AN AMMONIA OPTICAL SENSOR SILICA MIROSPHERES DOPED WITH NICKEL(II) ION AND REFLECTANCE TRANSDUCTION

A. Ulianas^{1,*}, O. Andini², Mawardi³, Ramli⁴ and T. Ling Ling⁵

^{1,2,3} Department of Chemistry, Faculty of Mathematics and Science, Universitas Negeri Padang
25131, Sumatera Barat, Indonesia

⁴ Department of Physic, Faculty of Mathematics and Science, Universitas Negeri Padang, 25131,
Sumatera Barat, Indonesia

⁵ Southeast Asia Disaster Prevention Research Initiative (SEADPRI-UKM), Institute for
Environment and Development (LESTARI), Universiti Kebangsaan Malaysia, 43600 UKM
Bangi, Selangor, Malaysia.

*E-mail: alizar_chem@yahoo.co.id

ABSTRACT

An optical sensor based on silica micromaterial doped with Ni(II) ion has been developed for quantitation of ammonia (NH₃) concentration using reflectometric transduction in an aqueous environment. The as-synthesized silica nanospheres were immobilized with Ni(II) ion via electrostatic interaction between positively charged divalent transition metal ion and negatively charged terminal silanol groups at silica microspheres surface. The optical microsensor demonstrated a colour change from green to blue upon introduced with NH₃ solution, as a result of the formation of blue-hued hexamminenickelate(II) ([Ni(NH₃)₆]²⁺) complex on the silica microspheres surface, and a maximum reflectance response was attained at the wavelength of 615 nm. The response time of the silica microspheres-based sensor is rapid towards the reflectance determination of NH₃, i.e. <1 min at optimum pH 6. The linear response range of the developed reflectometric NH₃ microsensor was acquired from 0.0003 M to 0.008 M (R²=0.9826) with a limit of detection (LOD) of 0.0012 M. The ammonia optical sensor response is good reproducibility with a relative standard deviation (RSD) obtained at 0.25% (n=7). The recovery test exhibited satisfactory results of 101.5% when the fabricated sensor was applied for the determination of NH₃ in a polluted water sample collected from landfill wastewater.

Keywords: Optical Sensor, Silica Microsphere, Reflectance, Transduction, Sensor Response

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INTRODUCTION

Ammonia (NH₃) is an important substance consisting of hydrogen and nitrogen elements that contribute significantly to the nutritional needs of earthly lives via serving as a precursor to food and fertilizers. Besides, NH₃ is a widely used source of nitrogen fertilizers, and as a building block in the production of pharmacy products, plastics, explosives, textiles, pesticides, dyes and a wide variety of chemicals. Also, much colorless ammonia is produced from agricultural practices, such as fertilizer application, animal feeding¹. However, exposure to low levels of NH₃ might affect human health especially people with asthma, whilst exposure to larger amounts of NH₃ could result in changes in various organs, decreases in lung function and effects on nerve conditions²⁻⁴.

If the ammonia concentration is higher than 25 µg/L in water it can be toxic to aquatic life^{5,6}. Furthermore, the World Health Organization shows that the odor threshold of ammonia concentration at alkaline pH is around 1.5 mg/L, while the taste threshold 35 mg/L⁷ and the norm for indoor air pollution of air for particulate matter is around 20 µg/m³⁸. Besides, The European Association for drinking water has set a maximum limit of ammonia in water is 0.5 mg/L⁹. Thus, it is necessary to monitor NH₃ concentrations in the environment, especially in the water body.

Some methods that have been reported to detect NH_3 including colorimetry, fluorometry, electrochemical analysis and titrimetric measurement. Nevertheless, these methods possess several disadvantages, such as low sensitivity, poor selectivity, complicated operating procedure or toxic organic reagents used¹⁰. And, the immobilization matrices, which have been adopted in the previous reported NH_3 optical sensor fabrications as the supporting substrates of receptors encompass fluorescent silver (Ag) nanoclusters¹⁰, chlorophenol red (CPR)-coated poly(methyl methacrylate) (PMMA) membrane¹, cholesteric film of Cu(II)-doped cellulose nanocrystals¹¹, amine-functionalized ZnO nanoflakes².

In this study, an optical reflectance sensor was developed for NH_3 detection in an aqueous environment. Silica microspheres immobilized with Ni(II) ion through ionic bonding was used to quantify NH_3 concentration with optical reflectance transduction method. Upon reaction with NH_3 in water surrounding, the green-hued Ni(II) ion-immobilized silica microspheres form blue-coloured hexamminenickelate(II) ($[\text{Ni}(\text{NH}_3)_6]^{2+}$) complex (Eqn.-1). The color change of the dye-doped microsensor in relation to the concentration of NH_3 in solution demonstrated high sensitivity, fast response time and facile assay of NH_3 concentration.

EXPERIMENTAL

Chemicals and Instruments

Ammonia (NH_3), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Merck. Tetraethyl orthosilicate (TEOS) and ethanol were supplied by Aldrich, whilst disodium hydrogen phosphate (Na_2HPO_4) was procured from Fluka. The instruments used in this study were ultra sonicator, UV-DRS Spectrophotometer (SPECORD 210 PLUS), Fourier-transform infrared spectroscopy (FTIR GX infra-red spectrophotometer, Perkin Elmer), X-Ray Diffraction (XRD-PW3040/60) and scanning electron microscopy (SEM, LEO 1450VP).

Preparation of Silica Microspheres

Silica microspheres were synthesized following the method reported before with some modifications¹². 2 mL of deionized water was mixed with 5 mL of concentrated NH_3 solution and 20 mL of ethanol. This mixture was sonicated at room temperature (25 °C) for 10 min. 2 mL of TEOS and 4 mL of ethanol were then added, and the sonication process was continued for another 30 min. The silica microparticles were isolated by centrifugation at 4000 rpm for 20 min followed by sequentially washing with abundant ethanol and deionized water, and dried in an oven at a temperature of 75 °C.

Optimization of NH_3 Sensor Optical Reflectance Response

Optimization of the silica microspheres-based NH_3 sensor was first carried out by varying the Ni(II) ion loading at 0.0005 M, 0.0010 M, 0.0030 M, 0.0050 M, 0.0100 M, 0.0300 M and 0.0500 M, whilst the concentration of NH_3 solution was fixed at 0.0100 M. The highest optical intensity of sensor response at maximum reflectance wavelength indicates optimum Ni(II) ion loading on the silica microspheres surface. The effect of pH on the NH_3 sensor response was conducted by changing the pH of 0.0100 M NH_3 solution pH from pH 5 to pH 8 with sodium phosphate buffer. The highest reflectance intensity shows the optimum pH of the NH_3 optical sensor. Response time and stability of the sensor are determined by exposing the Ni(II) ion-immobilized silica microspheres to a constant concentration of NH_3 solution at 0.0100 M, and optical reflectance response at 615 nm was taken intermittently during an experimental period of 180 min. The NH_3 optical sensor response time is indicated by the maximum plateau reflectance signal, whilst the stability of the developed sensor is estimated at the point when reflectance intensity begins to decline¹³. Calibration curve of the sensor was established with various NH_3 concentrations, i.e. 0.0003 M, 0.0005 M, 0.0008 M, 0.0010 M, 0.0030 M, 0.0050 M and 0.0080 M under sensor optimal conditions. Limit of detection (LOD) is the smallest analyte concentration that can be measured by the optical NH_3 sensor method.

Reproducibility and Recovery Studies

Reproducibility test of the transition metal-doped reflectance sensor involved batch production of seven units of NH_3 sensors under the same conditions and fabrication technique and the reflectance response of

each fabricated sensor with 0.0100 M NH_3 was recorded at 615 nm for subsequent calculation of sensor's reproducibility relative standard deviation (%RSD) percentage. The recovery performance of the NH_3 optical sensor is determined by calculating the percent recovery of NH_3 using Eqn.-2,

$$\% \text{ Recovery} = \text{Cs}/\text{C} \times 100\% \quad (2)$$

where C is the actual concentration of NH_3 being spiked into the water sample and Cs is the concentration of NH_3 determined by the developed reflectometric NH_3 sensor¹³. The developed optical sensor has been used to detect NH_3 content in wastewater collected within the landfill vicinity.

RESULTS AND DISCUSSION

Characterizations of Silica Microparticles

Figure-1 shows the FTIR and XRD spectra as well as SEM image of the as-synthesized silica microspheres. Stretching vibration of silanol functional groups, i.e. -OH from Si-OH can be perceived at 3279 cm^{-1} with the corresponding bending vibration observed at 2106 cm^{-1} (Fig.-1a) Siloxane groups can be seen with the emergence of the absorption band at 1083 cm^{-1} , indicating asymmetric stretching vibration of Si-O group in Si-O-Si, whilst the absorption peak at 797 cm^{-1} corresponds to the symmetric stretching vibration of Si-O group in Si-O-Si¹⁴. XRD spectrum in Fig.-1b reveals that the as-prepared silica microspheres formed non-crystalline solid with amorphous structure¹⁵. Scanning electron micrograph in Fig.-1c depicts the morphology of silica microparticles, whereby good spherical morphology and excellent homogeneous monodispersing¹⁶ was discernible with diameter in the micrometer range of 502 nm-614 nm.

Fig.-1: (a) FTIR and (b) XRD Spectra, and (c) SEM Image of the prepared Silica Microspheres

Optical NH₃ Sensor Response

The reflectance response of NH₃ sensor based on silica microspheres doped with nickel(II) ion is exhibited in Fig.-2. The green-hued Ni(II) ion-modified silica microspheres showed a maximum reflectance response at 615 nm. After reaction with NH₃ via a dative covalent bond, whereby the non-bonding electrons of NH₃ acted as Lewis base or electron donor, and the metal ion acted as a Lewis acid, the electron acceptor and that forming the charge-transfer complex, the hexamminenickelate(II) ([Ni(NH₃)₆]²⁺) immobilized on the silica microspheres surface, thereby resulted in a color change of the substrate from green to blue, and an enhancement in reflectance signal at 615 nm was observed. The addition of deionized water on the Ni(II)-doped silica microparticles was conducted as a controlled experiment and gave negligible optical reflectance response. Silica microparticles substrate alone demonstrated higher reflectance response compared to Ni(II) ion-immobilized silica microspheres, which was attributed to its white background color matrix that could reflect higher light intensity than dye-doped silica microspheres.

Fig.-2. Optical Reflectance Response of the Silica Microspheres-based Sensor in the Presence (a) and Absence (b) of 0.01 M NH₃

Optimizing Optical NH₃ Sensor Response in Terms of Ni(II) ion Loading and pH Effect

Figure-3a represents the effect of Ni(II) ion concentration on the microspheres sensor response towards reaction with 0.0100 M NH₃ solution. The NH₃ sensor response increased as increasing the Ni(II) ion

loading on the silica microspheres and reached an optimum reflectance response at 0.0030 M Ni(II) ion when the optical signal at 615 nm started to reach a plateau state. At this stage, the available NH_3 molecules have been entirely consumed to form immobilized $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complex¹⁷. The optimum Ni(II) ion loading at 0.0030 M was then employed in pH optimization of the NH_3 sensor.

The effect of pH on the NH_3 sensor response is illustrated in Fig.-3b. At pH below pH 6, NH_3 tends to convert to NH_4^+ ion due to the availability of excessive H^+ ions in acidic conditions, and that the formation of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complex was not favorable. In a highly basic environment, on the other hand, hydroxide (OH^-) ions are responsible for the alkalinity of a reaction medium. This resulted in the formation of nickel(II) hydroxide $[\text{Ni}(\text{OH})_2]$ precipitation in an alkaline environment. The charge effect to adsorption was reported before¹⁸. Therefore, lower reflectance response was obtained in both acidic and basic reaction media. Optimum NH_3 sensor response was attained at pH 6 ascribed to the formation of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complex was more favorable at this pH. The same pH was also reported before as the optimum pH for the $[\text{Ni}(\text{NH}_3)_6]^{2+}$ charge-transfer complex to form optimally¹⁹.

Fig.-3: The Effect of (a) Ni(II) Ion Concentration and (b) pH on the NH_3 Sensor Reflectance Response.

Response Time and Sensor Stability

The response time of the optical sensor referred to the time taken for the complexation reaction to go to completion. Based on the response time curve shown in Figure. 4, the optical sensor exhibited a fast response upon reaction with 0.0100 M NH_3 , whereby it took less than 1 min to achieve maximum reflectance intensity at 615 nm, and the reflectance sensor response was stable for up to 90 min. This implied that the formation of immobilized $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complex was rapid, and the charge-transfer complex was stable for 90 min before it was dissociated.

Dynamic Linear Range and Limit of Detection of NH_3 Optical Sensor

Dynamic linear range, i.e. the calibration curve of the optical sensor is the linear proportionality between the concentration of the analyte (NH_3) in sample²⁰ and reflectance response is presented in Fig.-5. The

fabricated reflectometric NH_3 sensor demonstrated a linear response concentration range from 0.0003 M to 0.0080 M NH_3 with a linear regression equation $y=20.997x+1.7728$, and correlation coefficient value, $R^2=0.9826$. The R^2 value approaching 1 shows that the data has a perfectly linear relationship between NH_3 concentration and reflectance response²¹. The limit of detection (LOD) that was obtained based on the lowest NH_3 concentration that can be quantified by the developed silica microspheres-based reflectance NH_3 sensor was estimated at 0.0012 M²².

Fig.-4: The Response Time Curve and Stability of the Immobilized $[\text{Ni}(\text{NH}_3)_6]^{2+}$ Complex at pH 6.

Fig.-5: The Linear Response Curve of the Optical NH_3 Sensor between 0.0003 M and 0.0080 M.

Reproducibility and Recovery Performance of Sensor

Reproducibility is the closeness of the agreement between reflectance responses of 7 similar microsensors, which were batch-produced with the same methodology and the same experimental conditions. Based on the reflectance responses obtained from the optical sensors in the presence of 0.0100 M NH_3 at 615 nm, a reproducibility RSD was calculated at 0.25%. The small RSD value implies that the fabricated optical sensors are identical with the proposed fabrication manner, and negligible variance between optical responses, and that the data points tend to be very close to each other with the same NH_3 concentration measurement.

The accuracy of an analytical method is calculated as the recovery percentage of the assay of known spiked target analyte concentration in the real sample. The ideal frame of an acceptable recovery percentage is 80.0-120.0%. In the present study, the percentage recovery of the known added amount of NH_3 in the polluted water sample by the proposed silica microspheres-based reflectance sensor was 101.5%, and this percentage recovery is fell within the ideal frame of recovery, and that the developed optical sensor is considered as an acceptable valid method for assessing NH_3 in environmental water samples.

Table-1 summarizes the analytical performance of previously reported optical sensors employing various immobilization matrices for comparison with the proposed Ni(II) ion-doped silica microspheres

reflectance sensor for NH₃ quantification. Based on this comparative analysis, it can be concluded that the proposed reflectometric optical NH₃ sensor is comparable to the other previously reported sensors concerning dynamic linear detection range and sensor detection limit.

Table-1: A Comparison of the Analytical Performance of Previously Reported Optical Sensors Employing Various Immobilization Matrices with Present Developed An Optical Sensor for NH₃ Detection.

Immobilization Matrix	Linear Range (M)	Limit of Detection (M)	References
Silica microspheres	3.0×10^{-4} - 8.0×10^{-3}	1.2×10^{-3}	This work
ZnO:Eu ²⁺ nanoparticles	3.0×10^{-4} - 4.7×10^{-3}	1.2×10^{-3}	²³
Plastic clad silica	5.9×10^{-4} - 5.9×10^{-2}	5.9×10^{-4}	²⁴
Guar gum biopolymer/silver nanoparticles nanocomposite	5.9×10^{-4} - 2.9×10^{-3}	5.9×10^{-4}	²⁵
Polyaniline/glycidyl ether of bisphenol composite film	5.4×10^{-3} - 2.7×10^{-1}	5.4×10^{-3}	²⁶

CONCLUSION

An NH₃ optical sensor based on silica microparticles doped with Ni(II) ions has been successfully developed, and carefully optimized with reflectance transduction technique. Ni(II) ions were immobilized to silica microparticles through electrostatic interaction and gave green coloration to the silica microspheres surface. Upon reaction with NH₃ molecules, the Ni(II) ion-modified silica microsphere rapidly turned to blue hue due to the formation of the immobilized charge-transfer complex. The NH₃ concentration was quantified by measuring the reflectance intensity of the sensor as the color change of the optical sensor from green to blue was proportional to the increasing NH₃ concentration. The proposed optical NH₃ sensor possessed good reproducibility and recovery performance with linear response range and limit of detection that are comparable to some other optical NH₃ sensors reported in the literature.

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