Int. J. Electrochem. Sci., 11 **(2016)** 9928 – 9940, doi: 10.20964/2016.12.03

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

An All-Solid-State Ammonium Ion-Selective Electrode Based on Polyaniline as Transducer and Poly (o-phenylenediamine) as Sensitive Membrane

Yating Kan[1], *Chenhua Han*[2,*], *Ying Ye*[1], *Xiao Zhang*[1], *Yuanfeng Huang*[1], *Liang Xing*[1], *Yifan Zhou*[1], *Huawei Qin*[3]

[1] Ocean College, Zhejiang University, Zhoushan 316021, China
[2] Laboratory of Marine Ecosystem and Biogeochemistry, Second Institute of Oceanography, State Oceanic Administration, Hangzhou 310012, China
[3] School of Mechanical Engineering, Hangzhou Dianzi University, Hangzhou 310018, China
[*]E-mail: hanchenhua@sio.org.cn

Received: 21 August 2016 / *Accepted:* 29 September 2016 / *Published:* 10 November 2016

An all-solid-state ammonium ion-selective electrode, with silver/nano-silver wire as the substrate, polyaniline as transducer and poly (o-phenylenediamine) as sensitive membrane, is presented. The nano-silver was prepared by electrodeposition in 0.1 M $AgNO_3$ standard solution with the half-sine wave at amplitude of 500 mV, frequency of 50 HZ and action time of 1 min. The polyaniline and poly (o-phenylenediamine) were electropolymerized on the surface of the silver/nano-silver substrate by cyclic voltammetry with the scanning potential from 0 to 0.45 V in solutions of 1.0 M aniline hydrochloride and 0.08 M o-phenylenediamine hydrochloride, respectively. Under the SEM, poly (o-phenylenediamine) with 0.5-5 μm in size was evenly and firmly embedded on the surface of the PANI. This ammonium electrode exhibited low impedance of approximately 70 Ohm. It can detect as low as 1.2×10^{-5} M of ammonium ion, with the slopes of 54.99-55.70 mV per decade ($R^2>0.99$) within a linear range between 2×10^{-5} M to 0.1 M. It responds as quickly as 0.5-2 s, as well as its lifespan extends to at least 147 days. The electrode showed a superior selectivity toward NH_4^+, and was successfully applied to detect the NH_4^+ concentration in real samples. In addition, this electrode is miniature and convenient for package and assembly, which will enable *in-situ* measurement and long-term monitoring of NH_4^+ concentration in rivers, lakes and industrial sewage.

Keywords: All-solid-state ammonium electrode; Low impedance; In-situ detection and longtime monitoring; Poly (o-phenylenediamine); Polyaniline

1. INTRODUCTION

Ammonium ion is one of the important elements in the biogeochemical cycle of nitrogen. It's generated by heterotrophic bacteria as the primary nitrogenous end product of decomposition of N-organic compounds [1], which are photosynthetically assimilated, stored, transformed [2]. The concentration of ammonium ion ($[NH_4^+]$) is one crucial index to evaluate the water quality. High $[NH_4^+]$ in water will cause eutrophication [3], and result in water bloom [4] and red tide [5] releasing the toxin and killing aquatic biota [6], and even causing cell death in the central nervous system of human body [7, 8]. Therefore, it is essential to quickly and accurately determine $[NH_4^+]$ in waters, such as rivers, lakes and industrial sewage, etc. Traditional methods to measure $[NH_4^+]$ are Nessler's reagent colorimetry [9, 10], titration method [11], ion chromatography [12] and nuclear magnetic resonance [13]. Nessler's reagent colorimetry is the most frequently used method. However, its result will be interfered by the nonferrous ions and the turbidity in the tested solution. In addition, the process of preparing Nessler's reagent is complex, as well as it always produces by-products which pollute the environment. The titration method uses discoloration of end point to determine $[NH_4^+]$, which is insensitive and makes significant errors. The procedures of nuclear magnetic resonance are too cumbersome and complicated to operate. Although ion chromatography is a simple method using non-toxic and pollution-free reagents and can rapidly measure $[NH_4^+]$, its detection limit is low. In recent years, ammonium ion-selective electrodes (ISEs) are applied to determine $[NH_4^+]$ directly and rapidly [14], which can monitor $[NH_4^+]$ nondestructively and conveniently.

According to the different fabricating process, NH_4^+ ISEs are mainly classified into four types: glass NH_4^+ electrode [15], ammonia gas sensing electrode [16], carriers-based NH_4^+ ISE [17-18], and organic polymer-based electrode [19-20]. Among these ISEs, the organic polymer-based electrode performs better. Schloer et al [21] first employed Nonactin as the NH_4^+ ion-sensitive component to fabricate NH_4^+ ISEs. And it showed higher NH_4^+ selectivity and a wide response range by adding polar plasticizer nitrophenyl octyl ether in the sensitive membrane [22]. Huang et al [19] prepared an all-solid-state by electrochemical method. With this method, the electrode can be used in solutions with wider pH range. However, its lifespan is not long enough to sustain the long-term online monitoring.

Recently, conducting polymers (CPs) have been found increasing influence on the fabrication of nano-devices [23] and chemical sensors [24] due to their favorable conductive property [25]. Among them, poly (o-phenylenediamine) (POPD) earned more focus due to its well conductive performances [26]. POPD was widely used for the construction of electrochemical biosensors, such as hydrogen peroxide sensor [27], reducing sugar [28], non-enzymatic glucose [29] and benzophenone [30] and permselectivity for the dissolved species [31].

In this study, a new all-solid-state NH_4^+ ISE was prepared by cyclic voltammetry (CV) method with electropolymerized films of polyaniline (PANI) and POPD which were doped by HCl. This ISE composed of a silver wire successively coated with silver nanoparticles, PANI film and POPD membrane. The electrode has a good selectivity and can be carried out *in-situ* monitoring. Its lifespan can be 5 months, which greatly improve the NH_4^+ ISE's lifespan. Moreover, this prepared sensor was applied for the analysis of the NH_4^+ ion in real samples.

2. EXPERIMENTAL

2.1 Materials and apparatus

O-phenylenediamine, aniline hydrochloride, rubidium chloride, calcium chloride dihydrate, aniline hydrochloride, 0.1 M $AgNO_3$ standard solution, 1.0 M HCl standard solution and magnesium chloride dihydrate were purchased from Aladdin. Silver wire (99.9%, 0.6 mm in diameter) was obtained from the Precious Materials Company of Changzhou, China. Sodium chloride, ammonium chloride, potassium chloride, copper (Ⅱ) chloride dihydrate, iron (Ⅲ) chloride hexahydrate, aluminum chloride hexahydrate, lithium chloride, cesium chloride, strontium chloride, nickel chloride hexahydrate and barium chloride dihydrate were purchased from Sinopharm Chemical Reagent Company, Shanghai, China. All reagents were analytical and used without further purification.

Ultrasonic cleaning KQ218 (Shumei Company, China) was used to clean electrode substrate and accelerate dissolving process. Electrodeposition of the nano-Ag was conducted by SG1020A function generator (Ruite Company, China) with MBR1045 Schottky diode. All electrochemical studies were made by CHI760D electrochemical workstation (Chenhua Company, China). Commercial Ag/AgCl electrode (3 M KCl; Zhenghao Electronic Technology Company, China) was utilized as reference electrode and platinum electrode (Leici Instrument Company, China) as auxiliary electrode. Morphology of electrode were obtained by SU70 (Hitachi, Japan) field-emission scanning electron microscope (SEM). Continuous flow analyzer Scan^{++} system (Skalar, Nertherlands) was used to determine the [NH_4^+] value in real samples for comparison.

2.2 Fabrication of ammonium electrode

50 mm of silver wire, as the electrode substrate, was polished using 0.05 mm-alumina powder, and washed ultrasonically with diluted HCl and deionized water, respectively. After this pretreatment, the silver nanoparticles were electroplated on the prepared Ag substrate with half-sine wave at a frequency of 50 HZ and amplitude of 500 mV for 1 min, in which the Ag wire was used as cathode electrode as well as 0.1 M $AgNO_3$ standard solution acted as electrolyte (Fig. 1a). And the Ag/nano-Ag substrate was prepared. Then a PANI membrane was coated on this substrate by electrochemical workstation using the CV method (Fig. 1b), in which the PANI was electropolymerized in 1.0 M aniline hydrochloride solution with a three-electrode system at room temperature to enhance the conductivity and chemical stability [32] of the electrode. In this procedure, the scanning circle and the rate were set 3 and 50mV/s, and the potential ranges from 0 to 0.45 V. Finally, a POPD membrane, which was sensitive to NH_4^+, was produced and coated by CV method scanning for 4 circles in 0.08 M o-phenylenediamine hydrochloric acid solution made up of 0.2163g o-phenylenediamine dissolved in 25 ml of 1 M hydrochloric acid with the same scanning rate and potential as those in the PANI membrane preparation (Fig. 1c). The filmed wire, i.e. fabricated electrode, was rinsed thoroughly alcohol and subsequently deionized water, and activated in 10^{-3} M NH_4Cl for six hours for use.

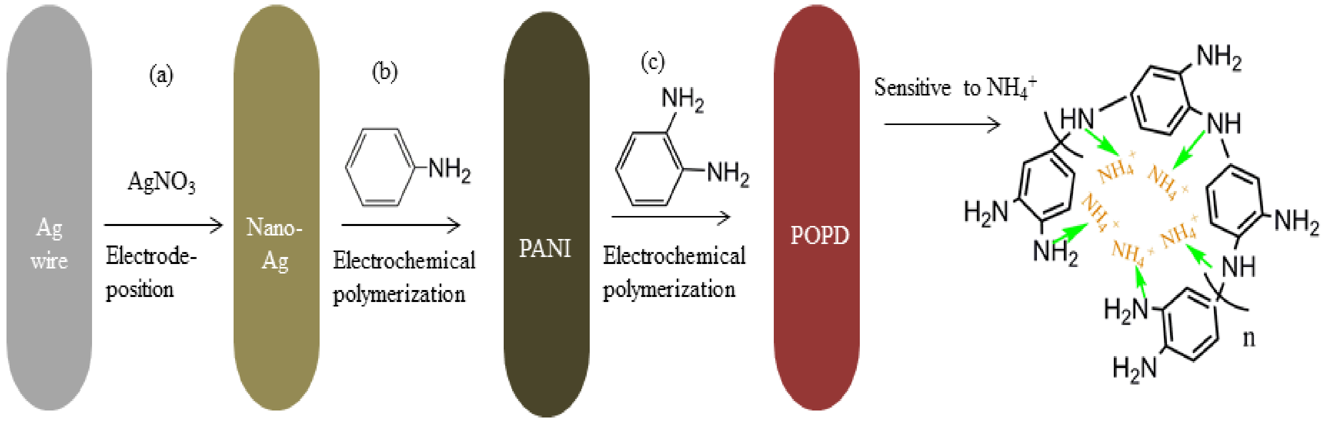

Figure 1. Fabrication processes of POPD-based NH_4^+ selective electrode.

2.3 Characterizations and performances of electrode

Microscopic morphology, structure and distribution of different layers (nano-silver, PANI and POPD) of this NH_4^+ ISE were characterized with SEM, respectively. And the electrochemical impedance spectroscopy (EIS) experiments were carried out between 0.01 and 10^5 Hz at the amplitude of 10 mV with the potential of 0.35 V in 0.1 M NH_4Cl solution (25℃) to measure the electron-transfer resistance [33]. The performance of this NH_4^+ ISE, such as stability, detection limit, repeatability, and life span, were evaluated by recording potentials in varied concentrations of NH_4Cl solutions which were 0.1 M standard NH_4Cl solution and 10^{-2}-10^{-9} M diluents obtained by stepwise dilution method with ammonium-free water, and each potential reading was taken at room temperature for 300 s.

In addition, the selectivity of this ISE was performed by fixed interference method (FIM) [34] and its coefficients were calculated on the basis of the following equation:

$$\log K^{pot}_{NH_4^+,J} = \alpha_{DL}/(\alpha_J)^{1/z} \qquad (1)$$

where α_{DL} is the lower detection limit of $[NH_4^+]$ when interfering ions existed, α_J the concentration of the interfering ion, and z the charge of the interfering ion. Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+},Cu^{2+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Na^+ and K^+ were used to investigate the selectivity and the concentration of interfering ions was all fixed at 10^{-2} M.

2.4 Application

The tap water, sampled from the Zhoushan campus of Zhejiang University, with standard addition of ammonium ion was used in this study to examine and verify the reliability of the proposed electrode in practical applications. In this procedure, three different samples were prepared at a standard addition of 0.1 M, 1.6×10^{-3} M and 4×10^{-4} M, respectively. $[NH_4^+]$ values were measured by the proposed NH_4^+ ISE, and each sample was tested repetitively for 5 times.

3. RESULTS AND DISCUSSION

3.1 Electro-polymerization of POPD and its effect

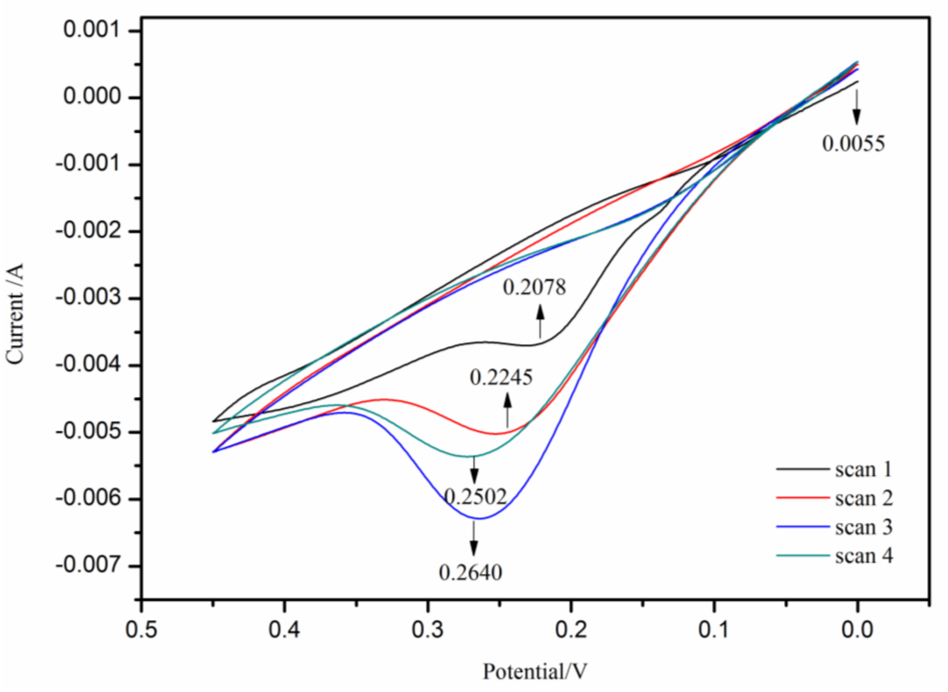

Figure 2. Cyclic voltammogram of o-phenylenediamine setting at 4 circles with a scan rate of 50 mV/s and potential range from 0 to 0.45 V in 0.08 M o-phenylenediamine hydrochloric acid solution.

POPD is one of the PANI derivatives and possess a good conductivity [35] as well as NH_4^+ selectivity. And the -NH and $-NH_2$ groups of POPD can be sensitive to NH_4^+ [36] (Fig. 1), and develop a stable response to NH_4^+ in the ammonium-bearing solution. The CV curves of o-phenylenediamine electrochemical polymerization were shown in Fig. 2. Weak oxidation of o-phenylenediamine was initially observed at the potential of 5.5 mV in the initial scan, and the main oxidation occurred at 0.2078 V, 0.2245 V, 0.2640 V and 0.2502 V, respectively. With the scanning circles increasing, oxidation peak increased and were in the similar pattern but each slope bigger, implying that POPD membrane continuously synthesized and deposited on the surface of the electrode.

3.2 SEM characterization

Silver nanoparticles, PANI and POPD membranes coated on the silver substrate surface were characterized by the SEM and the image was presented in Fig. 3. Nano-Ag is uniformly distributed on the surface of silver wire (Fig. 3A). The PANI sheets cover completely on the surface of nano-Ag and its structure is dense and uniform (Fig. 3B-C), which possibly enables a better binding between PANI and the substrate. The POPD films, compact-structured and appeared cross-linked sheets with 0.5-5 μm-sized particles, evenly and firmly bind with PANI (Fig. 3D-F). Thus, the well binding of PANI and POPD may be another reason for the good stability and long lifespan of the electrode.

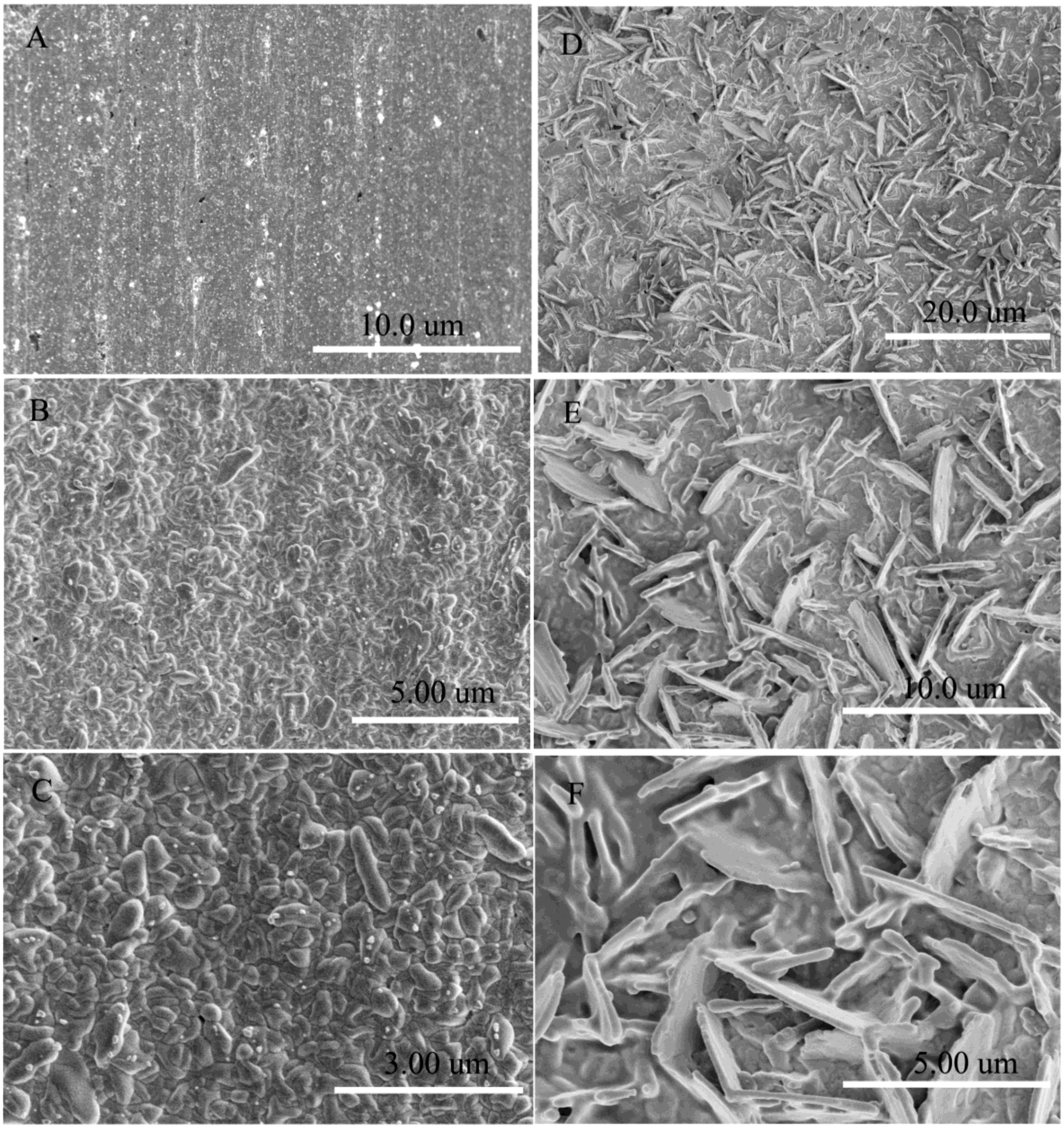

Figure 3. SEM images of different layers: nano-silver (A), PANI (B, C) and POPD (D, E and F) at 3.0 kV.

3.3 EIS studies

EIS was an effective technique to investigate the electron transfer properties of the modified surfaces and it is often used for understanding electrochemical transformations [37]. A well-defined semicircle curve and Warburg diffusion were observed in four electrodes (Ag/nano-Ag/PANI/POPD, Ag/nano-Ag/POPD, Ag/PANI/POPD and Ag/POPD electrodes) in Fig. 4. And a large semicircle diameter, corresponding to the electron transfer limit process, was obtained as a high electron transfer resistance (400 ohm) in the Ag/POPD electrode compared to the Ag/nano-Ag/PANI/POPD (70 Ohm), the Ag/PANI/POPD electrode (100 Ohm) and the Ag/nano-Ag/POPD electrode (200 Ohm). The low electron transfer resistance (70 Ohm) of Ag/nano-Ag/PANI/POPD electrode indicated that Ag/nano-

Ag/PANI/POPD-based NH_4^+ ISE possess high electron transfer ability and low resistance property, which was ascribed to the good conductivity of the silver nanoparticles and PANI film.

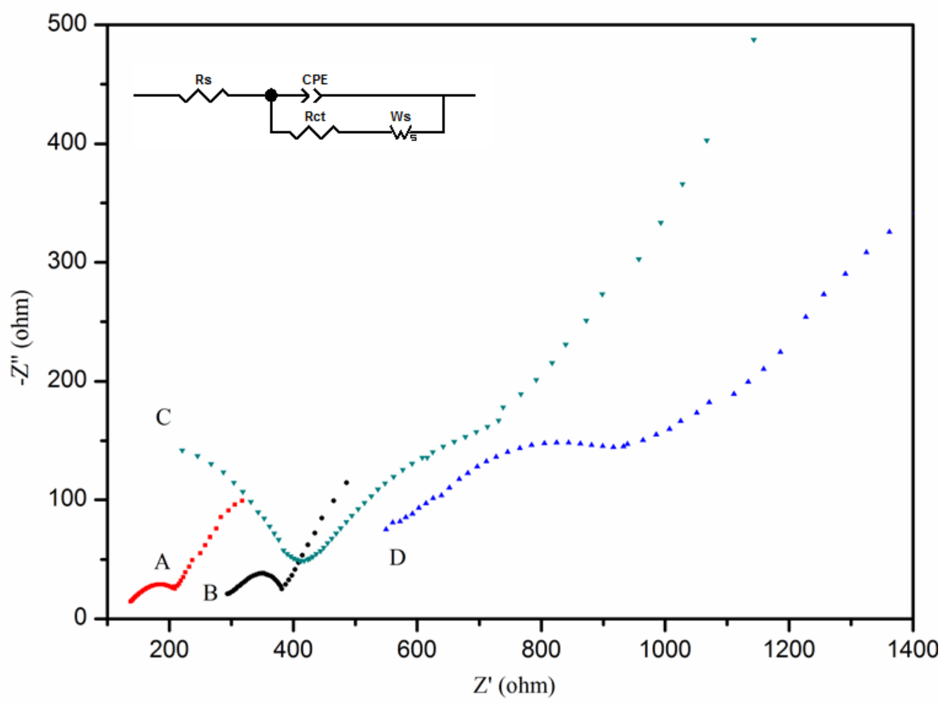

Figure 4. EIS of (A) Ag/nano-Ag/PANI/POPD; (B) Ag/ PANI/POPD; (C) Ag/nano-Ag/ POPD; (D) Ag/ POPD in 0.1 M NH_4Cl at potential of 0.35 V, frequency range of 0.01-10^5 Hz and amplitude of 10 mV.

3.4 Analytical performance of proposed electrode

3.4.1 Linear range and detection limit

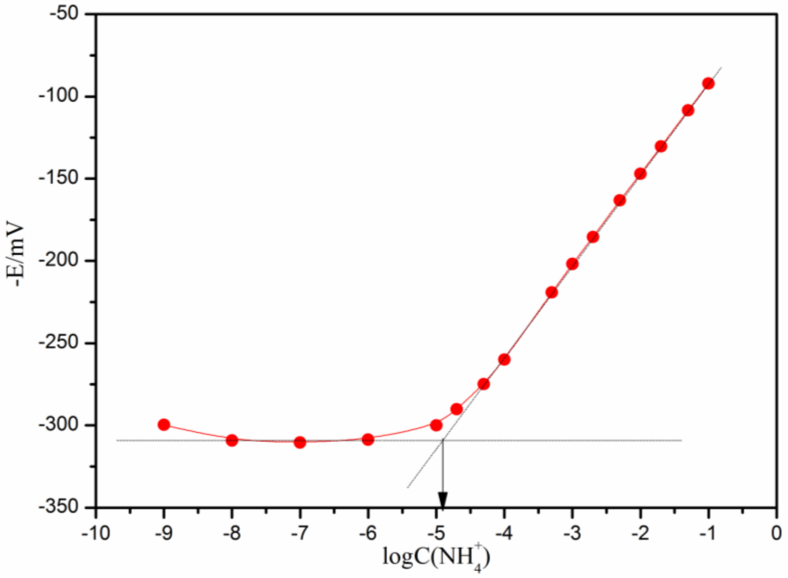

Figure 5. Performance curves of the NH_4^+ electrode in 10^{-9}-10^{-1} M NH_4Cl solutions.

The detection limit of the electrode was defined as the intersection of the extrapolated linear regions of the calibration graph [18]. Fig. 5 showed the calibration graph of Ag/nano-Ag/PANI/POPD-based NH_4^+ ISE in the concentration range of 10^{-9}-10^{-1} M NH_4Cl. It demonstrated that the linear range is 2.0×10^{-5} -1.0×10^{-1} M and the detection limit is 1.2×10^{-5} M.

3.4.2 Effect of PANI

To compare the effect of PANI, we fabricated two electrodes with (A) or without (B) PANI layer following the same procedures and the calibration curves were shown in Fig. 6. In Fig. 6A, the slopes of NH_4^+ electrodes were 54.99-55.70 mV per decade, which are close to the theoretical value of 59.16 mV per decade [38], and R^2 values of higher than 0.99, which means their coefficients is high. However, in Fig. 6B, the slopes were only between 49.24 mV per decade and 50.73 mV per decade, less than those in Fig. 6A. This result indicated that PANI as transducer strengthened response of POPD sensitive membrane toward NH_4^+.

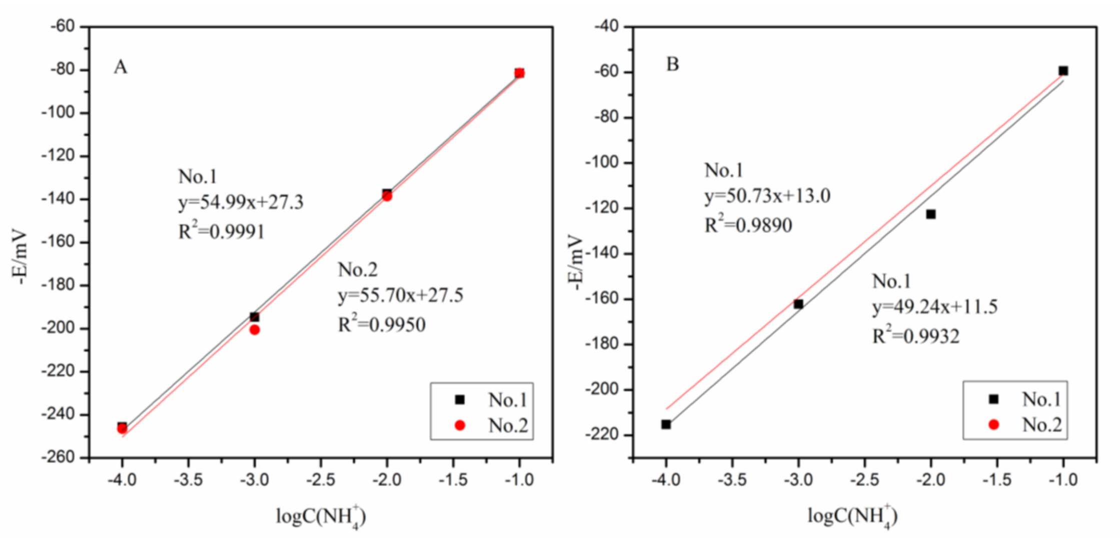

Figure 6. Calibration curves of electrodes with PANI (A) and without PANI (B) in 10^{-4}-10^{-1} M NH_4Cl solutions.

3.4.3 Potentiometric stability, response time and repeatability

The same electrode was measured in 10^{-4} -10^{-1} M NH_4Cl solutions alternatively on the 1st, 68th and 147th day (Fig. 7), respectively. Remarkably, the result showed the potential values on the 1st day were -241.3 mV, -199.7 mV, -140.4 mV, -82.33 mV in 10^{-4} to 10^{-1} M NH_4Cl, respectively, which were basically consistent with the data on the 147th day (-243.8 mV, -195.5 mV, -140.9 mV, -86.75 mV). This inaccuracy of the potential values might result from the experimental error of the calibration solutions which were obtained by step-wise dilution method.

The response time is calculated as the time which elapses between the instant at which the ISE and the Ag/AgCl reference electrode immerse in a sample solution and the first instant at which the E/time becomes steady [39]. This NH_4^+ electrode responses as fast as 0.5-2 s, while the previous ISEs needed a few seconds [39] or even a few minutes to obtain stable signals [40]. Meanwhile, the response time of non-PANI electrodes is longer than that of PANI-coated electrodes.

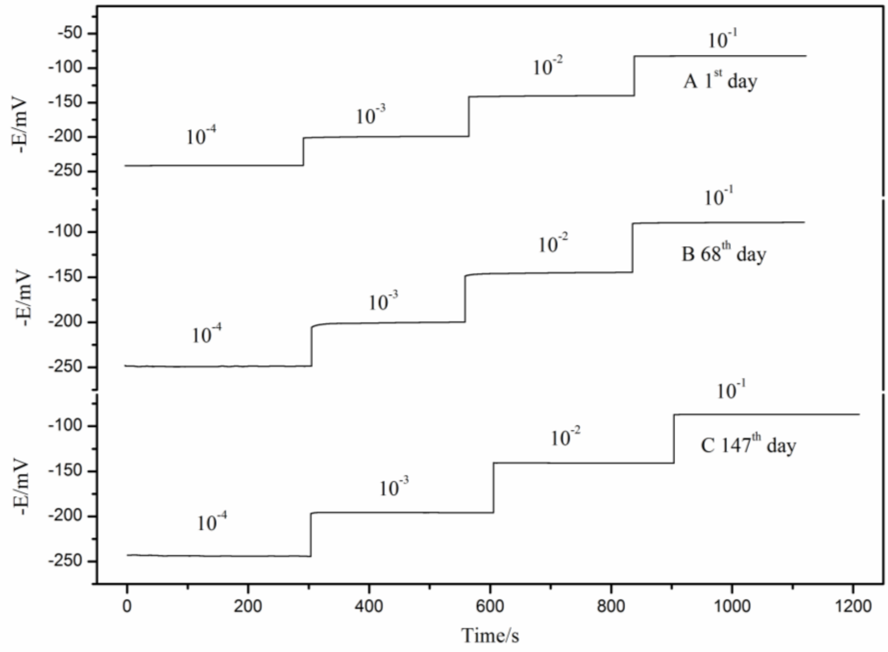

Figure 7. Response curves of the NH_4^+ ISE in 10^{-4} M to 10^{-1} M NH_4Cl solutions on the 1st day (A), 68th day (B) and 147th day (C).

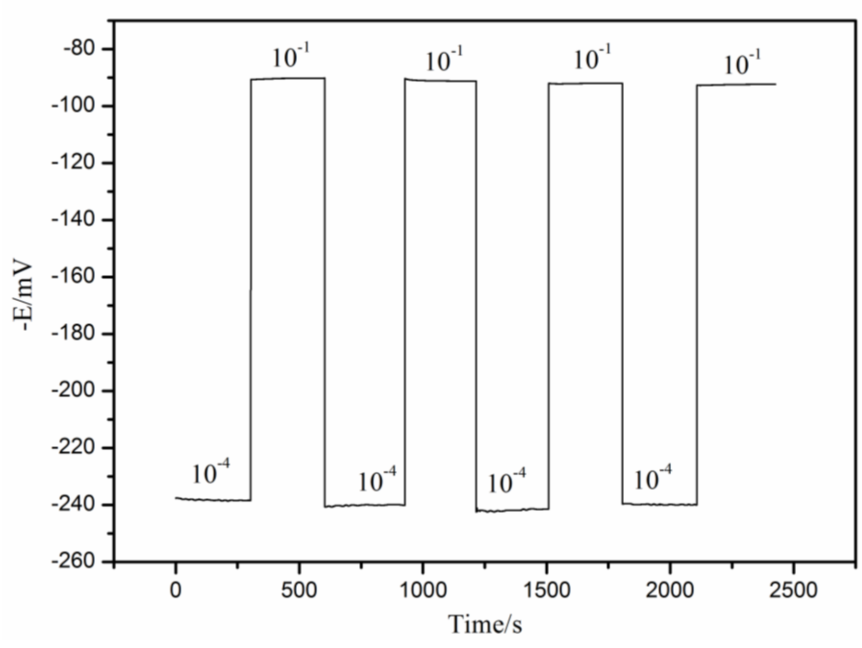

Figure 8. Repeatability performed by the same NH_4^+ electrode in 10^{-1} and 10^{-4} M NH_4Cl solutions.

In order to evaluate its repeatability, the NH_4^+ electrode was placed in the NH_4Cl solutions of high (10^{-1} mol/L) and low (10^{-4} mol/L) concentrations repeatedly for 4 times. And this NH_4^+ electrode performed excellent repeatable performance (Fig. 8), and the potential values were -90.16 mV, -91.22 mV, -91.97 mV, -92.34 mV in 10^{-1} M NH_4Cl solution as well as they were -238.4 mV, -240.1 mV, -241.4 mV, -240.0 mV in 10^{-4} M NH_4Cl solution.

3.4.4 Potentiometric lifespan

For testing the long-term stability, two NH_4^+ electrodes marked No.1 and No.2, respectively, were bathed in 10^{-3} M NH_4Cl solution at room temperature for 147 days. Table 1 exhibited the slopes and correlation coefficients (R^2) of the calibration curves, while Table 2 showed the lifespan comparison between this NH_4^+ electrode and others. During this stability test, these two electrodes performed reasonably stable and no obvious signal drift was observed.

Table 1. Slopes and correlation coefficients of the two ISEs continuously calibrated in 147 days.

Days	No.1		No.2	
	Slope	R^2	Slope	R^2
1	54.99	0.9991	55.70	0.9950
3	53.59	0.9919	55.41	0.9966
4	54.92	0.9969	53.98	0.9938
7	52.48	0.9951	52.19	0.9965
14	51.19	0.9951	51.90	0.9913
21	53.10	0.9951	52.70	0.9989
27	51.81	0.9970	52.54	0.9972
41	51.42	0.9958	53.47	0.9962
49	52.02	0.9982	51.75	0.9968
60	51.13	0.9973	50.72	0.9912
68	51.56	0.9957	53.31	0.9986
94	52.51	0.9957	53.47	0.9990
106	52.76	0.9989	52.98	0.9988
119	52.62	0.9998	52.01	0.9999
132	52.97	0.9997	55.32	0.9995
147	53.05	0.9941	52.75	0.9948

Table 2. Lifetime of ammonium ISE for comparison.

Ammonium ISE	Lifespan
Khadro, et al, 2009 [40]	12 weeks
Chandra, et al, 2006 [39]	45 days
Huang, et al, 2015 [19]	84 days
proposed electrode	147 days

3.4.5 Potentiometric selectivity

The potentiometric selectivity of this NH_4^+ electrode, responding to the target analyte ion in the presence of other ions, is always far from being ideal [41]. We fixed the concentration of the interfering ions (Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Na^+ and K^+) to 10^{-2} M to measure the selectivity coefficients $\log K_{NH_4^+,J}^{pot}$.

The calculated potentiometric selectivity coefficients are summarized in Table 3 and the selectivity factors $\log K_{I,J}^{pot} < 0$ indicates a preference for measuring ion I relative to the interfering ion J in theory [42]. All the $\log K_{NH_4^+,J}^{pot}$ values are less than -0.9 indicating the POPD-membraned NH_4^+ electrode exhibits a high selectivity of NH_4^+ in the appearance of the interfering species.

Table 3. Selectivity coefficients measured for NH_4^+ by fixed interference method (fixed at 10^{-2} M).

Interfering ions(j)	Selectivity coefficients $\log K_{NH_4^+,J}^{pot}$
Fe^{3+}	-2.179
Al^{3+}	-2.201
Mg^{2+}	-1.900
Ca^{2+}	-1.834
Cu^{2+}	-1.909
Sr^{2+}	-1.857
Ni^{2+}	-1.907
Ba^{2+}	-1.877
Na^+	-0.9449
K^+	-0.9461

3.5 Application

Each tap water sample was examined with the proposed electrode for 5 times and the determination results (average of five times) were given in Table 4. The actual [NH_4^+] values determined by continuous flow analyzer Scan^{++} system were 0.1 M, 1.6×10^{-3} M and 4×10^{-4} M, respectively, while those values were 0.09912 M, 1.527×10^{-3} M and 3.775×10^{-4} M determined by the proposed electrode. And the recovery rates of NH_4^+ range from 94–99%, indicating that this NH_4^+ electrode can be applied to measure the real samples.

Table 4. Recovery rates of NH_4^+ in local tap water.

Sample number	Real value (M)	Measured value (M)	Recovery (%)
1	0.1	0.09912	99.12
2	1.6×10^{-3}	1.527×10^{-3}	95.44
3	4×10^{-4}	3.775×10^{-4}	94.38

4. CONCLUSIONS

A novel solid state ammonium ion-selective electrode was developed by electrochemical method with Ag/nano-Ag as the substrate, PANI as the transducer providing good conductivity and POPD as the ammonium ionophore. This NH_4^+ electrode exhibits a Nernstian slope of 54.99-55.70 mV per decade in the ammonium-bearing solution ranging from 2.0×10^{-5} to 10^{-1} M and the response time was as quick as 0.5-2 s due to its low impedance of 70 Ohm. Meanwhile, this electrode has a favorable selectivity towards NH_4^+ than other interference ions, such as Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Sr^{2+}, Ni^{2+}, Ba^{2+}, Na^+ and K^+. Also, it successfully measured $[NH_4^+]$ in real samples with recovery rate of 94-99%. This NH_4^+ electrode is miniature in size with diameter of 0.6 mm and length of 50 mm, and it can be conveniently packaged and assembled with other sensors to obtain multiple signals. In addition, its lifespan is significantly expanded to 5 months, which means it could possibly be widely applied for *in-situ* measurement and long-term monitoring of ammonium ion concentration in waters, such as rivers, lakes and sewage water.

ACKNOWLEDGEMENTS
The work is supported by Development and Application of Real-time Monitoring System for Marine Environmental Buoy (529101-I21503), the Scientific Research Fund of the Second Institute of Oceanography, SOA (No.JG1521), Study on the Synchronous Observation and Comprehensive Development of the Wind Wave in Zhoushan Sea Area (529000-J31211), the project of China Ocean Mineral Resources R & D Association (No.DY125-11-R-04), the Postdoctoral Research Funds of Zhejiang Projects II (No.14010) and Wetland Ecological Restoration Project in the South Bank of Hangzhou Bay (529002-L91203).

References

1. R. Athavale, I. Kokorite, C. Dinkel, E. Bakker, B. Wehrli, Gastón A. Crespo, and A. Brand, *Anal. Chem.*, 87 (2015) 11990.
2. R. G. Wetzel, The Nitrogen Cycle. In Limnology, San Diego, (2001) CA, USA.
3. D. C. Gooddy, D. J. Lapworth, S. A. Bennett, T. H. E. Heaton, P. J. Williams and B. W. J. Surridge, *Water Res.*, 88 (2016) 623.
4. C. Wang, Z.Y. Wang, P. F. Wang and S. H. Zhang, *Environ. Model. Assess.*, 21 (2016) 247.
5. N. S. Kang, K. H. Lee, H. J. Jeong, Y. D. Yoo, K. A. Seong, E. Potvin, Y. J. Hwang and E. Y. Yoon, *Harmful Algae* 30 (c) (2013) 114.
6. S. Chen, X. Chen, Y. Peng and K. Peng, *Appl. Math. Model.*, 33 (2) (2009) 1097.
7. A. F. Gonçalves, I. Páscoa, J. V. Neves, J. Coimbra, M. M. Vijayan, P. Rodrigues and J. M. Wilson, *Dev. Comp. Immunol.*, 36 (2) (2012) 279.
8. D. J. Randall and T. K. N. Tsui, *Mar. Pollut. Bull.*, 45 (1-12) (2002) 17.
9. L. N. Demutskaya and I. E. Kalinichenko, *J. Water Chem. Techno+.*, 32 (2) (2010) 90.
10. H. Song, Z. Li, B. Du, G. Wang and Y. Ding, *J. Appl. Microbiol.*, 112 (2011) 79.
11. Z. K. He, B. Fuhrmann and U. Spohn, *Anal. Chim. Acta*, 409 (2000) 83.
12. A. Szterk and L. Pakuła, *Talanta* 152 (2016) 54.
13. F. Takasaki, K. Fujiwara, Y. Nakajima, T. Nishikawa, H. Masu, C. M. Imanari, Y. Hidakac, and N. Ogawa, *Dalton Trans.*, 44 (2015) 645.

14. C. Molins Legua, S. Meseguer Lloret, Y. Moliner Martinez and P. Campı´ns-Falco, *Trac-Trend. Anal. Chem.*, 25 (3) (2006) 282.
15. G. Mattock and R. Uncles, *Analyst*, 89 (1964) 350.
16. H. Malkeshi, and H. Milani Moghaddam, *J. Polym. Res.*, 23 (2016) 108.
17. M. S. Ghauri and J. D. R. Thomas, *Analyst*, 119 (11) (1994) 2323.
18. T. Katsu and N. Nishimura, *Anal. Sci.*, 16 (5) (2000) 523.
19. Y. Huang, J. Li, T. Yin, J. Jia, Q. Ding, H. Zheng, C.-T. Arthur Chen and Y. Ye, *J. Electroanal. Chem.*, 741 (2015) 87.
20. K. Suzuki, D. Siswanta, T. Otsuka, T. Amano, T. Ikeda, H. Hisamoto, R. Yoshihara and S. Ohba, *Anal. Chem.*, 72 (10) (2000) 2200.
21. R. P. Scholer and W. Simon, *Chimia*, 24 (1970) 372.
22. J. S. Benco, H. A. Nienaber, and W. G. McGimpsey, *Anal. Chem.*, 75 (1) (2003) 152.
23. H. Li, K. Xie, Y. Pan, M. Yao and C. Xin, *Synthetic Met.*, 159 (13) (2009) 1386.
24. E. S. Forzani, X. Li and N. Tao, *Anal. Chem.*, 79 (14) (2007) 5217.
25. P. Rameshkumar and R Ramaraj, *J. Electroanal. Chem.*, 741 (2015) 64.
26. K. OGURA, M. KOKURA, J. YANO and H. SHIIGI, *Electrochim. Acta*, 40 (17) (1995) 2707.
27. M. Shamsipur, Z. Karimi and M. A. Tabrizi, *Mater. Sci. Eng. C*, 56 (2015) 426.
28. Q. Wang, L. L. Paim, X. Zhang, S. Wang, and N. R. Stradiotto, *Electroanal.*, 26 (2014) 1612.
29. L. Liu, Y. Chen, H. Lv, G. Wang, X. Hu and C. Wang, *J. Solid State Electr.*, 19 (3) (2015) 731.
30. H. Li, H. Guan, H. Dai, Y, Tong, X, Zhao, W. Qi, S. Majeed and G. Xu, *Talanta*, 99 (2012) 811.
31. U. Olgun and M. Gülfen, *React. Funct. Polym.*, 77 (2014) 23.
32. B. Narayanasamy and S. Rajendranb, *Prog. Org. Coat.*, 67 (2010) 246.
33. V. H. Nguyen, T. H. Tran and J. J. Shim, *Mat. Sci. Eng. C-Mter.*, 44 (2014) 144.
34. F. Deyhimi, *Talanta*, 50 (5) (1999) 1129.
35. J. Stejskal, *Prog. Polym. Sci.*, 41 (2015) 1.
36. J. YANO, *J. Polym. Sci. Pol. Chem.*, 33 (1995) 2435.
37. Ç. C. Koçak, A. Altın, B. Aslışen and S. Koçak, *Int. J. Electrochem. Sci.*, 11 (2016) 233.
38. T. Lindfors and A. Ivaska, *Anal. Chim. ACTA*, 404 (1) (2000) 111.
39. S. Chandra, R. Buschbeck, and H. Lang, *Talanta*, 70(5) (2006) 1087.
40. B. Khadro, P. Namour, F. Bessueille, D. Leonard and N. Jaffrezic-Renault, *Intern. J. Environ. Anal. Chem.*, 89 (1) (2009) 1.
41. K. N. Mikhelson, Ion-selective electrode, *Springer-Verlag*, (2013) New York.
42. H. Berlin, Ion-Selective Microelectrodes Principles, Design and Application, *springer-Verlag*, (1986) New York.