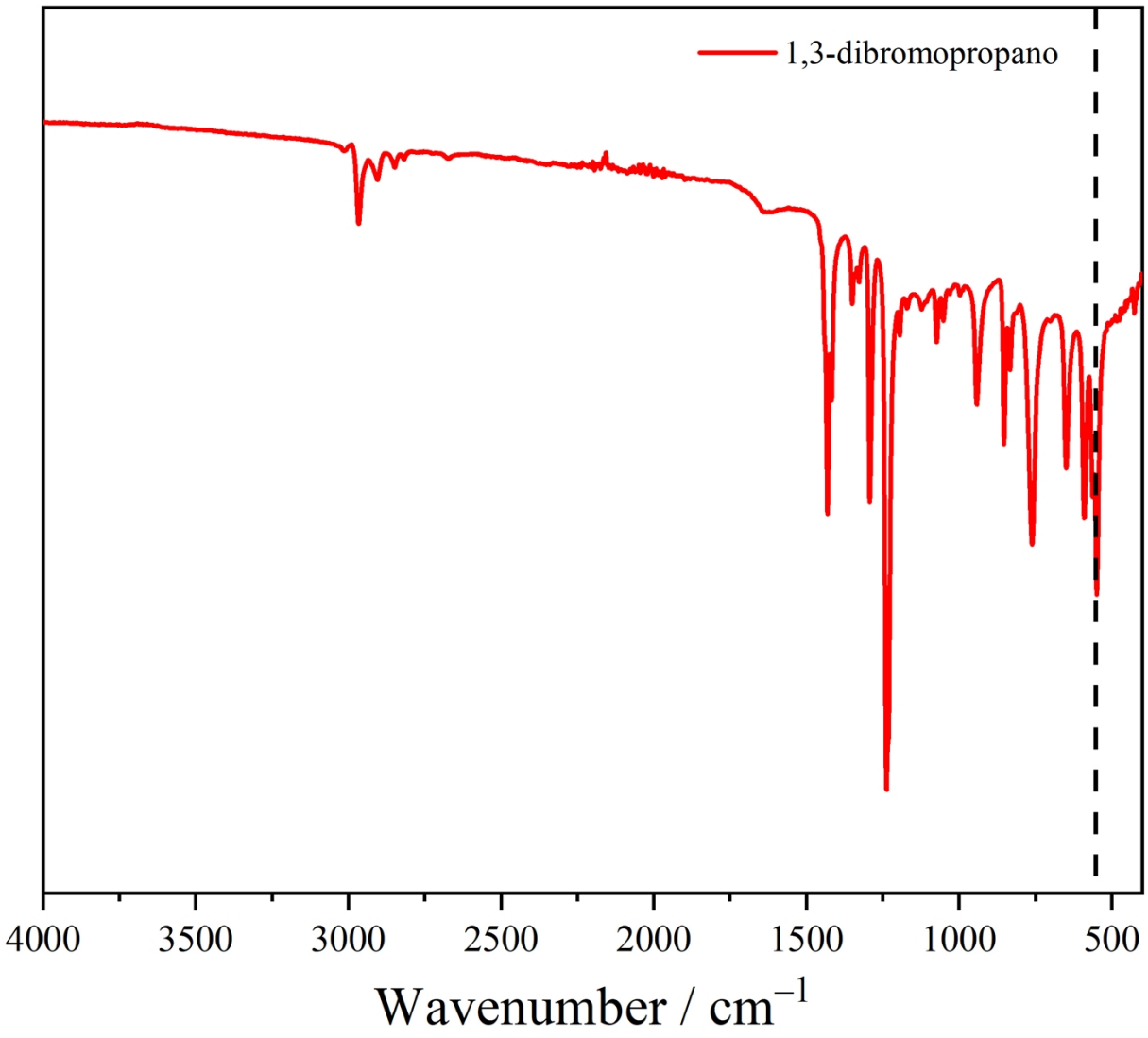

Figure. 2 FT-IR spectra of 1,3-dibromopropane.

(Wavenumber from 400-4000 cm^{-1})

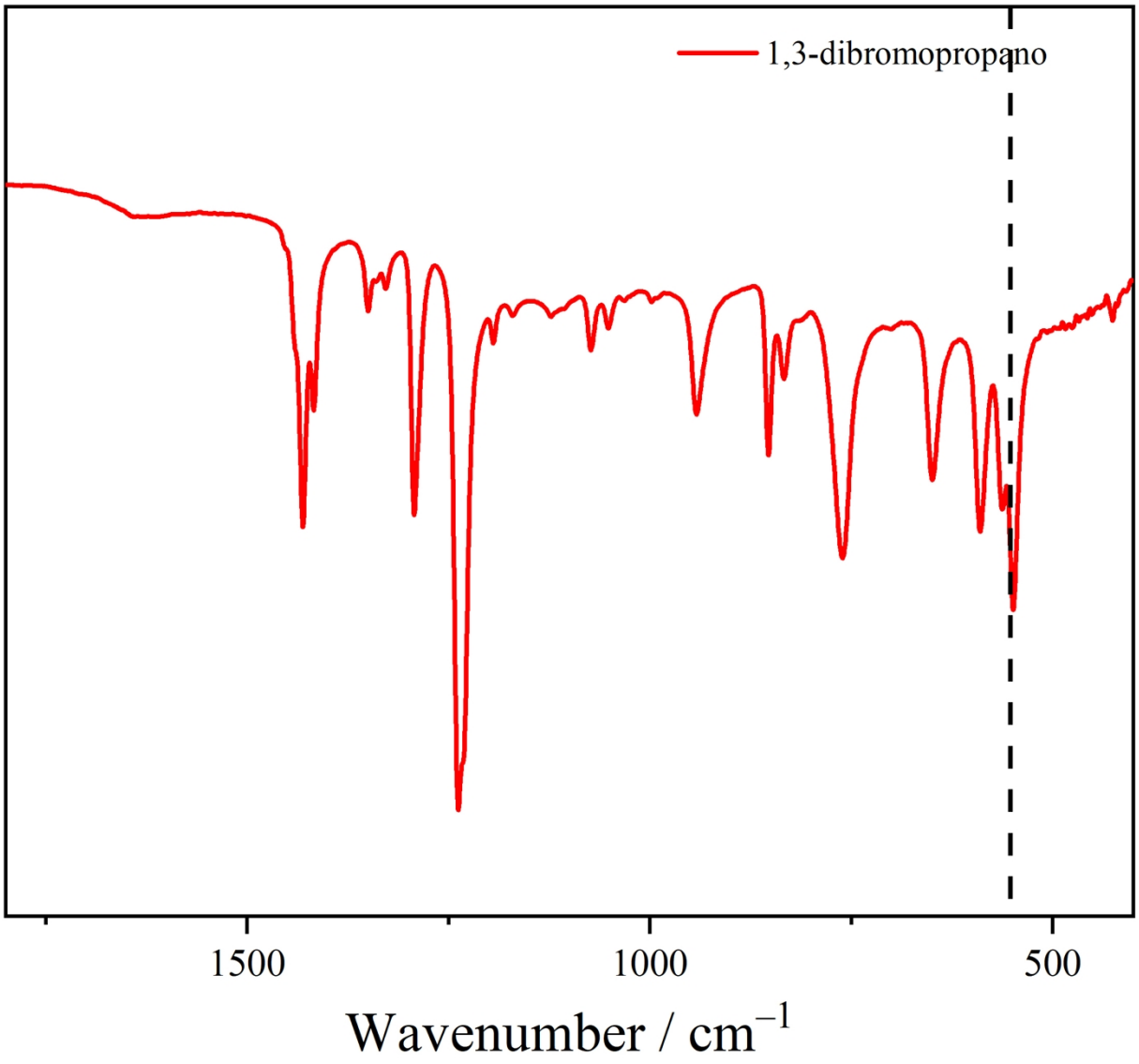

Figure. 3 FT-IR spectra of 1,3-dibromopropane.

(Wavenumber from 400-1800 cm^{-1})

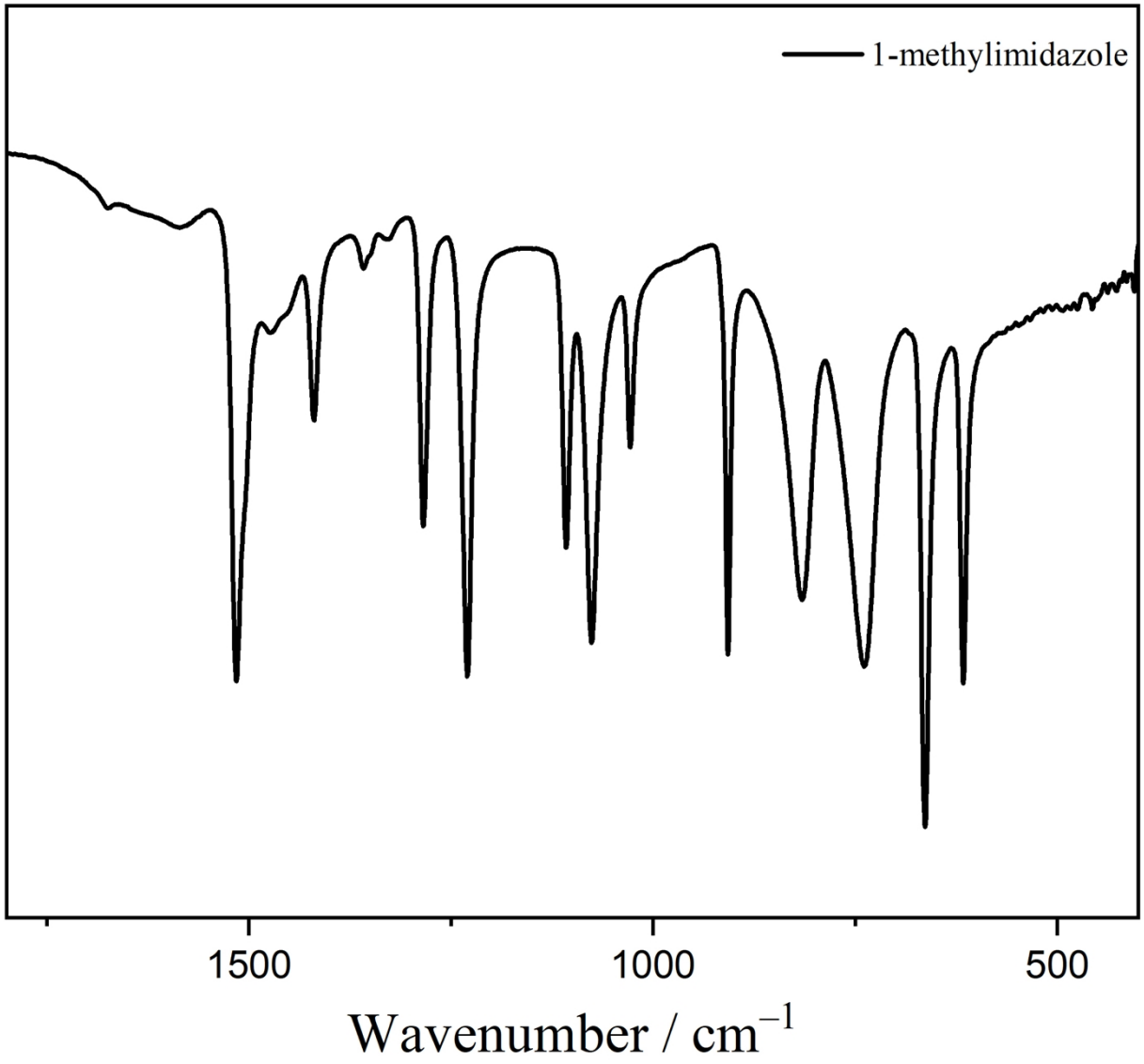

Figure. 4 FT-IR spectra of 1-methylimidazole.

(Wavenumber from 400-1800 cm^{-1})

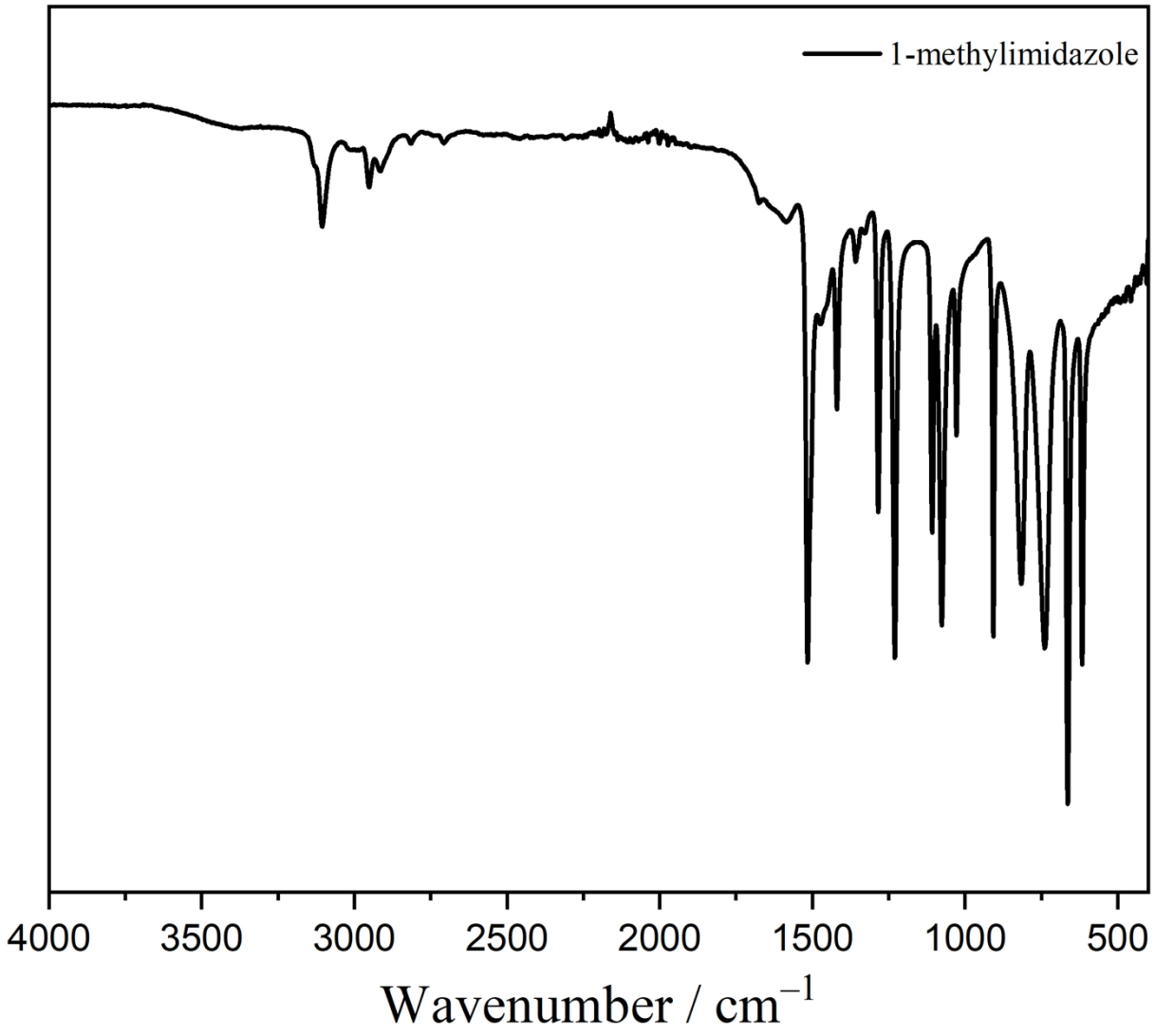

Figure. 5 FT-IR spectra of 1-methylimidazole

(Wavenumber from 400-1800 cm^{-1})

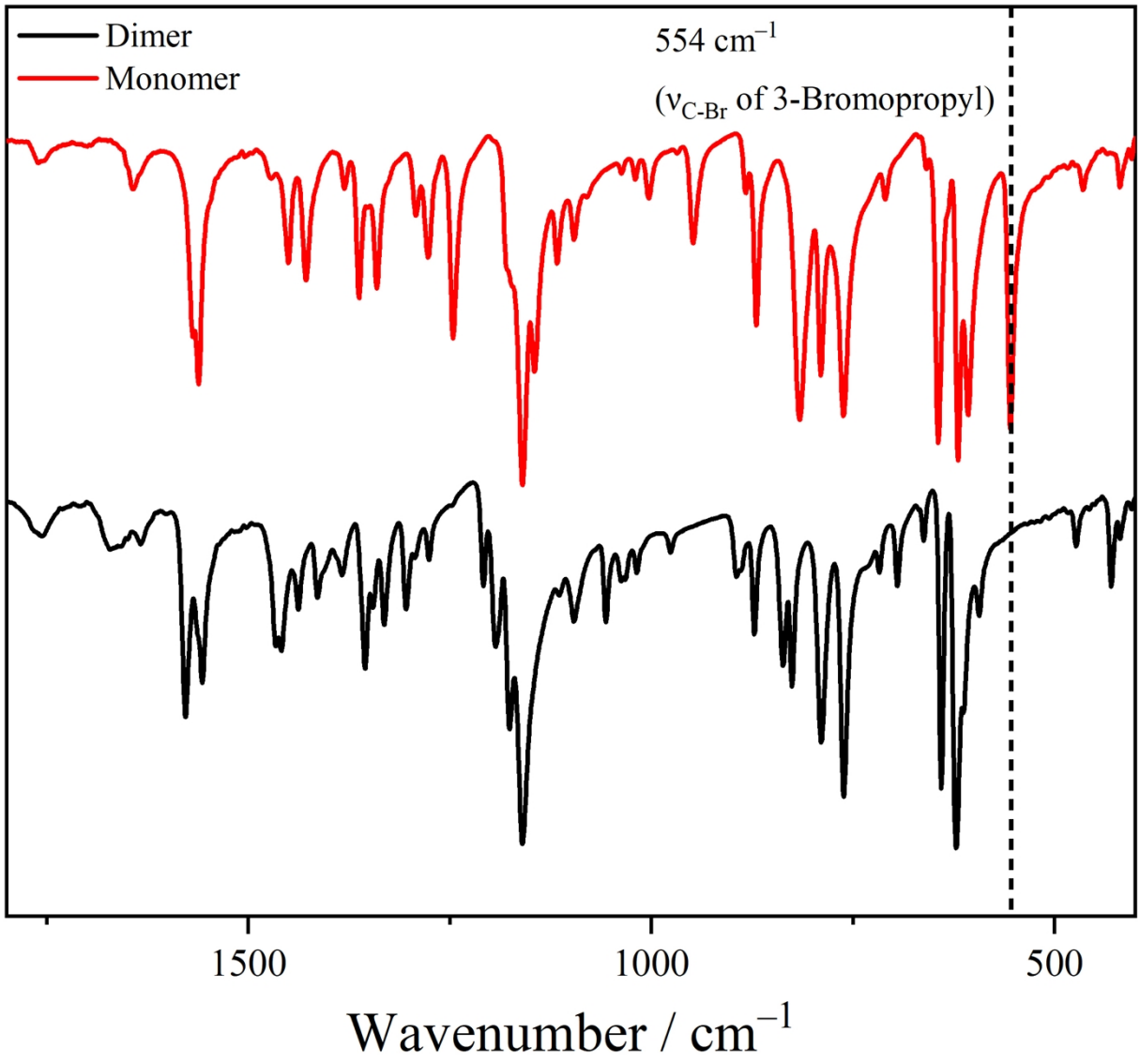

Figure. 6 FT-IR spectra of dimer and monomer.

(Wavenumber from 400-1800 cm^{-1})

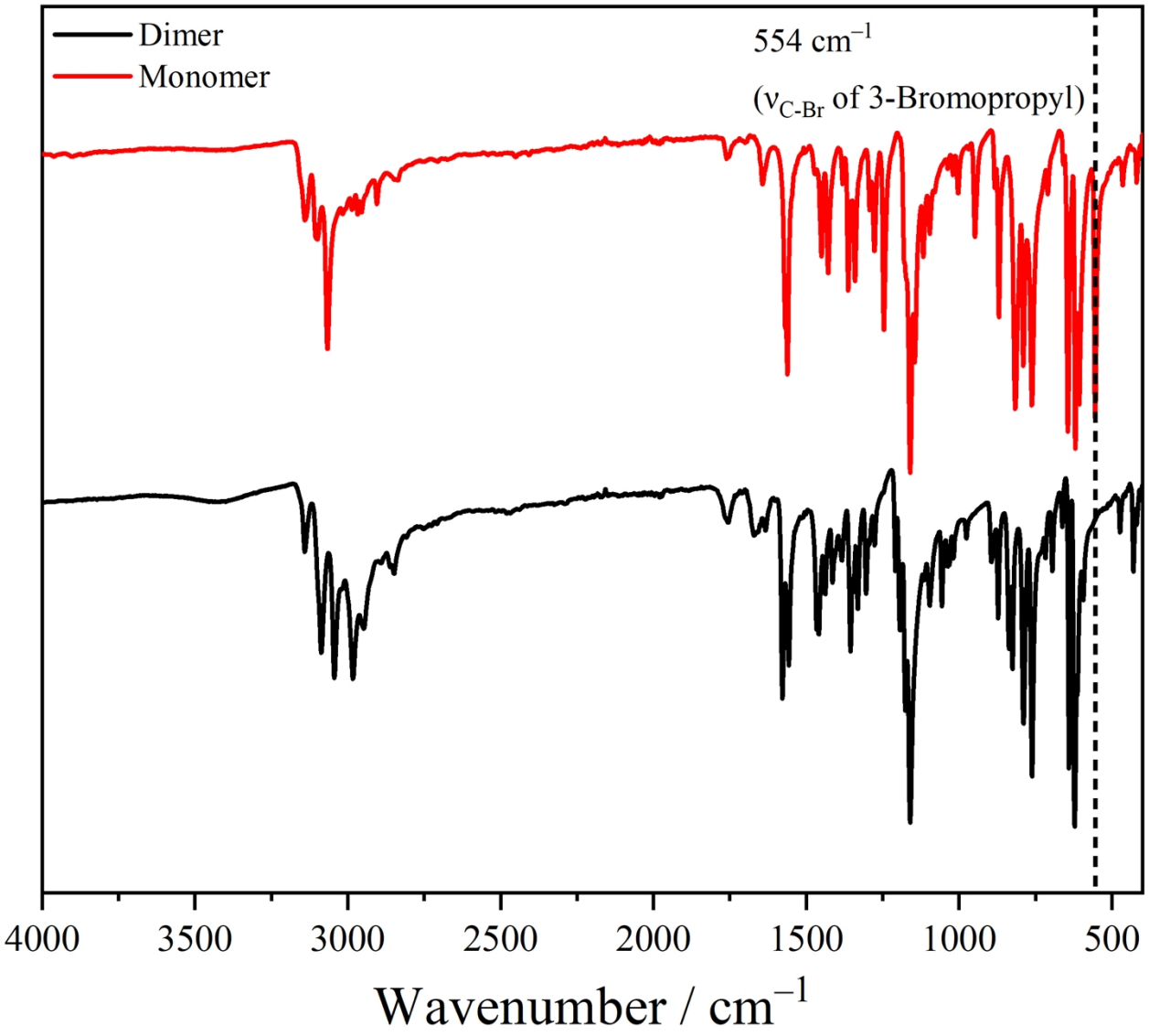

Figure. 7 FT-IR spectra of dimer and monomer.

(Wavenumber from 400-4000 cm^{-1})

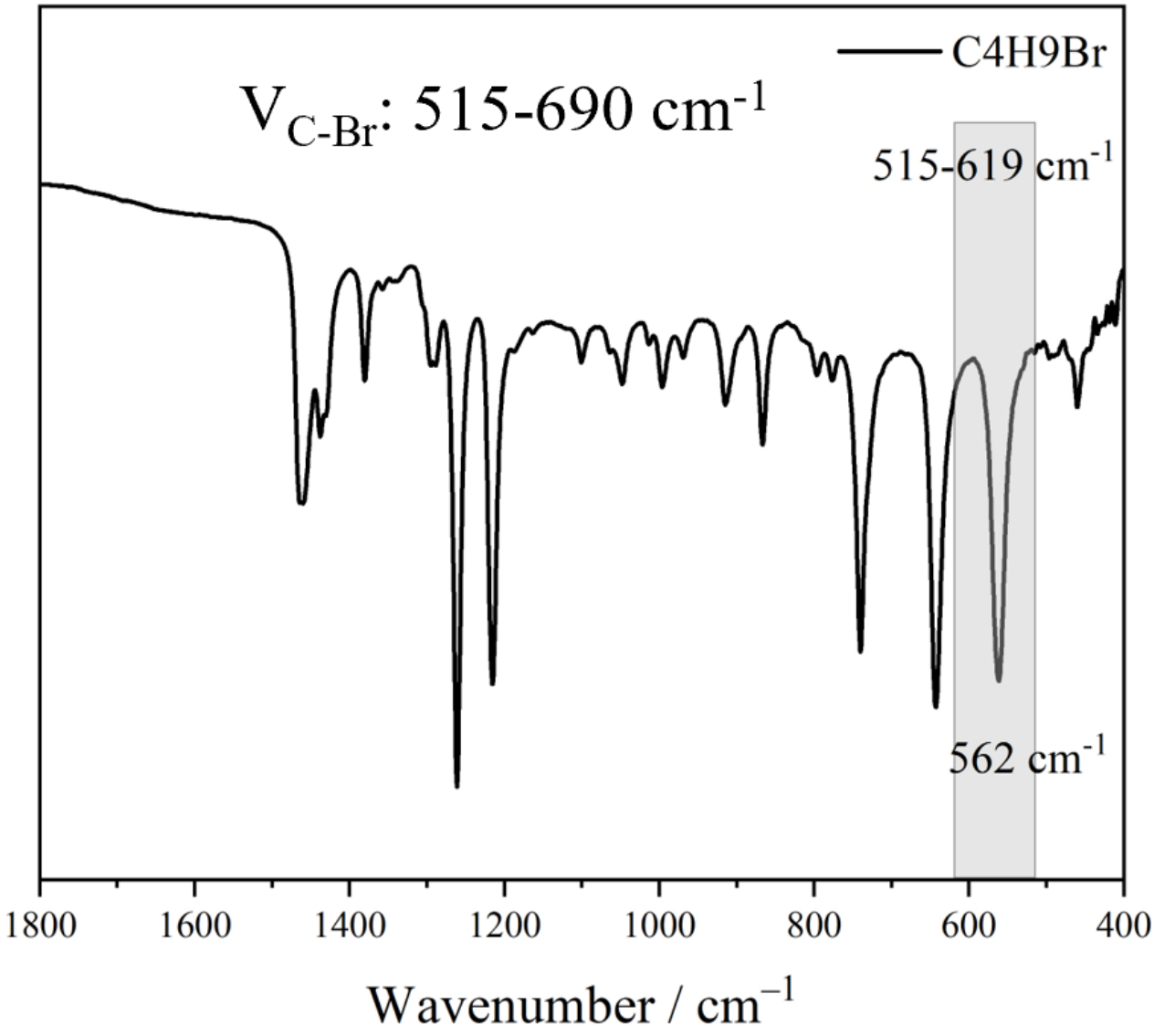

Figure. 8 FT-IR spectra of 1-Bromobutane, as a comparison to monomer.

(Wavenumber from 400-1800 cm^{-1})

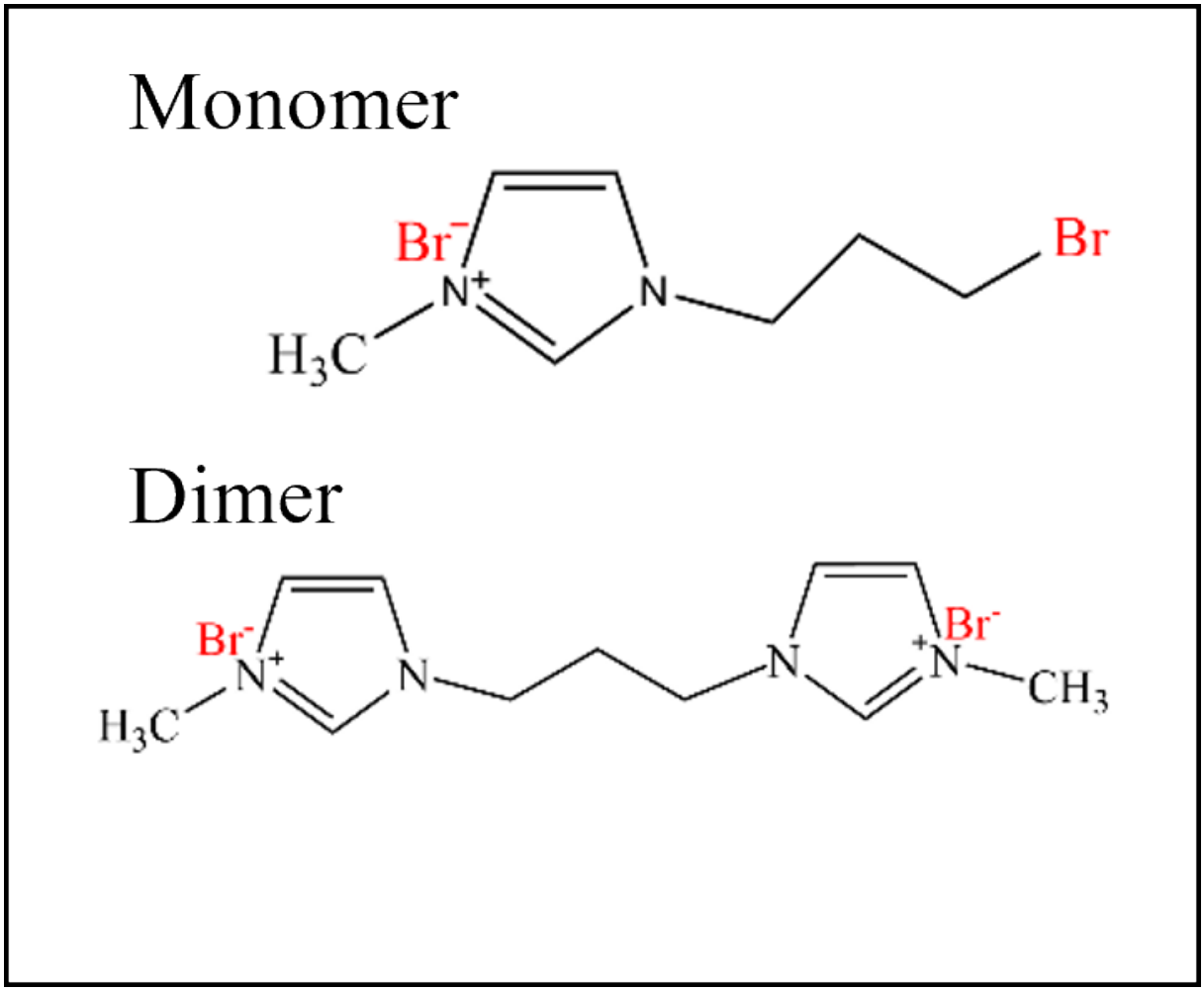

Figure. 9 Molecular structures of monomers and dimers.

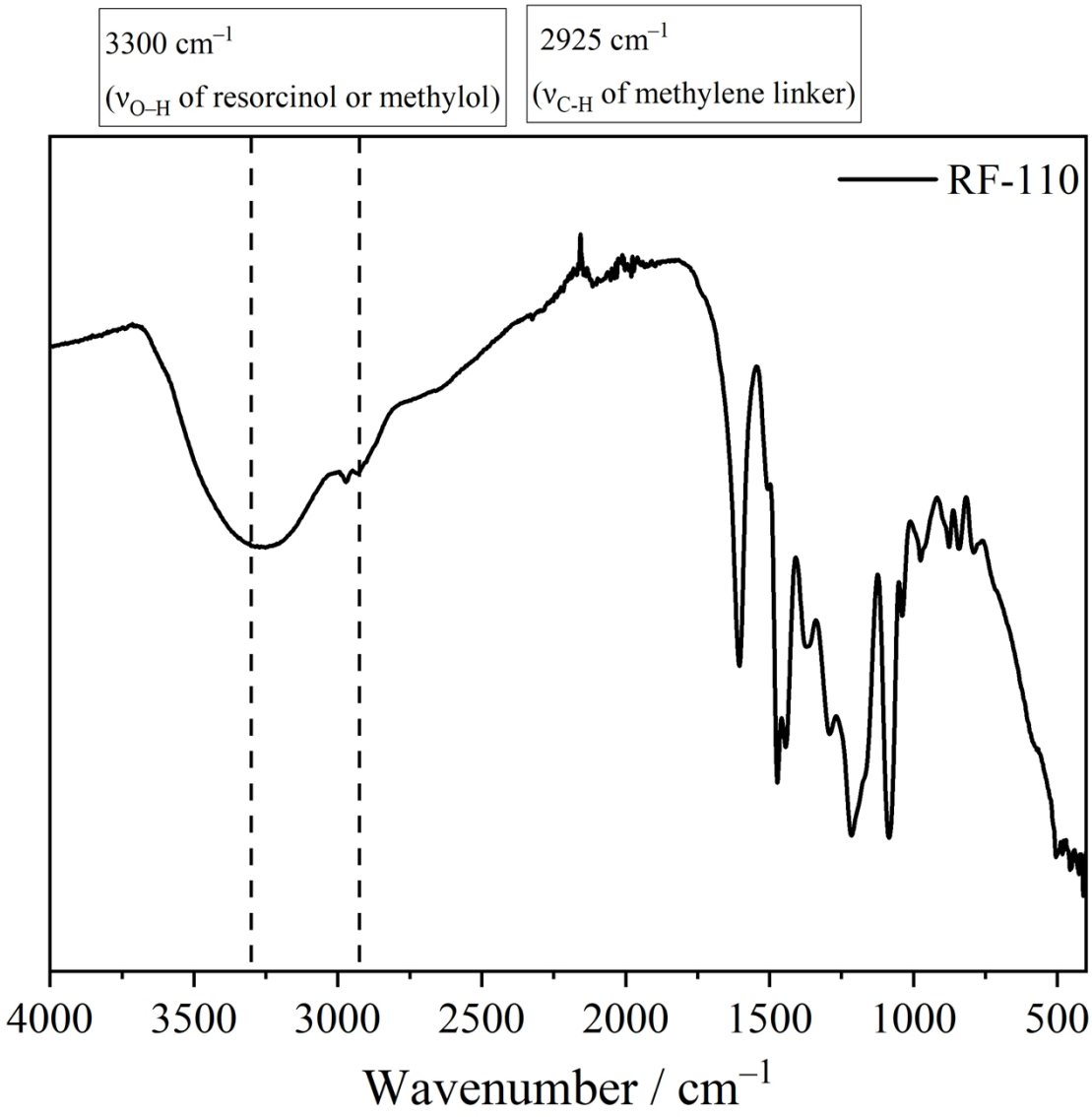

Figure. 10 FT-IR spectra of RF-110.

(Wavenumber from 400-4000 cm^{-1})

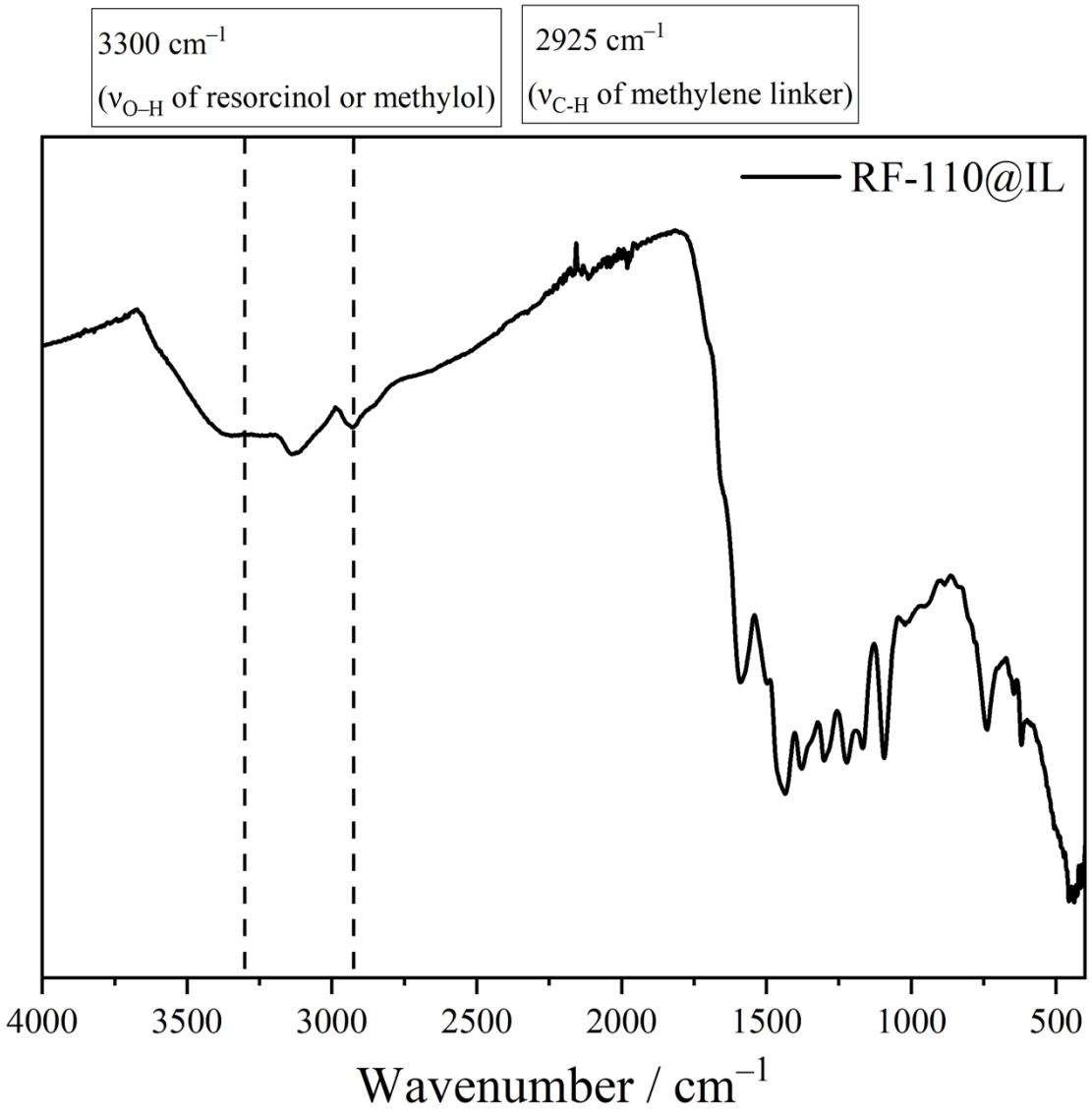

Figure. 11 FT-IR spectra of RF-110@IL.

(Wavenumber from 400-4000 cm^{-1})

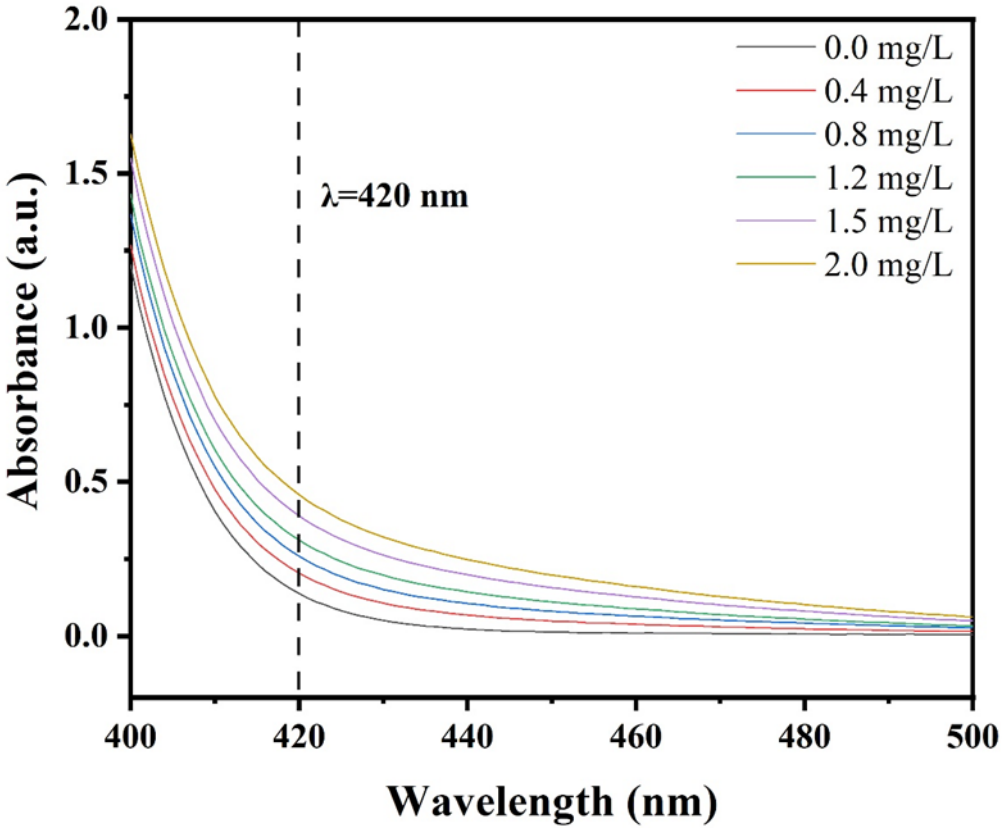

Figure. 12 UV-vis absorption spectra of Nessler's reagent method at different concentrations of NH_4Cl.

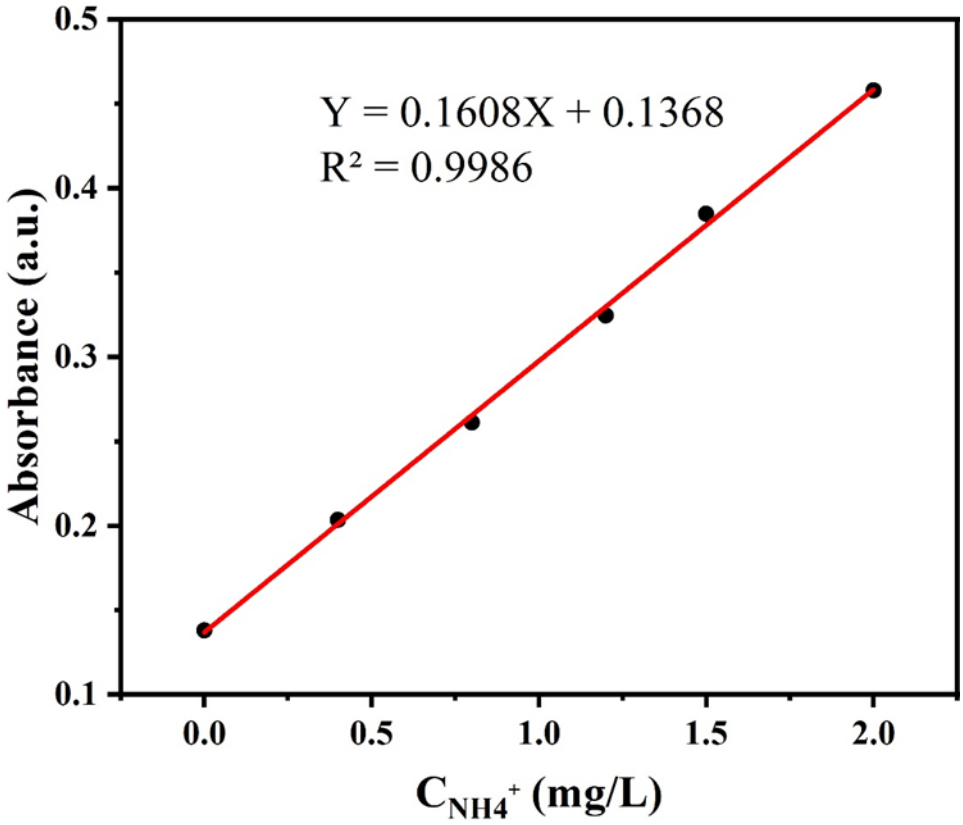

Figure. 13 The resulting calibration curve with the absorbance at 420 nm.

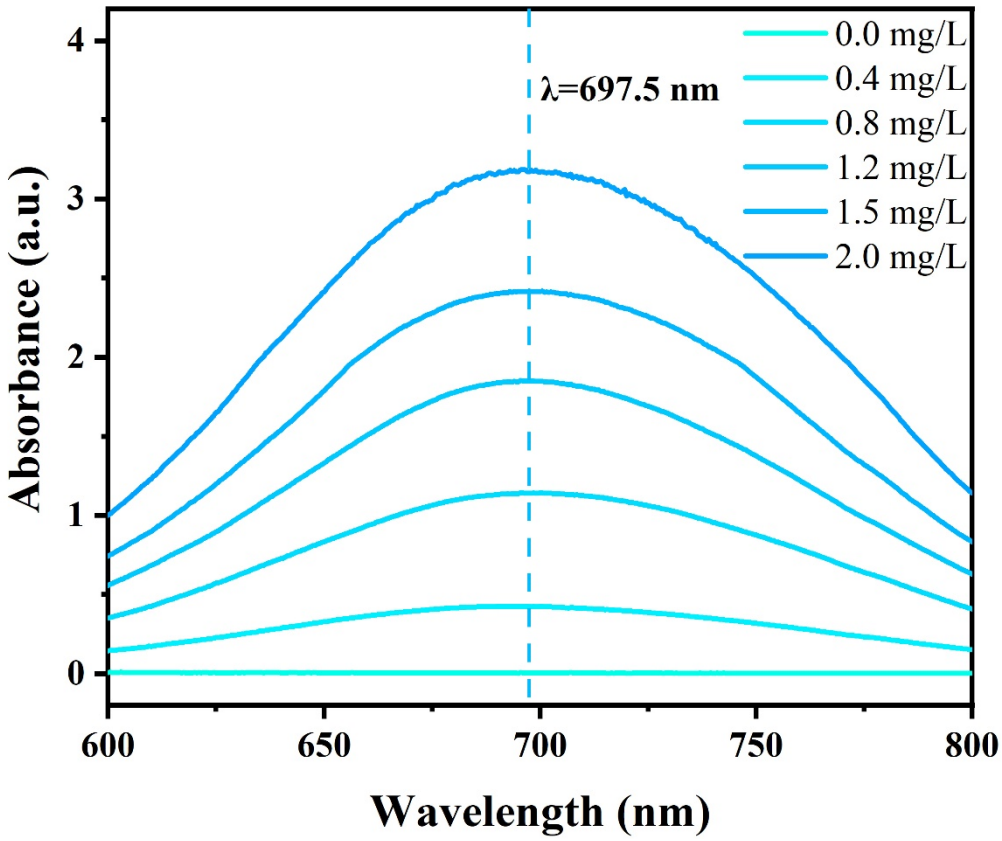

Figure. 14 UV-vis absorption spectra of indophenol blue method at different concentrations of NH_4Cl.

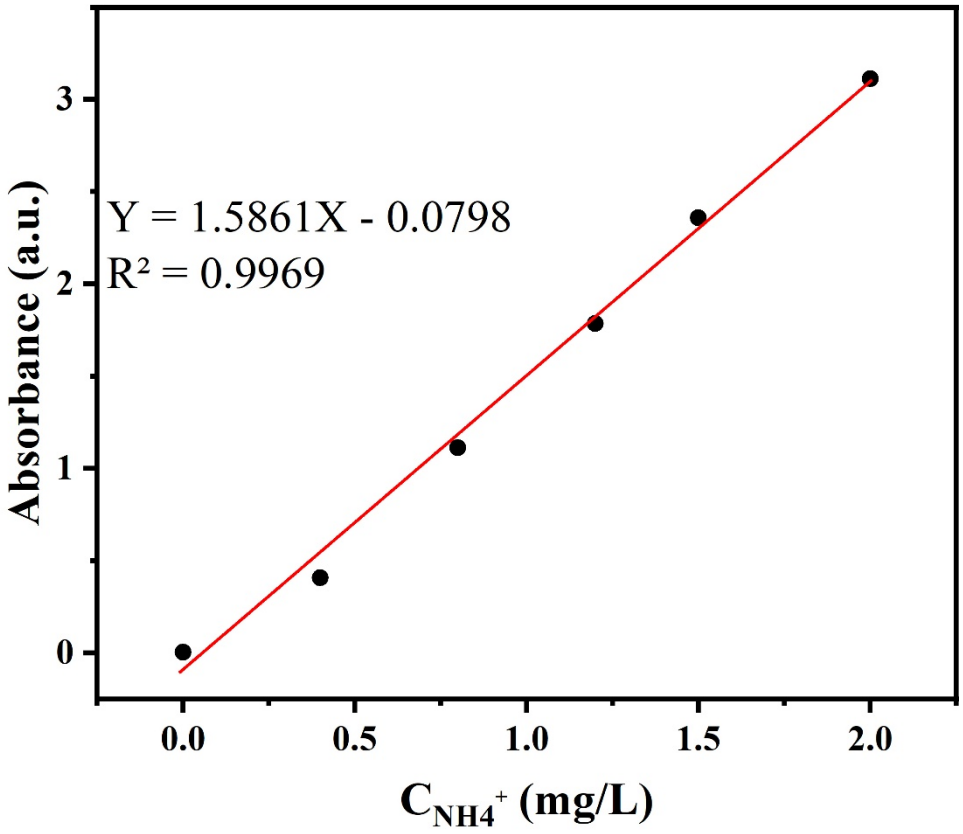

Figure. 15 The resulting calibration curve with the absorbance at 697.5 nm.

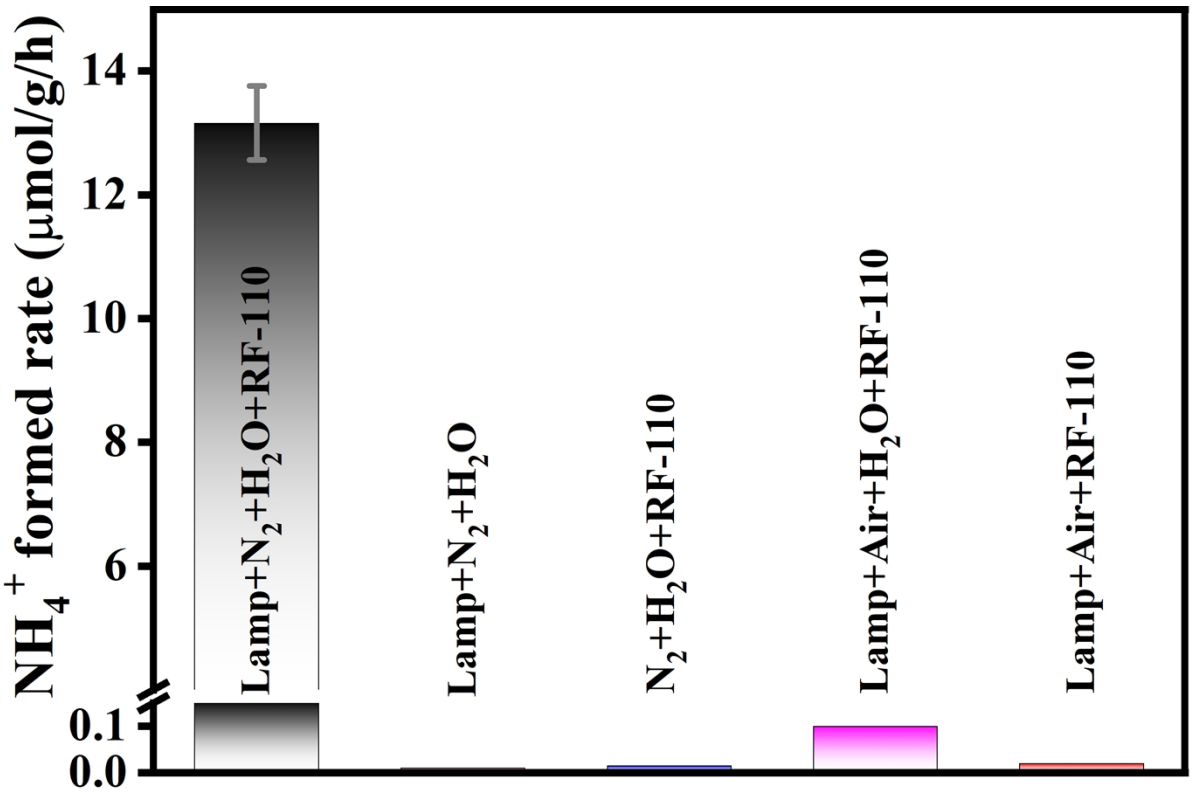

Figure. 16 Ammonia detection under different reaction conditions.

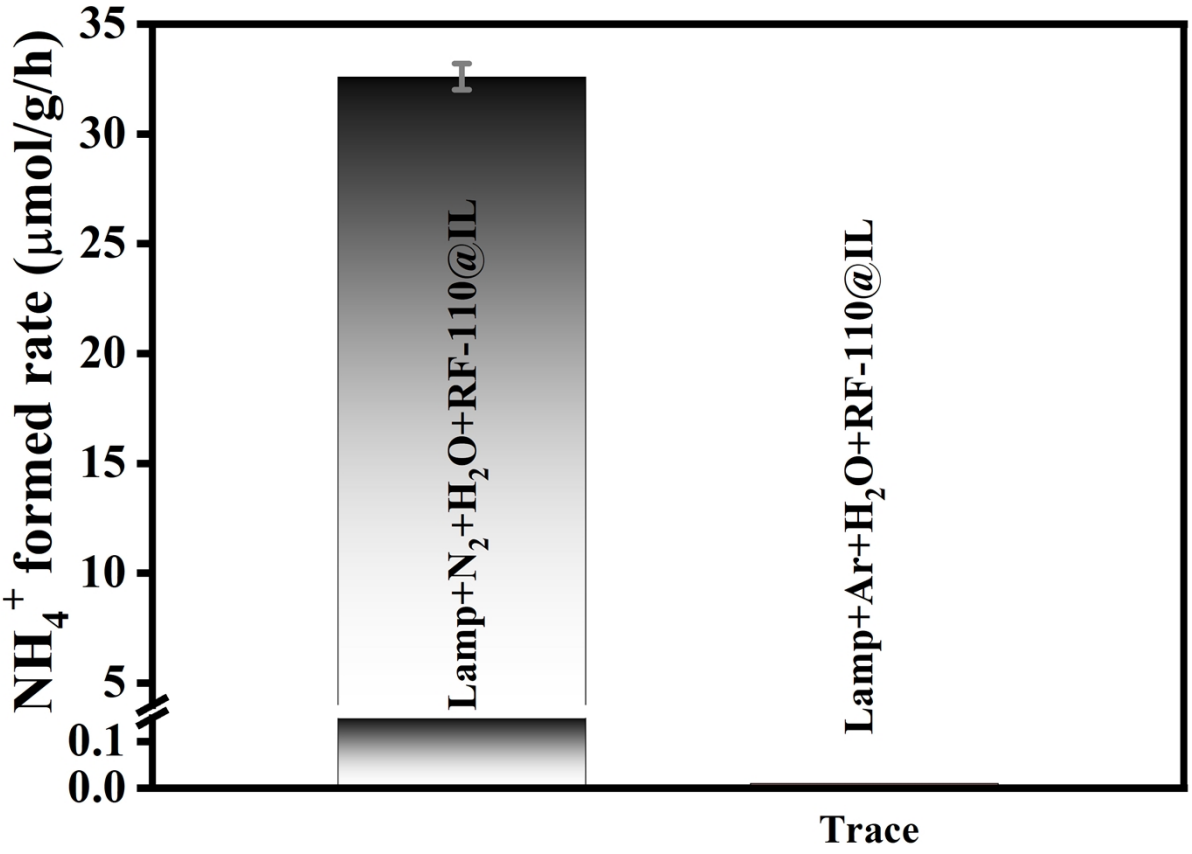

Figure 17. Photocatalytic ammonia yield of RF-110@IL under N_2 and Ar atmospheres.

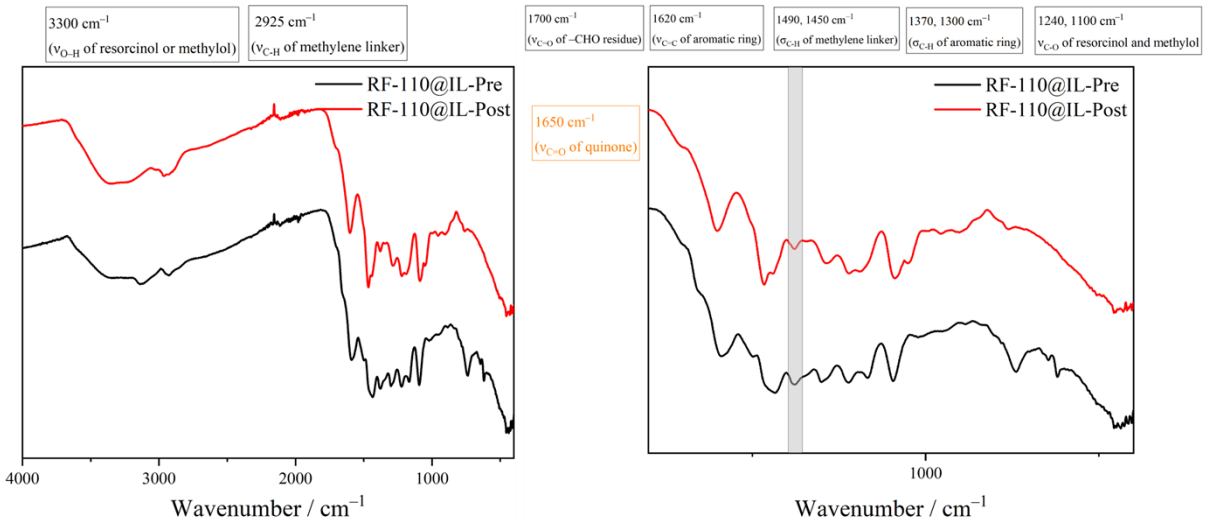

Figure 18. FT-IR spectra of RF-110@IL before and after the photocatalytic reaction.

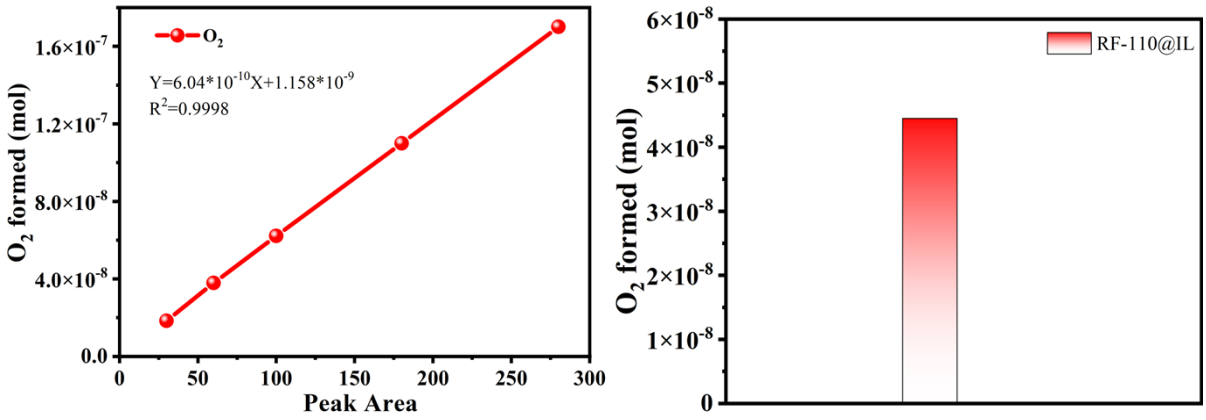

Figure 19. Standard calibration curve for O_2 evolution and the yield of photocatalytic O_2 synthesis by RF-110@IL.

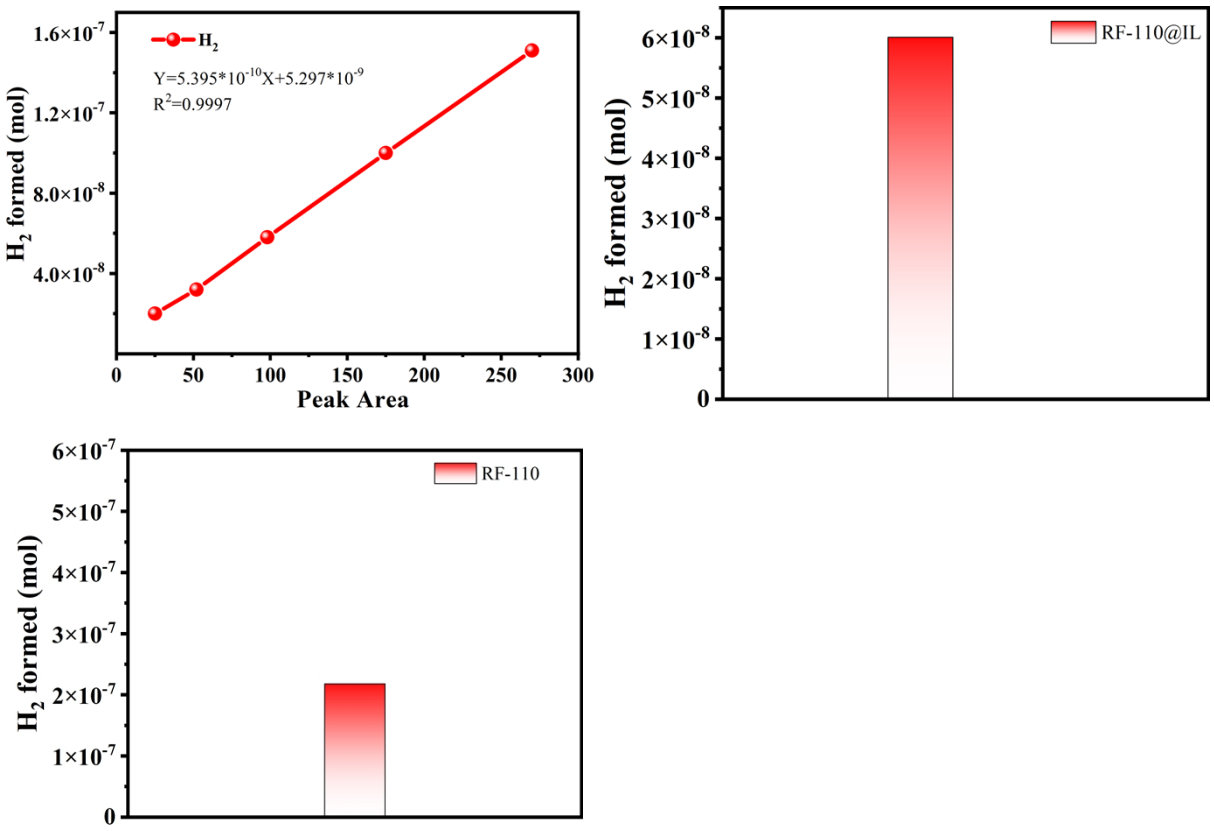

Figure 20. Standard calibration curve for H_2 evolution and the yield of photocatalytic H_2 synthesis by RF-110@IL and RF-110.

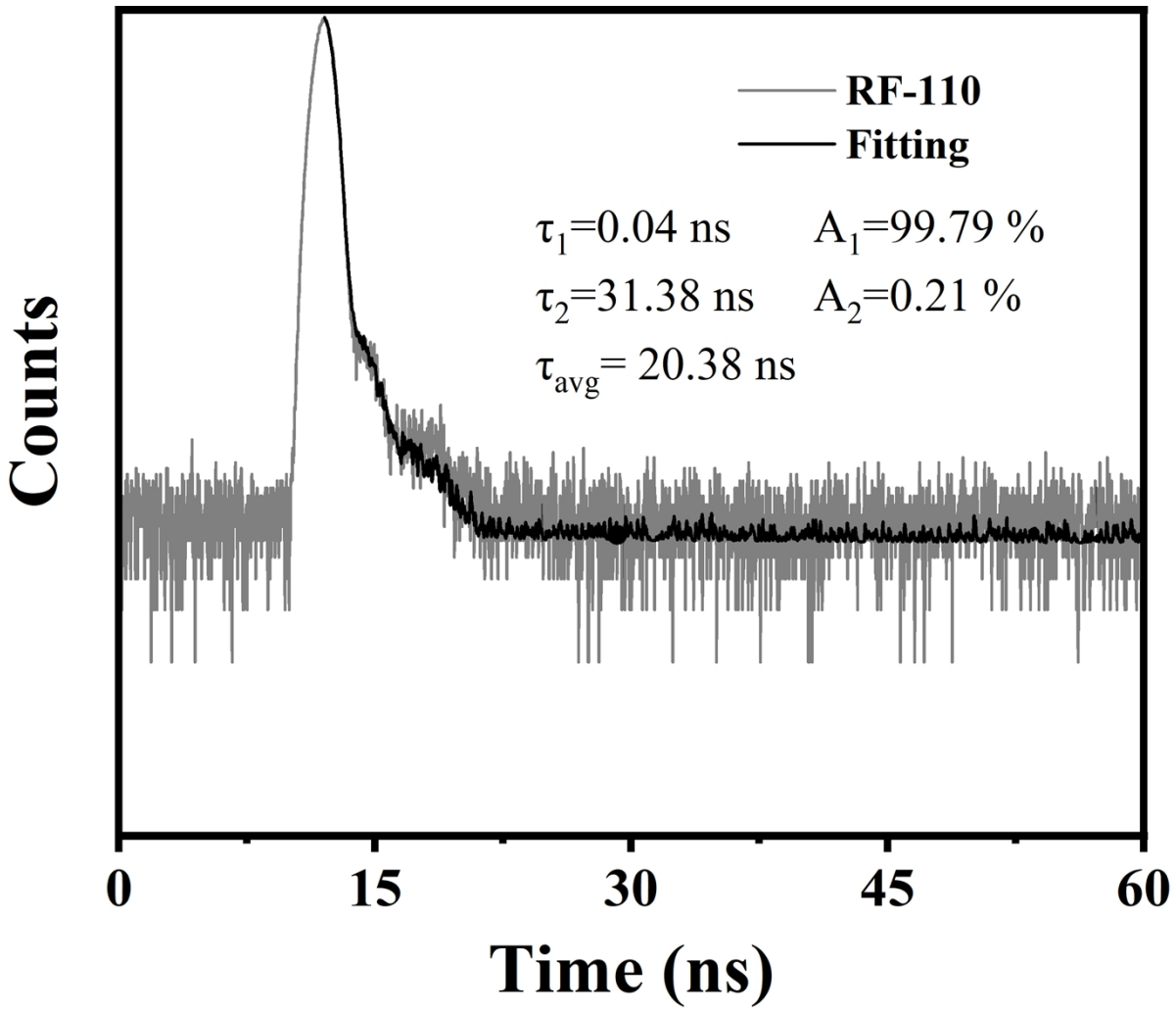

Figure. 21 Time-resolved fluorescence spectra of RF-110.

$$\tau_{avg} = \frac{\tau_1^2 \times A_1 + \tau_2^2 \times A_2}{\tau_1 \times A_1 + \tau_2 \times A_2}$$

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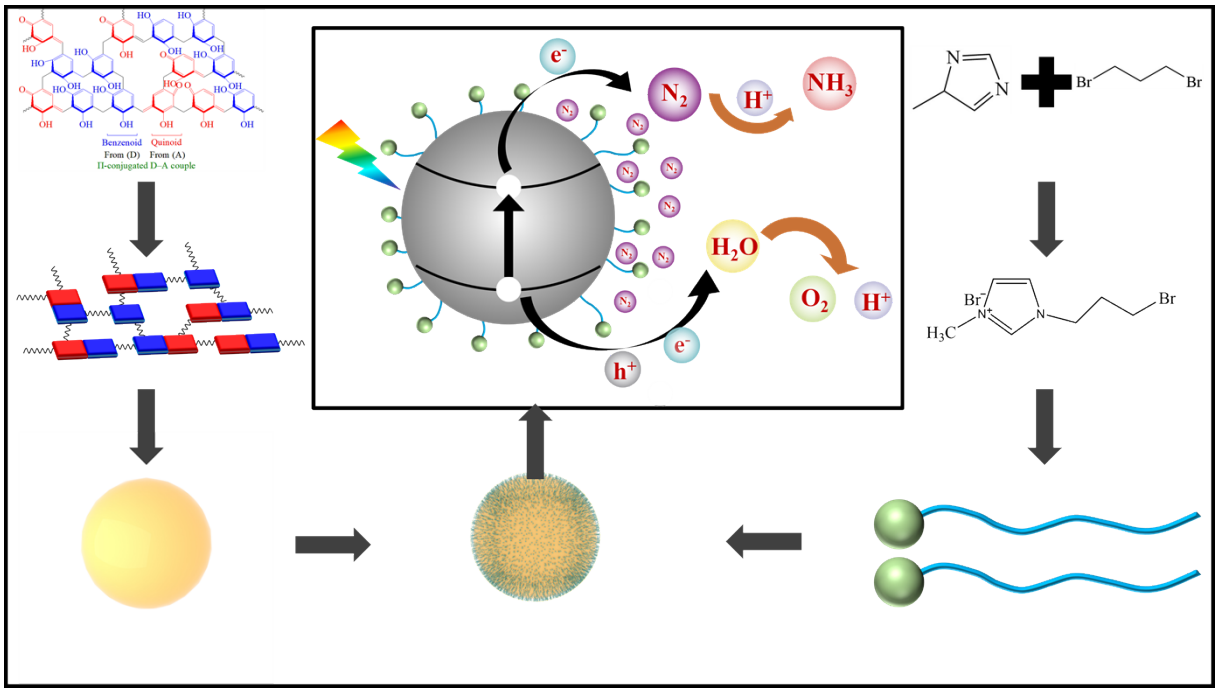

Figure. 22 Illustrations for photocatalytic nitrogen reduction procedures

Table 3. Consolidated XPS fitting parameters for RF-110 and RF-110@IL.

Element	Component	Position (eV)	FWHM (eV)	RF-110 (Area %)	RF-110@IL (Area %)
C 1s	C=C	284.6	1.8	73.21%	72.94%
	C-O	286.2	1.5	23.01%	22.50%
	C=O	288	1.43	3.78%	4.56%
O 1s	C=O	531.4	1.8	15.79%	75.58%
	C-O	533	1.86	84.21%	24.42%
N 1s	C=N−C	398.8	1.6	N/A	21.67%
	C−N−H_2	401.2	1.6	N/A	78.33%

Table 4. Apparent specific surface area calculation resultsfor RF-110 and RF-110@IL.

Sample	Observed BET (m^2/g)	IL Mass Fraction (Z%)	Apparent BET (m^2/g)
Bare RF-110	10.58	0%	10.58
RF-110@IL	5.21	18.50%	6.39