Synthesis of Optode Thin Layer using Sol Gel Hybrid of Trietoxysiloxane monomer and 3-(Trimethoxysilyl) Propilamine with Ionophore 4-(2-Pyridilazo)-1,3-Benzenadiol (PAR)

S Wahyuningsih, F Rahmawati, S Kamal, S Slamet, M Yunianto, P Rahmawati, F N Aini

1Inorganic Material Research Group, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Ir. Sutami Street No. 36 A, Surakarta, Central Java, 57125, Indonesia.

*E-mail: sayeki@mipa.uns.ac.id

Abstract. Optode (Optical sensors) is one of the modern chemical sensors in the field of analytical chemistry that has utilized of inorganic polymers. The optode based on MLCT (Metal to Ligand Charge Transfer) (or MMLL’CT, Mixing Metal-Ligand to Ligand Charge Transfer) or LMCT (Ligand to Metal Charge Transfer) phenomenons have been generated from oktyltrietxysilane, aminopropyltrimethoxysilane and 4-(2-pyrydilazo) resorcinol (abbreviated as OTES-APTS-PAR) for Cu(II), Cr(III), Ni(II), Fe(III), Cd(II), and Zn(II) ions target. The syntheses of thin layer optode were performed by sol gel method followed by evaporation in glass substrat. The formation of 4-(2-pyrydilazo) resorcinol complexes with ions target have gained strong absorption spectras in visible region because of charge transfer phenomenons. The optical sensor of OTES-APTS-PAR was analysed thermal properties using Differential Thermal Analysis (DTA). DTA thermogram showed a glass transition peaks at a temperature of 315.5 °C. Fourier transform Infrared (FTIR) spectras have showed that the optode materials consisted NH aryl groups indicated IR absorption at 1577.7 cm⁻¹ and also –CH aromatic at 1469.0 cm⁻¹. Synthesized optode materials have strong broad visible absorption with the maximum wavelengths (λmax) = 405 nm and 508.5 nm, respectively. This material have excellent optical responds to several metal ions such as Cu(II), Cr(III), Ni(II), Fe(III), Cd(II), and Zn(II) that was showed from huge Δλmax and the increase of Ktotal.

1. Introduction
Optode (optical sensor) is one of chemical sensor that brings unique properties. This optical sensor doesn’t need a comparative material, so that it becomes easier maintenance, reproducible and portable. Optode can be used without magnetic field’s interference thereby it will decrease mistaken measurement and increase its accuracy [1]. Optode technology is based on MLCT (Metal to Ligand Charge Transfer) (or MMLL’CT, Mixing Metal-Ligand to Ligand Charge Transfer) or LMCT (Ligand to Metal Charge Transfer) phenomenons. Those phenomenons have huge benefit as a recorder of gas optical sensor luminescent, PH sensor, standpoint technology, sensitizer on dye-sensitized photovoltaic cells and photocatalytic material [2].
pH optical sensor has been used based photoluminescent on europium and terbium complex [3]. Other researches have been introduced a ruthenium complex which has long excitation MLCT period and strong absorption for O₂ sensor [4] and the use of 4-desiloxo-2-(2-pyridilazo-1-naphtol) (PAN) ligand mobilized on polyvinylchloride (PVC) matrix as optode material for determining Cu(II) ion [5]. PAN is first line transition metal strong bonded ligand because charge transfer that is occurring along with building of bond produces sharp complex’s color intensity. Color changing concept resulted in maximum absorption alteration of visible light absorption is the basic of choosing optical sensor.

Some of the previous researchers argue that the use of plasticizer in optical sensor material is always necessary to produce lipophilization and prevent exfoliation and rigidity. Plasticizer can be obtained from organic compounds with long hydrocarbon chain. PVC membrane plasticizer based optical sensor has several problems such as bad adhesive property and active surface which easy to collapse. But, the problem of plasticizer can be handled with the use of long hydrocarbon chain organic compound ligand or polymer matrix which has hydrocarbon group. Bond strength between organic compound and supported material, an inorganic material can be engineered through chemical merging using ‘silylating agent’ compound.

Organic compound can be used as ionophore dyes, plasticizer or additive material (selectophore). Ionophore dyes can be used as plasticizer because of hydrocarbon chain existence. PAN is one of ionophore dye. Ionophore which can give a color when attached to ion target is chromoionophore. Chromoiononophore has big molar absorptivity (ε > 10⁵ L mol⁻¹ cm⁻¹), maximum wavelength and stolen color change. In addition, inorganic material as supported material which is usually used is silica. Porous silica has high surface area and volume ratio so that it becomes very sensitive to chemical species. tetramethoxysilane and tetraethoxysilane with their derivatives are usually used.

In this paper, thin layer material is synthesized from triethoxysilane (n-octyltriethoxysilane, OTES), 3-(trimethylsilyl)propylamine (aminopropyltrimethoxysilane, APTS) and 4-(-pyridylazo)-resorcinol (PAR) using sol-gel and chemical deposition methods. Material performances for optical sensor and metal ion target-ionophore study are also being analyzed.

2. Experimental
2.1 Materials
The materials were used for synthesis are octyltrimethoxysilane, aminopropyltrimethoxysilane, 4-(-2 pyridilazo) resorcinol (PAR), methanol, and NH₄OH. The instruments were used for analysis are UV-Vis spectrophotometer Lambda 25 (Pelkin Elmer), Fourier Transform Infra Red (FTIR) Prestige 21 (Shimatuzu), and Differential Thermal Analysis (DTA).

2.2 Preparation
Optode thin layer material was synthesized by sol gel method followed by solvent evaporation using borosilicate glass as substrat. Synthesis of another optode material with the same method also was conducted without glass substrat. The synthesis formula as shown in Table 1.

| Optode preparation formula | OTMS    | APTS    | Methanol | NH₄OH  | PAR       |
|---------------------------|---------|---------|----------|--------|-----------|
|                           | 8.1 mL  | 3 mL    | 20 mL    | 6 mL   | 10⁻⁴ M    |

Table 1. Thin-layer material synthesis conditions of OTES-APTS-PAR optode
3. Results and Discussion

3.1 Thermal Analysis of the Optode Materials

Synthesis of OTES-APTS material was done through sol-gel methods using NH₄OH as a catalyst. Polymerization process of octyltriethoxysilane and monomer of aminopropyltrimethoxysilane was built and through their branch chain results three dimension structures. DTA thermogram (Figure 1) shown excellent thermal stability of OTES-APTS polymer where there was not structural transformation until temperature of 206.32 °C. Exothermic peak at relatively huge heat released (2472.24 J) at 315.53 °C was estimated as glass transition (Tg) of the polymer. Over this temperature, polymer structure was flexible.

Figure 1. DTA Thermogram of OTES-APTS Polymer

3.2 Identification of Functional Group using FTIR spectroscopy

OTES shows Si-O-C group represented at 1188.1 cm⁻¹, while APTS shows two adjacent absorptions of Si-O-C at 1103.2 cm⁻¹ and 1088.1 cm⁻¹. Weak absorption of –NH aryl appears at 1627 cm⁻¹ and 1593 cm⁻¹. OTES-APTS polymer shows sharp absorption at 1134.1 and 1033.8 cm⁻¹ as an asymmetric stretching of Si-O-Si and Si-O-C respectively. Other functional groups such as –CH aliphatic show absorption region at 2927.7 cm⁻¹ and 2854.5 cm⁻¹. The presence of PAR in the optical sensor materials is proven by addition absorptions at 1577.7 cm⁻¹ and 1469 cm⁻¹ as –NH aryl and –CH aromatic from C=C bond respectively.

3.3 Study response optical material

The presence of PAR on OTES-APTS polymer improved λmax respond to materials and probably absorb visible light as showed at Figure 2.
The formation of complexes compound between ions of Cu(II), Cr(III), Zn(II), Cd(II), Ni(II) and Fe(III) with PAR created optical shift respond of electronic spectrums (Figure 3). PAR and metal complexes have high molar existing coefficient ($\varepsilon$) about $10^4$ L mol$^{-1}$ cm$^{-1}$. Maximum wavelength shifts occurred was based on optical responding. PAR spectrum has two peaks as a deprotonated and protonated stage. Interaction between metal ions as ions target and PAR through complexes formation mechanism. It shows that there was a maximum peak at protonated state from several complexes spectrums.

**3.4 Calculation of optical respond of maximum wavelength shift ($\Delta\lambda_{\text{max}}$)**

The interaction of optode materials with metal ions of Cd(II), Zn(II), Cr(III), Ni(II), Fe(III) and Cu(II) produced $\Delta\lambda_{\text{max}}$ as summarized in Table 2. The result obtained show that $\Delta\lambda_{\text{max}}$ which was determined from the difference of $\Delta\lambda_{\text{max}}$. $\Delta\lambda_{\text{max}}$ of PAR was increased in order : Cr(III), Ni(II), Zn(II), Fe(III), Cd(II) and Cu(II).
Table 2. Determination of maximum absorbance values and $\Delta \lambda_{\text{max}}$ after the interaction between target metal ions and optode materials at a contact time 10 seconds ($\lambda_{\text{max}}$ of optode materials = 405 nm)

| Target metal ion | $\lambda_{\text{max}}$ (nm) | $\Delta \lambda_{\text{max}}$ (nm) |
|------------------|---------------------------|-------------------------------|
| Cd(II)           | 513                       | 108                           |
| Zn(II)           | 488                       | 83                            |
| Cr(III)          | 298                       | 7.0                           |
| Ni(II)           | 480                       | 75                            |
| Fe(III)          | 508                       | 103                           |
| Cu(II)           | 520.5                     | 114.5                         |

3.5 Relatively respons of optodes with metal ions target to within Cu$^{2+}$ ion

Relatively respond of optodes with metal ions compared within Cu$^{2+}$ were valued as $A/A_{\text{Cu(II)}}$ at their $\lambda_{\text{max}}$ (Table 3).

Table 3. Relative respon value of absorbance ($A/A_{\text{Cu(II)}}$ )

| Metal ions target ($10^{-4}$ M) | $\lambda_{\text{max}}$ | Abs | $A/A_{\text{Cu(II)}}$ |
|---------------------------------|------------------------|-----|------------------------|
| Cu(II)                          | 520.5                  | 0.0169 | 1.00                     |
| Cr(III)                         | 398.0                  | 0.0427 | 2.52                     |
| Ni(II)                          | 480.0                  | 0.0101 | 0.60                     |
| Fe(III)                         | 508.5                  | 0.0126 | 0.75                     |
| Cd(II)                          | 513.5                  | 0.0236 | 1.40                     |
| Zn(II)                          | 488.0                  | 0.0210 | 1.24                     |

Relatively respond of optodes with metal ions compared within Cu$^{2+}$ gained various values. Cr(III) has the highest $A/A_{\text{Cu(II)}}$ value but only has a small $\Delta \lambda_{\text{max}}$. Nevertheless, this condition was unfavorable for optode based measurement.

3.6 Separation facor (1-\(\alpha\))

Based on the $\lambda_{\text{max}}$s of M-Optode complex can be calculated of $\alpha$:

$$\alpha = \frac{\lambda_{\text{maxM1}}}{\lambda_{\text{maxM2}}}$$

If $\lambda_{\text{maxM1}} = \lambda_{\text{maxM2}}$, $\alpha$ value = 1, but (1-\(\alpha\)) value = 0, in this situation the separation factor does not exist, it can’t be distinguished M1 and M2 analytic response.

Figure 4. The separation factor (1-\(\alpha\)) of Cr(III), Ni(II), Fe(III), Cd(II) and Zn(II) metal ions to Cu(II) metal ions (contact time 1 seconds, $\alpha = \frac{\lambda_M}{\lambda_{\text{Cu(II)}}}$)
The separation factors (1-α) of Cr (III), Ni (II), Fe (III), Cd (II) and Zn (II) metal ions are calculated on the Cu (II) metal ion increased in the order of Cd (II), Fe (III), Zn (II), Ni (II), and Cr (III) (separation factor for zero Cu ions) (Figure 4). Qualitative measurements of Cu (II) ions with optode material are interference in magnitude inversely proportional to the separation factor values. The presence of metal ions Cd(II) and Fe(III) most interferes with the qualitative measurement of Cu(II) ions by this optode.

3.6 Determination of total displacement constant (K\text{total})

\[
K_{\text{total}} = \frac{[\text{M}^{n+}]_o}{[\text{M}^{n+}]_a}
\]

\([\text{M}^{n+}]_o\) is the concentration of target metal ions in the sensor material whereas \([\text{M}^{n+}]_a\) is the concentration of target metal ions remained in the water phase. Measurement of each the metal ions is carried out with an atomic absorption spectrophotometer (AAS).

Total displacement constant value (K\text{total}) was determined by comparing target metal ion concentration on optode with target metal ion as residual in water phase that is showed at Figure 5. Measurement of Cu (II) ion has great interference with Fe(III) and Cd(II) ions.

![Figure 5. Total transfer constant (K\text{total}) of metal ions target to the optode, 10 ppm concentration of metal ions target along 10 seconds contact time](image)

4. Conclusion

Thin layer optode built from OTES-APTS-PAR was succesfully prepared by sol gel method and evaporation. Bond formation of the polymer matrix and PAR on optode materials was identified by the appearance of –NH aryl at 1577.7 cm\(^{-1}\) and –CH aromatic in 1469.0 cm\(^{-1}\), While the electronic transitions was absorb visible ligh at 404 nm and 508.5 nm. The glass transition (Tg) optode was present at a temperature of 315.5 \(^\circ\)C. The use of Cr(III), Ni(II), Zn(II), Fe(III), Cd(II) and Cu(II) by arrange as metal ion target decreases \(\Delta\lambda_{\text{max}}\), nevertheless K\text{total} increase by the following arrangement Cr(III), Ni(II), Zn(II), Fe(III) Cu(II) and Cd(II). Measurement of Cu (II) ions with this optode has great interference with Fe(III) and Cd(II) ions, respectivelly.
References
[1] Dybko A 2001 Sensors 1 29-37
[2] Whittle C Ed, Weinstein J A, George M W, Schanze K S 2001 Inorg Chem 40 4053-4062
[3] Blair S, Lowe M P, Mathieu C E, Parker D, Senanayake P K, Kataky R 2001 Inorg Chem 40 5860-5867
[4] Arvidsson J, Stean Hulth 2000 Göteborg University
[5] Amiet 2001 J. Chem 54 27-30