Revealing Ammonia Quantification Minefield in Photo/Electrocatalysis

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Abstract: Photo/electrocatalytic ammonia synthesis—a low carbon and sustainable process has developed fast over the past decade while the ammonia yield over state-of-the-art photo/electrocatalysts are still very moderate (typically < 1 mmol g^{-1} h^{-1}, roughly ~ 1 ppm taking xx volume solution and xx mass of catalyst used as one example). Such low concentration of NH3 synthesised brings about a challenge on the reliable quantification of the product in both photocatalysi and electrocatalysis. Notably, we found that the quantitative detection of ammonia concentration below 0.2 ppm is error-prone, which is likely the case happening in the majority of photocatalytic or electrocatalytic NH3 synthesis, thus arising concerns about the rationality and accuracy for low-concentration ammonia quantification in these processes. Herein, we discuss the methodology used and analyse the reliability of various detection methods (e.g., indophenol blue method, nessler's reagent method, ion chromatography method and ^{1}H nuclear magnetic resonance method) for the detection of trace ammonia in aqueous media. By regulating the parameters of detection methods, the experimental detection limitation can be expanded from 0.2 ppm to 0.1 ppm, even lower. The challenges facing in detection of low concentration of ammonia in photo/electrocatalysis can be overcome by integration of with multiple detection methods. According to the data presented, we also propose an effective criteria for precise quantification of ammonia, avoiding the unreasonable comparisons in photo/electrocatalytic ammonia synthesis..

Introduction

Ammonia (NH_3) is one of the essential commercial chemicals in today's chemical industry.[1] The industrially artificial catalytic reduction of nitrogen (N_2) to ammonia *via* the Haber-Bosch process over a metallic Fe-based catalyst needs harsh reaction conditions (200-250 bar, 400-500 ºC).[2] Conversely, the enzyme nitrogenases in nature containing cationic Fe and FeMo active sites can fixate N_2 to NH_3 under ambient conditions.[3] Taking inspiration from these biocatalytic systems, more and more researchers work on N≡N bond activation under ambient conditions through photo/electrocatalytic routes.[4] The photo/electrocatalytic ammonia synthesis driven by sunlight or electricity over the catalysts was widely explored and investigated, revealing the possibility of the nitrogen fixation under ambient reaction conditions.[5] As shown in Figure 1a, publications about photo/electrocatalytic nitrogen reduction reaction (NRR) research had been increasing during the past 5 years, indicating that the noticeable promise and potential of NRR.

Whilst significant fundamental advancements have been made in recent years regarding the photo/electrocatalytic ammonia synthesis, production rates and selectivity of the current catalytic systems still fails to warrant industrial interests.[6] At present, the evaluation of photo/electrocatalytic activity based on the production rate (μmol g^{-1} h^{-1}) or coulombic efficiency possibly causes a misunderstanding on exploiting low current/overvoltage or low usage catalyst to attain attractive ammonia yield. Thus, how to reasonably evaluate the activity of synthetic ammonia is still a controversial issue. Besides, owing to the low catalytic ammonia production rates and environmental ammonia contamination problem, more attention has to be paid to the accurate and reproducible quantification of ammonia,[7] which is highly desirable and vital though technically challenging.

Results and Discussion

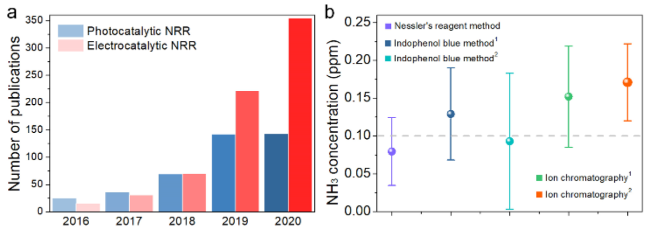

Figure 1. (a) Present status of photo/electrocatalytic NRR research (Publications about NRR during the past 5 years). The counts were obtained from Web of Science. (b) The measured results of 0.1 ppm of ammonia in aqueous media (pH = 7) using widely used ammonia quantification methods (For different methods, see supporting information). To guarantee the accuracy of the detected results, we used fresh ultrapure water every time to minimise the interference of environmental ammonia. All testing experiments were repeated 3 times.

Generally, the qualitative and quantitative analysis of ammonia depends on various methods, such as colorimetric methods (indophenol blue and Nessler's reagent method),[8] ion chromatography method (IC),[9] fluorescence method,[10] ammonia ion-selective electrode and ^{1}H nuclear magnetic resonance (NMR) method.[11] All of these methods theoretically show considerable consistency and high accuracy in wide-ranging ammonia concentrations under ideal conditions. However, when it comes to a complicated chemical environment (such as harsh pH conditions, impurity ions and other N-containing contaminations), the validity and accuracy, especially at nano/micromolar concentrations, need to be verified carefully.[12] Additionally, the detection and quantification of low-concentration ammonia (particularly below 0.2 ppm) become the pressing priority, considering that they are involved in the majority of the reported photo/electrocatalytic ammonia synthesis. Unfortunately, the accurate detection of low-concentration ammonia using typical methods is not optimistic as shown in Figure 1b. The detection errors for standard NH_3 solution (0.1 ppm) increase, ranging from 20.5% for Nessler's reagent method to 71.2% for the ion chromatography method. Almost all testing methods exhibit unsatisfactory reproducibility when the ammonia concentration is below 0.2 ppm, leading to more inaccurate and unreliable detected results. The standard curves of NH_4^+ in pure water with indophenol blue, Nessler's reagent and ion chromatography methods are presented in Figure S1 (supporting information) and Table 1. In the case of high ammonia concentration (≥ 0.2 ppm), strong linear relationships are established between intensity and the concentration in aqueous media (pH = 7) (the coefficient of determination value (R^2) = 0.9990 for Nessler's reagent method, 0.9995/0.9996 for indophenol blue methods and 0.9952/0.9989 for IC, respectively), which are in accordance with reported results. With the ammonia concentration decreases less than 0.2 ppm, the poor correlation coefficient of the three methods can be observed (Figure S2) probably due to the practical detection limitation of three different methods. It hints that the measured ammonia concentration lower than 0.2 ppm using normal quantification methods would be questionable.

Table 1. The R^2 values of different detection methods for quantifying ammonia concentration in pure water.

Ammonia Detection Methods	R^2 (> 0.2 ppm)	R^2 (lower than 0.2 ppm)
Nessler's reagent method	0.9990 ± 0.0029	-0.208 ± 70.419
Indophenol blue method[1]	0.9995 ± 0.0007	0.9799 ± 0.0431
Indophenol blue method[2]	0.9996 ± 0.0009	0.9376 ± 0.0373
Ion chromatography[1][a]	0.9952 ± 0.0013	0.8047 ± 0.4946
Ion chromatography[2][b]	0.9989 ± 0.0021	0.9033 ± 0.3529
NMR[c]	/	0.9985

[a] Ion chromatography[1]: the loop size is 10 μL, ICS 600, Thermo Fisher Scientific.

[b] Ion chromatography[2]: the loop size is 20 μL, 930 compact IC Flex, Metrohm.

[c] NMR: ^{1}H nuclear magnetic resonance spectroscopy method (0.02-0.5 ppm).

Typically, the habitually precise IC was found to have a terrible performance in the case of the ammonia concentration lower than 0.2 ppm. To further optimize IC with the acceptable sensitivity and accuracy at low ammonia concentration, we firstly tuned the loop size from 10 to 200 μL. As shown in Figure S3 and Table S1, the values of R^2 ranged from 0.8047 to 0.9999 and optimal loop sizes of IC from different manufacturers are also distinct at low-concentration ammonia (100 μL for ion chromatography[1] and 50 μL for ion chromatography[2]). The experimental results indicated that the IC can be optimized to meet the low-concentration quantitative requirements and the optimized ion chromatography with customized loop size was employed in our following experiments. Furthermore, the frequency-selective NMR method as an advanced ammonia quantification method offers many advantages (high sensitivity, good reproducibility, straightforward discrimination against contaminant NH_3, and convenience without the need for NH_3 transfer or advanced chemical manipulation).[11b] For the NMR method, the Bruker 800MHz AVANCE III HD with a cryoprobe equipping and maleic acid as an internal standard was utilized to quantify the concentration of ammonia in aqueous media (see supporting information). Each ^{1}H NMR spectrum consists of an accumulation of 128 scans for a total experiment time of ~10 min, which is comparable to the detection efficiency of ion chromatography. Figure 2a shows that NH_4^+ is a 1:1:1 triplet in the region near 7.05~7.20 ppm and peaks of maleic acid appear at 6.36 ppm. The repetitive experiments in Figure 2b further verify the high reliability of NMR method. Moreover, this method fits different deuterated reagents using for a spin-lock field (i.e., DMSO-d_6, D_2O, CD_3OD and CD_3CN) (Figure 2c). On basis of the above data, we developed a calibration curve using the NMR method. It can be noticed that the relative intensity is highly correlated with ammonia concentration (lower than 0.2 ppm) and the corresponding R^2 can reach 0.9985 (Figure S4 and Table 1), exhibiting the high accuracy and repeatability of NMR method in quantifying low-concentration ammonia.

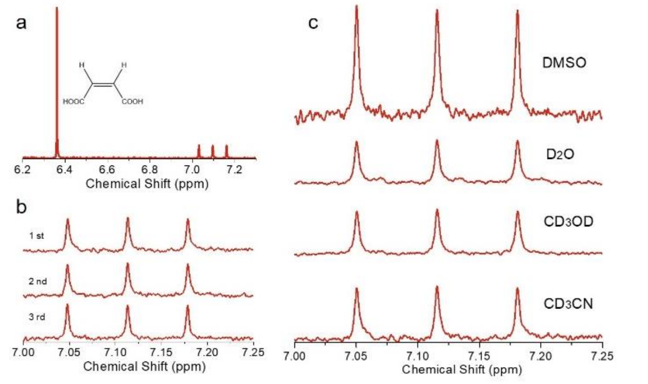

Figure 2. (a-b) ^1H NMR spectra of NH_4^+ (0.1 ppm) in aqueous media included a stand reference (maleic acid) and repetitive experiments using DMSO-d_6. (c) NMR spectra of NH_4^+ (0.1 ppm) solution in DMSO-d_6, D_2O, CD_3OD and CD_3CN. One ppm equals the 1 mg of NH_4^+ in 1 L of H_2O.

Table 2. The R^2 values of different detection methods for quantifying ammonia concentration in different electrolytes.

Ammonia Detection Methods	Electrolytes	R^2 (lower than 0.2 ppm)
Nessler's reagent method	0.05M H_2SO_4	0.8979 ± 0.3424
Nessler's reagent method	0.5M Na_2SO_4	0.9960 ± 0.0761
Nessler's reagent method	0.1M KOH	0.9818 ± 0.0019
Indophenol blue method[1]	0.05M H_2SO_4	0.9999 ± 0.0093
Indophenol blue method[1]	0.5M Na_2SO_4	0.9987 ± 0.0062
Indophenol blue method[1]	0.1M KOH	0.9901 ± 0.0172
Ion chromatography[1][a]	0.05M H_2SO_4	0.9953 ± 0.0004
Ion chromatography[1][a]	0.5M Na_2SO_4	/
Ion chromatography[1][a]	0.1M KOH	/
NMR[b]	0.05M H_2SO_4	0.9961
NMR[b]	0.5M Na_2SO_4	0.9960

[a] Ion chromatography[1]: the loop size is 100 μL, ICS 600, Thermo Fisher Scientific.

[b] ^1H NMR: ^1H nuclear magnetic resonance spectroscopy method.

In addition to the testing requirement of low-concentration ammonia in neutral water (pH = 7), other aqueous media (pH = 1 or pH = 13) are extensively employed in electrocatalysis. Considering the interference of ions on the ammonia quantification, we selected the electrolytes with different concentrations as a comparison, including 0.05 M H_2SO_4, 0.1 M KOH and 0.5 M Na_2SO_4 (Table 2 and Figure S5-8). For Nessler's reagent method, it showed a great linear relationship between absorption intensity and the concentration of ammonia in 0.5 M Na_2SO_4 (R^2 = 0.9960), whereas the linearity is unsatisfactory in 0.05 M H_2SO_4 and 0.1 M KOH. Compared with Nessler's reagent method, the indophenol blue method presented a remarkable correlation coefficient in three different pH solution (R^2 = 0.9999 for 0.05 M H_2SO_4, R^2 = 0.9987 for 0. 5 M Na_2SO_4 and R^2 = 0.9901 for 0.1 M KOH). Nevertheless, the reproducibility of spectrophotometric/colorimetric assessment is unsatisfactory in the low ammonia concentration range, thus each examination needs to be recalibrated rigorously. The IC method would be more suitable for acidic and neutral aqueous media at low ammonia concentration (R^2 = 0.9953 for 0.05 M H_2SO_4) since the interference of Na^+/K^+ ions in different electrolytes. Alternatively, the NMR method exhibited dramatical reproducibility and stability in different electrolytes and a considerable R^2 of 0.9961 for 0.05 M H_2SO_4 and 0.9960 for 0.5 M Na_2SO_4. We also found that the high-concentration electrolytes present the higher challenge under the same test parameters. The brand new test parameters and specific NMR tubes are required (such as shape tube), otherwise it would cuase damages to NMR instrumentation if we need to quantify low ammonia concentration dissolved in high-concentration electrolytes.

Many advantageous recommendations regarding ammonia quantification in photo/electrocatalysis have been made in reported work.[6b, 12a, 13] On the basis of the foregoing and to further enhance the consistency and accuracy of measurement at low ammonia concentration (especially lower than 1 ppm or even 0.2 ppm), particular attention should be paid as summarized in Figure 3: i) firstly, the quantitative measurement with ammonia concentration below 0.2 ppm is error-prone. The detection minefield should be realized and valued in the photocatalytic and electrocatalytic experiments; ii) For the accuracy and scientific rigor, it is recommended that the detection of ammonia concentration below 0.2 ppm requires two different quantitative methods to cross check; iii) The appropriate ammonia determination method should be derived from the concentration of NH_3 production in photo/electrocatalysis (> 0.2 ppm or < 0.2 ppm). Additionally, the choice of NH_3 quantification methods is also dependent on the pH of electrolytes. For neutral electrolytes, three methods (NMR, Nessler's reagent and indophenol blue methods) are consistent to achieve accurate detection of NH_3 concentrations below 0.2 ppm. The indophenol blue method is also suitable for alkaline and acid electrolytes. For photocatalysis, the ammonia concentrations (< 0.2 ppm) are recommended to be confirmed using IC or NMR methods. It is certainly more rigorous to confirm these quantitative results of ammonia by more than two different detection methods. Meanwhile, as the existence of trace ammonia in the air, the ammonia rates generated (especially lower than 0.2 ppm) with quantitatively isotopically labelled NMR would make this measurement more convincing (Figure S9).

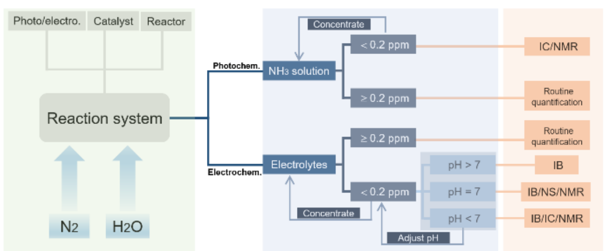

Figure 3. Flow diagram of suggested protocols to rigorously conduct ammonia quantification (IB = indophenol blue method, NS = Nessler's reagent method, IC = ion chromatography method, and NMR = ^1H nuclear magnetic resonance method).

Moreover, we give prominence to the significance of accurate and reproducible quantification of ammonia, especially lower than 1 ppm or even 0.2 ppm (Figure 4). The previously reported catalysts are systematically summed up in accordance with the mass-normalized ammonia evolution rates and produced ammonia concentration (Table S2). Regrettably, in 65% electrocatalytic statistics, the generated NH_3 concentration is unable to be calculated due to deficient information provided. For another 35% electrocatalytic reported results and all photocatalytic statistical results, most of the mass-normalized ammonia production ranges from 0.013 to 1.0 mmol g^{-1} h^{-1}.[14] Notably, the generated ammonia concentrations are still at the ppm level (mg L^{-1}), or even the ppb level (μg L^{-1}), which puts forward a higher quantitative requirement for ammonia detection. Furthermore, the production rate (μmol g^{-1} h^{-1}) or coulombic efficiency could be unreasonably raised, exploiting low usage catalyst or low current/overvoltage.[15]The obtained data are challenging to reflect actual catalytic performance directly, sometimes would cause misunderstanding. Reporting quantitative ammonia concentration can assist in providing another reference standard for comparison, thereby advocating researchers to provide the final NH_3 concentration and absolute ammonia yield (μmol or μmol h^{-1}) for appraising the catalytic performance of a new catalytic system.

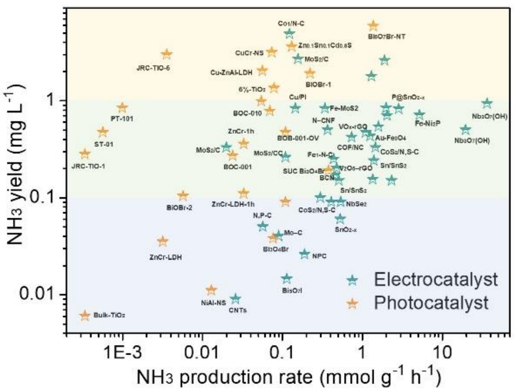

Figure 4. Ammonia concentration and mass-normalized NH_3 production rates of reported NRR photo/electrocatalysts. The NH_3 evolution rates, ammonia concentration and other detailed information are from the literature and summarized in Table S2.

Conclusion

In summary, we present the advantages and detection limitation and application scope of various detection methods (indophenol blue method, Nessler's reagent method, ion chromatography method and ^1H nuclear magnetic resonance method), especially when ammonia is below the detection limitation of 0.2 ppm in photo/electrocatalytic ammonia synthesis. On the basis of the data presented, a rigorous ammonia detection flow diagram and another reference standard were proposed for more accurate and reliable NH_3 quantification (especially lower than 1 ppm or even 0.2 ppm), together with the positioning and evaluation of the catalytic activity. It is highly recommended that the low-concentration ammonia quantification should be paid sufficient attention, so as to bypass detection minefield and push the development of the online and fast characterization techniques for accurate and reliable ammonia quantification in the future.

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Keywords: ammonia • detection • photo/electrocatalysis • quantification • 0.2 ppm.

[1] a) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84-87; b) J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, *Science* **2018**, *360*, eaar6611.

[2] a) J. W. Erisman, M. A. Sutton, J. N. Galloway, Z. Klimont, W. Winiwarter, *Nat. Geosci.* **2008**, *1*, 636-639; b) R. Schlogl, *Angew. Chem. Int. Ed.* **2003**, *42*, 2004-2008.

[3] A. Banerjee, B. D. Yuhas, E. A. Margulies, Y. Zhang, Y. Shim, M. R. Wasielewski, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2015**, *137*, 2030-2034.

[4] C. Guo, J. Ran, A. Vasileff, S.-Z. Qiao, *Energy Environ. Sci.* **2018**, *11*, 45-56.

[5] X. Chen, N. Li, Z. Kong, W.-J. Ong, X. Zhao, *Mater. Horiz.* **2018**, *5*, 9-27.

[6] a) S. Zhang, Y. Zhao, R. Shi, G. I. N. Waterhouse, T. Zhang, *EnergyChem.* **2019**, *1*, 100013; b) C. Tang, S. Z. Qiao, *Chem. Soc. Rev.* **2019**, *48*, 3166-3180; c) W. Guo, K. Zhang, Z. Liang, R. Zou, Q. Xu, *Chem. Soc. Rev.* **2019**, *48*, 5658-5716.

[7] a) Y. Chen, H. Liu, N. Ha, S. Licht, S. Gu, W. Li, *Nat. Catal.* **2020**, *3*. 1055-1061; b) J. Choi, B. H. Suryanto, D. Wang, H.-L. Du, R. Y. Hodgetts, F. M. F. Vallana, D. R. MacFarlane, A. N. Simonov, *Nat. Commun.* **2020**, *11*, 1-10; c) G. F. Chen, S. Ren, L. Zhang, H. Cheng, Y. Luo, K. Zhu, L. X. Ding, H. Wang, *Small Methods* **2019**, *3*, 1800337; d) C. Tang, S.-Z. Qiao, *Joule* **2019**, *3*, 1573-1575.

[8] L. Zhou, C. E. Boyd, *Aquaculture* **2016**, *450*, 187-193.

[9] D. H. Thomas, M. Rey, P. E. Jackson, *J. Chromatogr. A* **2002**, *956*, 181-186.

[10] Y. Zhu, D. Yuan, H. Lin, T. Zhou, *Anal. Lett.* **2016**, *49*, 665-675.

[11] a) A. LeDuy, R. Samson, *Biotechnol. Lett.* **1982**, *4*, 303-306; b) A. C. Nielander, J. M. McEnaney, J. A. Schwalbe, J. G. Baker, S. J. Blair, L. Wang, J. G. Pelton, S. Z. Andersen, K. Enemark-Rasmussen, V. Čolić, S. Yang, S. F. Bent, M. Cargnello, J. Kibsgaard, P. C. K. Vesborg, I. Chorkendorff, T. F. Jaramillo, *ACS Catal.* **2019**, *9*, 5797-5802.

[12] a) Y. Zhao, R. Shi, X. Bian, C. Zhou, Y. Zhao, S. Zhang, F. Wu, G. I. Waterhouse, L. Z. Wu, C. H. Tung, *Adv. Sci.* **2019**, *6*, 1802109; b) G. Y. Duan, Y. Ren, Y. Tang, Y. Z. Sun, Y. M. Chen, P. Y. Wan, X. J. Yang, *ChemSusChem* **2020**, *13*, 88-96.

[13] a) S. Z. Andersen, V. Colic, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg,

M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Norskov, I. Chorkendorff, *Nature* **2019**, *570*, 504-508; b) G. F. Chen, S. Ren, L. Zhang, H. Cheng, Y. Luo, K. Zhu, L. X. Ding, H. Wang, *Small Methods* **2018**, *3*, 1800337.

[14] Y. Chen, H. Liu, N. Ha, S. Licht, S. Gu, W. Li, *Nat. Catal.* **2020**, *3*, 1055-1061.

[15] B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nat. Catal.* **2019**, *2*, 290-296.

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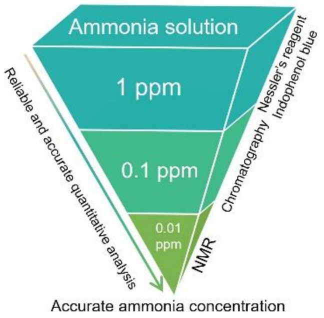

The analytical methods for the detection of ammonia concentration below 0.2 ppm in photo/electrocatalytic N_2 fixation are evaluated rigorously, reliably and insightfully. We motivate to indicate the low-concentration ammonia quantification minefield and conclude a rigorous ammonia detection flowchart as well as another reference standard to achieve a more accurate and responsible ammonia detection in photo/electrocatalysis.