As a key industrial nitrogenous product and a critical environmental pollutant, ammonia broadly affects our daily lives. Rapid and sensitive detection of ammonia is essential to both environmental monitoring and process control for industrial manufacturing. Here, we present a protocol for rapid detection of low amounts of ammonia in the aqueous phase, via surface-enhanced Raman spectroscopy. We believe the mechanism and speed of the approach demonstrate its potential toward applications in operando electrochemical catalysis and in situ ammonia detection.
Protocol

Protocol for rapid ammonia detection via surface-enhanced Raman spectroscopy

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https://doi.org/10.1016/j.xpro.2021.100599

SUMMARY

As a key industrial nitrogenous product and a critical environmental pollutant, ammonia broadly affects our daily lives. Rapid and sensitive detection of ammonia is essential to both environmental monitoring and process control for industrial manufacturing. Here, we present a protocol for rapid detection of low amounts of ammonia in the aqueous phase, via surface-enhanced Raman spectroscopy. We believe the mechanism and speed of the approach demonstrate its potential toward applications in operando electrochemical catalysis and in situ ammonia detection.

For complete details on the use and execution of this protocol, please refer to Liu et al. (2020).

BEFORE YOU BEGIN

Since surface enhanced Raman spectroscopy for the detection of low concentration chemicals is a very sensitive technique, the SERS substrate pretreatment, ammonia solution handling and the set-up of the detection assembly are all critically important for optimal Raman signal output.

Commercial SERS substrate and its pretreatment

⊙ Timing: 12 h

1. ~3 × 3 mm commercial SERS substrates (SERStrate, Silmeco, Denmark) have been used. These substrates are ion etched Silicon nanopillars covered by metal (e.g., Ag and Au). As plasmonic resonance position is both metal and structure size dependent, we used Ag coated Si nanopillar substrates with a broad surface plasmon resonance around 500 nm – 550 nm to efficiently enhance the field of the 532 nm excitation source.

2. To increase substrate efficiency, the nanopillars were leaned by depositing a drop of Millipore water to cover the whole surface, followed by ambient drying without any other purification and treatment. The procedure is discussed in detail in (Schmidt et al., 2012).

△ CRITICAL: Due to the fragility of the metal covered Si nanostructures, substrates have to be handled with extra care, i.e., via the use of tweezers. Any direct contact by any material
(including paper and other relative soft materials) will result in damage to the surface, hence enhancement efficiencies. However, some enhancement improvements have been observed if signals are measured near shallow scratches on the substrate surface. Such signals are highly irreproducible and associated with the exposure of fresh, non-oxidized metal surfaces and accidental sharp metal structure formation near the edge of the scratch.

Preparing homemade SERS substrates

⊕ Timing: 12 h

3. For homemade SERS substrates, commercial Ag ink from Sigma Aldrich was employed. The ink is composed of silver nanoparticles of ~100 nm diameter, as precharacterized by the vendor using optical and electron microscopy approaches.

4. The ink was manually pasted on a flat mica substrate by a small wooden stick, and then spread evenly.

5. The substrate was dried for 1 h and used immediately or stored in inert/vacuum environment for future use. Figure 1, SEM images of the prepared substrate were taken to confirm the film morphology and particle size.

△ CRITICAL: A thin Ag film is expected to easily oxidize. We did not observe any visible signs of oxidation (change of coloration) within the time frame of the experiments (<6 h). The noticeable changes were observed if the substrate was left for over two days in an open lab environment. Moreover, the surface of the film turned brown, indicating strong oxidation. As expected, oxidized films exhibited reduced enhancement.

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Software and algorithms | | |
| Gaussian09 quantum chemistry program | Gaassian Inc. | (Frisch et al., 2010) |
| M06-2X/aug-cc-pVTZ level of theory | N/A | (Zhao and Truhlar, 2008) |
| Other | | |
| Commercial SERS substrate | Silmeco | 55 |
| Ammonium hydroxide solution | VWR | CAS No. 1336-21-6 |
| Ag ink | Sigma-Aldrich | 796042-5G |
| Water | Millipore | N/A |
| Renishaw inVia Raman microscope | Renishaw | N/A |
| Water immersion objective | Olympus | UPLSAPO60XW |
MATERIALS AND EQUIPMENT

**Alternatives:** This protocol uses a pure ammonia hydroxide solution as the initial stock solution for all sequential diluted ammonia solutions. The pH value of the diluted ammonia solutions are between 10 and 12, wherein over 95% of the ammonia in the solution are ammonia molecules (NH$_3$), as compared to its ammonium counterpart (NH$_4^+$). Also, this recipe minimized the possible interference from other counter ions and chemical species, focusing the experimental and modeling work on the Raman spectrum of the ammonia monomer, ammonia dimmer, ammonia water complex and water molecules. Other precursors such as ammonia chloride (NH$_4$Cl) can also be used, but consideration must be given regarding the impact of pH changes and interference from additional counter ions.

| Reagent            | Final concentration | Stock concentration | Amount | Final volume |
|--------------------|---------------------|---------------------|--------|--------------|
| Ammonia Solution-1 | 10,000 p.p.m.       | 28 wt% (NH$_3$ vs H$_2$O) | 10 mL  | 253.2 mL     |
| Ammonia Solution-2 | 100 p.p.m.          | 10,000 p.p.m.       | 1 mL   | 100 mL       |
| Ammonia Solution-3 | 50 p.p.m.           | 100 p.p.m.          | 10 mL  | 20 mL        |
| Ammonia Solution-4 | 20 p.p.m.           | 100 p.p.m.          | 4 mL   | 20 mL        |
| Ammonia Solution-5 | 10 p.p.m.           | 100 p.p.m.          | 2 mL   | 20 mL        |
| Ammonia Solution-6 | 5 p.p.m.            | 100 p.p.m.          | 1 mL   | 20 mL        |
| Ammonia Solution-7 | 3 p.p.m.            | 100 p.p.m.          | 0.6 mL | 20 mL        |
| Ammonia Solution-8 | 1 p.p.m.            | 100 p.p.m.          | 0.2 mL | 20 mL        |
| Ammonia Solution-9 | 0.5 p.p.m.          | 5 p.p.m.            | 2 mL   | 20 mL        |
| Ammonia Solution-10| 0.1 p.p.m.          | 1 p.p.m.            | 2 mL   | 20 mL        |

⚠️ CRITICAL: Throughout the experiments, no signal contribution from chemical contamination or impurities has been noticed in the spectral region of interest. Important to notice, a linear dependence of the ammonia related signal on the concentration over several octave changes down to sub-1ppm levels indicates no change in the anticipated solution concentration. The initial handling of all ammonia solutions has been done in a fume hood. The glassware involved in the solution preparation was thoroughly cleaned before use as discussed below. The prepared solutions have been briefly handled in an open laboratory environment prior to being sealed between mica microscope cover slips.

STEP-BY-STEP METHOD DETAILS

Preparation of ammonia solutions

⏰ Timing: 12 h

1. Soak all glassware in Caro’s acid for 1 h. Then, rinse the glassware 10 times with Millipore water, followed by 5 times with ethanol and 3 times with acetone. Dry the glassware thoroughly in an oven at approximatley 80 °C for 12 h before use.

2. In a fume hood, create a 10,000 ppm (1.0 wt%) ammonia solution by taking 10 mL of a 28 wt% ammonium hydroxide (NH$_3$ H$_2$O) solution and diluting with Millipore water to a total volume of 250 mL. Next, compensate with an additional 3.2 mL of water using a 5 mL pipette tip, for a total 10,000 ppm solution volume of 253.2 mL.

⚠️ CRITICAL: Use a small graduated cylinder to measure 5 mL of the ammonia water stock solution, because the insufficient surface tension will cause severe leakage when using pipettes.
3. Dilute the obtained solution to 100 ppm. First, take 1 mL of the 10,000 ppm solution (using a pipette) and add it to ~50 mL of MilliQ water in a 100 mL measuring flask. Then, fill the flask with water to 100 mL.

4. Prepare other less concentrated samples in glass vials (20 mL).
   a. For 50 ppm, mix 10 mL of the 100 ppm sample and 10 mL of water in a glass vial.
   b. For 20 ppm, mix 4 mL of the 100 ppm sample and 16 mL of water in a glass vial.
   c. For 10 ppm, mix 2 mL of the 100 ppm sample and 18 mL of water in a glass vial.
   d. For 5 ppm, mix 1 mL of the 100 ppm sample and 19 mL of water in a glass vial.
   e. For 3 ppm, mix 0.6 mL of the 100 ppm sample and 19.4 mL of water in a glass vial.
   f. For 1 ppm, mix 0.2 mL of the 100 ppm sample and 19.8 mL of water in a glass vial.
   g. For 0.5 ppm, mix 2 mL of the 5 ppm and 18 mL of water in a glass vial.
   h. For 0.1 ppm, mix 2 mL of the 1 ppm and 18 mL of water in a glass vial.

5. Seal all glass vials with built-in caps and parafilm.

**Surface-enhanced Raman detection with the confocal and wide-field setup**

**Timing:** [≤15 min for preparation, <1 s per measurement]

6. Raman spectra of the ammonia solutions near the metal surface have been measured using a commercial Raman microscopy system (InVia, Renishaw Corp., UK). The system is designed for epi geometry detection and through the control of the spectrometer input slit and beam profile on the sample, the system can be operated in both a confocal and quasi wide field geometry (see Figure 2 for concept of confocal and wide field approaches).

The following parameters have been used:

| Instrument                  | Specification                                      |
|-----------------------------|----------------------------------------------------|
| Grating                     | 2400 grooves/mm<sup>−1</sup>                        |
| Excitation wavelength       | 532 nm                                             |
| Focusing objective          | 60×, 1.2 NA, water immersion (Olympus, Japan)      |
| Detector                    | High speed CCD camera (Hamamatsu, Japan)           |

| Spectra acquisition parameters |                                  |
|--------------------------------|----------------------------------|
| Accumulation                   | 1                                |
| Exposure time                  | 1 s (unless stated otherwise)     |
| Excitation power               | 1.5 mW                            |
| Immersion liquid               | DI water                          |
| Slit width for confocal detection | 40 μm                           |
| Slit width for wide field detection | 500 μm                           |
| Beam size for confocal detection | 500 nm                           |
| Beam size for wide-field detection | 60 μm                            |

*Assuming the same diffraction efficiency, grating periodicity mainly influences spectral resolution, thus the use of 1200 gr/mm or even smaller is possible.

7. In each analysis, the substrates were immersed with an analyte ammonia solution that also served as the immersion liquid for the water objective.

8. The sample has been brought to focus based on an optical image of substrate surface and beam reflection image.

△ CRITICAL: The direct use of an analyte as an immersion material for the high numerical aperture objective simplifies experimental logistic and avoids any additional immersion materials.

△ CRITICAL: The SERS approach utilizes modest experimental parameters (low light flux, large spot size) and has virtually no geometrical restrictions that have limited other optical
techniques such as surface-enhanced attenuated total reflection infrared spectroscopy. It also allows ammonia detection at relatively high speeds (detection in under <1s). These factors enable in situ and on-site detection of the local concentration of ammonia, something that is much harder to achieve with existing methods. These conditions are particularly important for operando electrochemical experiments, where sample volumes are small and rapid quantification is advantageous.

**DFT calculations of the vibrational spectrum of ammonia aqueous solution**

© Timing: [< 48 h per calculation]

Calculations based on Density Functional Theory were performed to support the interpretation of the Raman spectra of ammonia in water (Figure 3).

9. The structure of the ammonia molecule, ammonium ion, ammonia-ammonia dimer, water-ammonia dimer, and ammonia-water complex were built using Avogadro, a molecule editor and visualizer (Hanwell et al., 2012) and optimized using M06-2X/aug-cc-pVTZ level of theory (Zhao and Truhlar, 2008). Harmonic frequency calculations were performed in the same step to obtain Raman mode intensities. Optimization and frequency calculations were performed using Gaussian09 quantum chemistry program Revision C.01 (Frisch et al., 2010). We used tight convergence criteria and an ultrafine integration grid. For example, route section for the Gaussian09 calculation was defined as

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**Figure 2. Concept of the experimental set-up**

(A) Optical pathway with an immersed objective. (B) Conventional confocal mode. (C) Wide-field set-up for large volume probing. Figures are adopted from Ref. (Liu et al., 2020).
The harmonic frequencies and Raman intensities were then read from the output of the Gaussian09 program. The normal models were inspected and assigned using visualization software, in this case ‘Jmol, an open-source Java viewer for chemical structures in 3D’.

10. The anharmonic frequencies were calculated using structures optimized in the previous step. Anharmonic frequencies are calculated using numerical differentiation along corresponding vibrational modes as implemented in the Gaussian09 software. The route section for the Gaussian09 calculation was defined as

```
# M062X/aug-cc-pVTZ integral=ultrafine freq=anharmonic
```

Anharmonic correction for each fundamental normal mode is read from the output of the Gaussian09 program.

**Optional:** Two steps (i.e., optimization, Raman intensities and anharmonic frequency calculations) can be combined in one calculation using Gaussian16 version and route

```
# opt=(maxcycles=250,gdiis,tight) M062X/aug-cc-pVTZ integral=ultrafine freq=(anharmonic,raman)
```

Figure 3. Ammonia-related vibrational modes
Figure was adopted with minor change from Ref. (Liu et al., 2020).
In addition, the anharmonic correction can be evaluated only for a certain number of normal modes that are of interest to the user by using the following route section:

```
# M062X/6-31+G(d) integral=ultrafine freq=(anharmonic,raman,SelectAnharmonicModes)
```

A list of the nodes was included after the molecule specification section following the blank line. For example, due to the computational cost of the calculations with the solvated ammonia model, we calculated the anharmonic correction for the stretching modes only using "mode=95–105".

**EXPECTED OUTCOMES**

Water Raman spectrum is comprised of many broad and overlapped features within 3000 cm\(^{-1}\) - 3700 cm\(^{-1}\) spectral range associated with OH-stretching vibrations (Figure 4). Using conventional spontaneous Raman spectroscopy and for given experimental parameters, ammonia spectroscopic signatures cannot be distinguished from water contributions, unless its concentration exceeds 1000 ppm (0.1 wt%) as seen in Figure 4B. The most pronounced peak is associated with the NH\(_3\)-NH\(_3\) dimer stretching at 3300 cm\(^{-1}\), as clearly seen in Figure 4B for 1000 ppm and confirmed in Figure 4C for 30,000 ppm.

Using a commercial silver SERS substrate (Schmidt et al., 2012) an ammonia concentration as low as 1 ppm is clearly detectable in just a 1 s exposure time (Figure 5A), showing the impact and functionality of a SERS substrate. As shown in Figure 5B, the ammonia related line scales linearly with

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**Figure 4. Ammonia signals and water backgrounds without SERS**

(A and B) Spontaneous Raman spectra of water and 1000 ppm ammonia solutions. (C) Raman spectrum of concentrated ammonia solution (3 wt%, 30,000 ppm) and calculated ammonia-related formations represented by column bars. All Raman spectra in this figure were conducted without a SERS substrate and with an exposure time of 1 s.

Figures were adopted with minor change from Ref. (Liu et al., 2020).
concentration. Similar detection sensitivity is also observed with the homemade SERS substrate from Ag ink (Figure 5C), showing the simplicity of the approach and sensor preparation.

With the wide-field detection approach (Figure 2C), the signals associated with ammonia are drastically boosted, resulting in sub-1 ppm detection limits (Figure 6A). The wide-field approach would be the method of choice when spatial resolution is of less importance to the overall detection sensitivity.

Figure 6B demonstrates the reversibility of the ammonia molecules in the vicinity of the SERS substrate surface, wherein the pure water spectrum can be fully recovered after the measurement of a 200 ppm solution on same SERS substrate. This experiment confirms the absence of surface adsorption of ammonia molecules by the metal surface, allowing for full detection of solution concentration dynamics.

QUANTIFICATION AND STATISTICAL ANALYSIS

The pH values of the ammonia solutions were measured to estimate the ratio of ammonia molecules (NH₃) and ammonium ions (NH₄⁺). The pH of Millipore water in this protocol was measured at ~6.6 due to small amounts of dissolved ambient carbon dioxide. The pH values of 0.1 ppm, 10 ppm and 500 ppm solutions were 10.7, 10.2 and 11.1 respectively. The NH₃/NH₄⁺ value was calculated by using the acidity of ammonium (pKa = 9.25), according to:

$$\log_{10}(\text{NH}_3 / \text{NH}_4^+) = \text{pH} - \text{pKa}$$

Consequently, the ammonia molecule (NH₃) content of all dilute ammonia solutions were more than 95%, as compared to its ammonium ion (NH₄⁺) counterpart. This explains the absence of the calculated NH₄⁺ signal around 1500 cm⁻¹ (Figure 4C insert).

Quantitative analysis of Raman spectra

Quantitative analysis, i.e., calibration of the integrated spectral intensity as a function of concentration is rather limited due to the SERS substrate reproducibility. It is important to note, the error in Figure 5B. Here, the integrated signal intensity has been determined for each concentration through a fit of the spectral line using a Lorentz function, with broad OH spectral features being subtracted as a constant background within the discussed narrow spectral window (~50 cm⁻¹). We determined that intensity deviations do not stem primarily from the water background related to OH bands, but from the irreproducibility of the SERS substrate. Even for the highest quality substrates, the enhancement factor can vary significantly. The added error bars represent the observed variation of the enhancement factor, based
on multiple experiments for several concentrations at different spatial positions. We found an error of under 10% for the smallest concentration. The signal fluctuations are considered negligible compared with the spatial reproducibility within the same substrate, that varies on average by a factor of 2 (error over 10 experiments for each given concentration).

Number of molecules in the detection volume.

Per simple estimation outlined below, the confocal volume is determined to be ~1.2 μm³ (fL), which means only 10⁴ - 10⁵ molecules for 1 ppm concentration (Table 1).

![Figure 6. Ammonia signals with different detection mode and reversibility test](image)

(A) Detection of a 500 ppm ammonia solution using confocal and wide-field approaches. The spectra were obtained with a commercial SERS substrate with an exposure time of 0.3 s.

(B) Sequential ammonia detection of 200 ppm, water and 1 ppm solutions on the same SERS substrate, demonstrates the reversibility of the methodology. Figures were adopted from (Liu et al., 2020).

We would like to emphasize here that not all the molecules in confocal volume contribute to the signal, but only those in close proximity to the metal hot spots. In this case the detection volume must be corrected with the near field contribution range of only 10 nm, compared to Raleigh range z ~2 μm. This allow us to speculate that only <10³ molecules are being detected.

**LIMITATIONS**

Though the nature of the signal enhancement does not rely on the solvent origin, the compatibility of this method to other organic/inorganic solvents, such as THF and ethanol,

| Vertical resolution | Index of refraction | Numerical aperture of the objective | Beam waist |
|---------------------|---------------------|-------------------------------------|------------|
| \( \kappa \)        | \( n \)             | \( \text{NA} \)                      | \( \omega \) |
| 2.52                | 1.3                 | 1.2                                 | 500 nm     |

\[
\kappa = \frac{2.33n}{\text{NA}}
\]

\[
V_{\text{confocal}} = \pi^{3/2} \kappa \omega^2
\]

We would like to emphasize here that not all the molecules in confocal volume contribute to the signal, but only those in close proximity to the metal hot spots. In this case the detection volume must be corrected with the near field contribution range of only 10 nm, compared to Raleigh range \( z \sim 2 \mu m \). This allow us to speculate that only <10³ molecules are being detected.

**LIMITATIONS**

Though the nature of the signal enhancement does not rely on the solvent origin, the compatibility of this method to other organic/inorganic solvents, such as THF and ethanol,
need to be further determined. At the same time, organic solvents are expected to improve the approach sensitivity as their contribution in the spectral region of interest are limited by the CH-stretching mode, which are much narrower and remain aside of the ammonia signatures.

The SERS detection concept does not put any limitations on the identity or morphology of the electrode as long as it can be put close enough to the SERS structure. The separation distance between the electrode and the SERS active particles/surface is dictated by experimental conditions and may vary from the micro- to macro-scale.

**TROUBLESHOOTING**

**Problem 1**
Thin Ag films are easily oxidized. If left for several days in an open lab environment, the surface of the film turns brown, indicating strong oxidation. As expected, oxidized films exhibit reduced enhancement. (steps 4 and 5)

**Potential solution**
The substrate should be dried for ~1 h and used immediately or stored in inert/vacuum environment for future use.

**Problem 2**
Untreated commercial SERS substrates may have insufficient enhancement factor. (steps 1 and 2)

**Potential solution**
Plasmonic enhancement factor, hence the signals are highly dependent on the substrate structure, composition, and geometry. Leaning of the substrate is thoroughly discussed in the manuscript and appear to simply enhance the interaction surface. Thus, the similar level of signals can be observed using home-made substrates from silver ink comprised of metal nanoparticles. Leaning of commercial substrate is recommended to increase efficiency but is not absolutely required. Moreover, the leaning will naturally occur for a flowing solution device design. It can also be anticipated that better and more efficient substrate designs can increase both the quantity of plasmonic hot spots and large areas of interaction.

**Problem 3**
The analyte concentration may be inaccurate or unstable if the initial handing of ammonium hydroxide (NH$_3$ H$_2$O) is not appropriate. (step 2)

**Potential solution**
The low surface tension of the stock solution or less diluted analytes can not be firmly held within normal pipette tips. Always use a measuring cylinder or flask even for small amounts of solutions with higher ammonia concentrations.

**Problem 4**
Ammonia related signals around 3250 cm$^{-1}$ are overlapped with a broad response of the OH band coming from the aqueous solution. (step 6)

**Potential solution**
For sub-ppm concentration detection, a background comparison of pure water may benefit the method sensitivity. Moreover, such a broad background should not be present for non-aqueous solvents, including D$_2$O, indicating a broader application of the current method to other chemical environments. Potential contribution of CH stretching modes for organic solvents is away of the spectral region of interest.
Problem 5
Calculation of anharmonic frequencies is computationally too demanding. (steps 9 and 10)

Potential solution
Anharmonic correction can be evaluated only for a certain number of normal modes that are of interest by using the following route section in Gaussian09 or Gaussian16:

```
"# M062X/6-31+G(d) integral=ultrafine freq=(anharmonic,raman,SelectAnharmonicModes)".
```

A list of modes has to be included after the molecule specification section following the blank line. For example, due to the computational cost of the calculations with the solvated ammonia model, we calculated the anharmonic correction for the stretching modes only using “mode=95–105”.

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Dr. Yuanchao Liu (yuanchao.liu@uci.edu).

Material availability
This study did not generate any new unique reagents.

Data and code availability
The Python code (Jupyter Notebook) for confocal volume and molecules calculations can be found in our Github repository.

https://github.com/ycliu1987/Paper-of-SERS-for-Ammonia

The above link also includes the ammonia geometry for DFT simulation.

ACKNOWLEDGMENTS

This work was supported in part by a subcontract from DOE-EERE Advanced Manufacturing Office award to Sandia National Laboratories (AOP 34920). D.A.F. would like to thank Prof. Var tkess A. Apkarian for inspiring discussions. D.A.F. acknowledges NSF grant CHE-0960179. I.M. wishes to thank the UNM Center for Advanced Research Computing, supported in part by the National Science Foundation, for providing the high-performance computing resources used in this work. We are thankful to Dr. Andrea Perego, National Fuel Cell Research Center (NFCRC), University of California Irvine, for the SEM images obtained at Irvine Materials Research Institute (IMRI).

AUTHOR CONTRIBUTIONS

D.A.F. and P.A. conceived the idea and supervised the study. Y.L. and E.M. prepared ammonia solutions directed general logistics of chemical experiments. I.M. performed DFT calculations. D.A.F. designed experimental concepts, conducted optical experiments, and analyzed the data. Y.L. drafted the manuscript. All authors contributed to manuscript editing.

DECLARATION OF INTERESTS

The authors declare no competing interests.
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