



## Preparation and Characterization of CdS Intercalated Montmorillonite for Potentiometric Sensor Fabrication

Kemawadee Udomphan<sup>1\*</sup>, Atchana Wongchaisuwat<sup>2</sup> and Ladda Meesuk<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science and Technology, Thepsatri Rajabhat University, Lop Buri, 15000, Thailand

<sup>2</sup>Department of Chemistry, Faculty of Science Kasetsart University, Bangkok, 10900, Thailand

\* Corresponding author. E-mail address: udomphankemawadee@gmail.com

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### Abstract

In this investigation, CdS intercalated montmorillonite (CdS-MMT) was prepared by an *in situ* solid-solid reaction between Cd-montmorillonite (Cd-MMT) and Na<sub>2</sub>S as 1:1 molar ratio. The intercalated material was characterized by using X-ray diffraction (XRD), Fourier Transform Infrared Spectrophotometry (FT-IR) and Field Emission Scanning Electron Microscopy with Energy X-ray Dispersive (FE-SEM-EDX). According to XRD and FT-IR results, the basal spacing of interlayer space was significantly increased and also the intensity of Si-O-Si vibration stretching at wavenumber 1,000 cm<sup>-1</sup> was decreased after treated by ion exchange. FE-SEM showed that clay crystal has flake like shape, resemble pillar structure. EDX quantitative data exhibited atomic (%) of Cd and S to be 7.64 and 5.23 % respectively. The ratio of sulfur and cadmium (S/Cd) was found 0.68 which closed to 1:1 molar ratio. The use of CdS-intercalated montmorillonite for electrochemical sensor is proposed.

**Keywords:** montmorillonite, intercalation compounds, potentiometric sensor, clay modified electrode

### Introduction

Bentonite is known as a clay mineral which consists of montmorillonite as main composition. Montmorillonite is a layered silicate which composed of two silica tetrahedral sheets with a central of alumina octahedral sheets. Substitution within the lattice structure of Al<sup>3+</sup> for Si<sup>4+</sup> in tetrahedral sheet and Mg<sup>2+</sup> for Al<sup>3+</sup> in octahedral sheet resulted imbalance charge in the structure of montmorillonite. The charge imbalance is compensated by exchangeable cations such as, Na<sup>+</sup>, Ca<sup>2+</sup> and/or Mg<sup>2+</sup> on the layer surface. Sodium bentonite (Wyoming bentonite) has a natural swelling ability and will maintain its swelling ability throughout its use (Manning, 1995). Cadmium sulfide (CdS) is a bright yellow crystalline solid and sparingly soluble. CdS is one of the important semiconductors and exhibits direct band gap at 2.4 eV. Due to its excellent chemical, physical and luminescence properties, CdS has been widely used in many applications such as semiconductor, light emitting diode, solar cell, photo optic devices and sensor (Ip, Wang, Quan, & Hark, 2004; Wei Guicun Li & Zhang, 2005; Li, Peng & Zhang, 2007; Dumbrava, Badea, Prodan, & Ciupina, 2010; Kochubey, Konyukhova, Zabenkov, Tatarinov, & Volkova, 2010; Sankar, Jothibas, Muthuvel, & Aran Kumar M. et al., 2020). Khaorapong et al reported that CdS in the interlayer space of montmorillonite could be prepared by solid-solid reaction between Cd(II)-montmorillonite and Na<sub>2</sub>S at room temperature. XRD, FT-IR, TG-DTA and TG-MS analyses were performed to observe the formation of CdS in the interlayer space of montmorillonite (Khaorapong, Ontam, & Okawa 2008; 2010). Na<sup>+</sup>-Cloisite (which is sodium montmorillonite) was used to fabricate modified electrodes in several methods and its properties have been studied to improve analytical characteristic for electrochemical sensor due to excellent adsorption, cationic exchange capacity and highly large specific surface area (Seleci, Ag, Evrim Yalcinkaya, Odaci Demirkol, Guler, & Timur, 2012; Loudiki et al.,

2016; Barros, Jose Leopoldo Constantino, Cristino da Cruz, Nilson, & Ferreira, 2017; Sajid, 2018; Lucena, Miyazaki, Shimizu, Constantino, & Ferreira, 2018). In our previous studied, we prepared and constructed CdS intercalated in calcium montmorillonite for potentiometric electrode to determine sulfide ion in aqueous solution. The electrode was selective to sulfide ion, showed good precision, durability and low cost (Udomphan, Wonchaisuwat, & Meesuk, 2010; 2011 and 2014). In this work, we prepared and characterized CdS-intercalated in Na<sup>+</sup>-Cloisite (sodium montmorillonite) in order to use for poentiometric sensor fabrication.

## Methods and Materials

### Materials

Clay mineral (Na<sup>+</sup>-Cloisite) was purchased from BYK-Chemie GmbH Germany Inc. Particle size was less than 25 μm which included 4–9% of moisture with density of 2.86 g/cm<sup>3</sup> and exhibited off white color. The cation exchange capacity (CEC) of Na<sup>+</sup>-Cloisite was 92.6 meq/100 g as reported before (Mallakpour & Dinari, 2012). All chemical solutions were prepared from analytical grade, cadmium chloride (CdCl<sub>2</sub>·2.5H<sub>2</sub>O, Univar), sodium sulfide (Na<sub>2</sub>S·xH<sub>2</sub>O, Panreac), silver nitrate (AgNO<sub>3</sub>, Carlo Erba) and deionized water.

### Apparatus

X-ray diffraction data were obtained from Bruker D8 with Cu anode and Ni filter diffractometer for all montmorillonite samples. Infrared spectra were performed on attenuated total reflectance (ATR-IR) by using Shimadzu GladiATR10. Field-emission scanning electron microscope (FE-SEM) FEI NOVA Nano SEM 230 was used to produce topological images of montmorillonite samples which were attached on carbon tap without conductive coating. This instrument was equipped with energy dispersive X-ray (EDAX) Apollo 10 SDD detector in order to characterize composition. Hanna 420A ion meter was used to measure potential of the solution. Silver-silver chloride (Ag/AgCl) electrode was used as a reference electrode.

### Preparation of CdS intercalated montmorillonite (CdS-MMT)

Cd-montmorillonite (Cd-MMT) was prepared from Na<sup>+</sup>-Cloisite by conventional ion exchange reaction. Na<sup>+</sup>-Cloisite was mixed with 1 M CdCl<sub>2</sub> and stirred at room temperature for 24 h. The resulting Cd-MMT was washed with deionized water for several times and tested for free Cl<sup>-</sup> ion with 5% AgNO<sub>3</sub>.



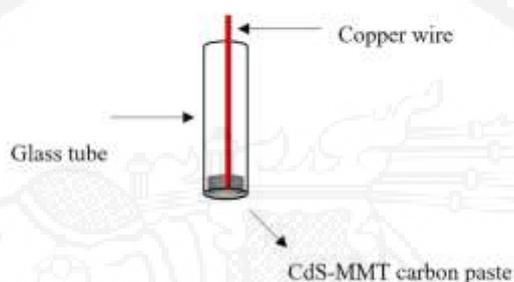
**Figure 1** Schematic diagram for preparation of CdS intercalated montmorillonite (CdS-MMT)



CdS intercalated montmorillonite was prepared from Cd-montmorillonite mixed together with  $\text{Na}_2\text{S}$  in in situ solid solid reaction by grinding about 15–20 minutes. The bright yellow solid product was washed with deionized water to remove excess  $\text{Na}_2\text{S}$ .

#### Construction of CdS–MMT carbon paste potentiometric electrode

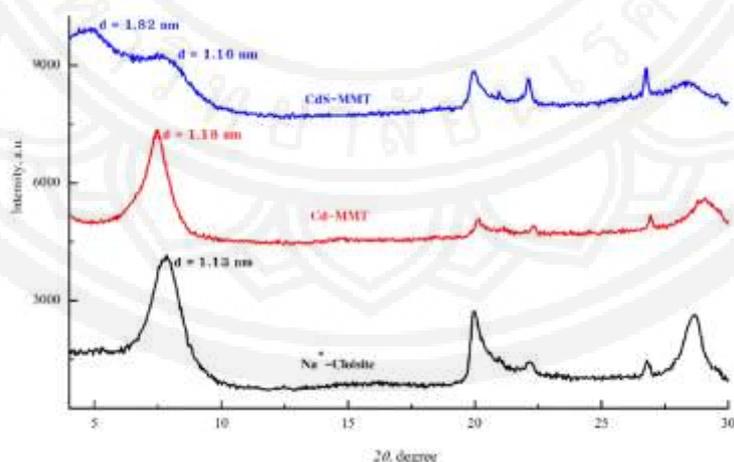
A 0.1 g. CdS–MMT was mixed with spectroscopic grade graphite in an appropriate composition and paraffin oil was added to the CdS–MMT–graphite mixture, as binder. The mixture was ground for 15 minutes in agate mortar. The CdS–MMT–graphite paste was then packed into a glass tube of diameter about 6 mm. The electrical contact was established by a copper wire. The sensor was conditioned in 0.001 M  $\text{Na}_2\text{S}$  and  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  solution for 1.30 h. before using. The potentiometric measurement was performed by using HI 2211 pH/ORP meter HANNA. The surface of the electrode can be reused by cleaning with soft paper after finishing the measurement.



**Figure 2** Schematic diagram of CdS–MMT carbon paste electrode

## Results

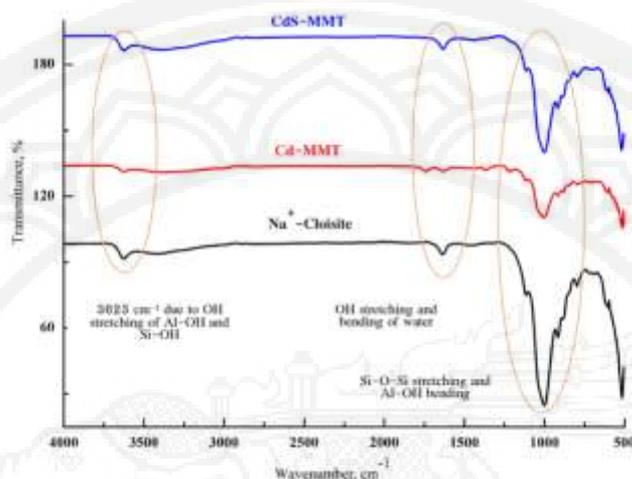
### XRD patterns



**Figure 3** XRD patterns of  $\text{Na}^+$ –Cloisite (black), Cd–MMT (red) and CdS–MMT (blue)

XRD patterns of Na<sup>+</sup>-Cloisite (black), Cd-MMT (red) and CdS-MMT (blue) are shown in Figure 3. The characteristic patterns of Na<sup>+</sup>-Cloisite, Cd-MMT and CdS-MMT exhibited the silicate reflection peak d(001) at 2 $\theta$  of 7.83 $^{\circ}$ , 7.47 $^{\circ}$  and 4.87 $^{\circ}$  which are consistent with basal spacing of 1.13 nm, 1.18 nm and 1.82 nm respectively. According to the Bragg's law the basal spacing of Na<sup>+</sup>-Cloisite was significantly increased 0.69 nm after ion exchange and in situ solid-solid reactions, indicating that CdS was completely intercalated in the interlayer space of Na<sup>+</sup>-Cloisite.

#### FT-IR spectra

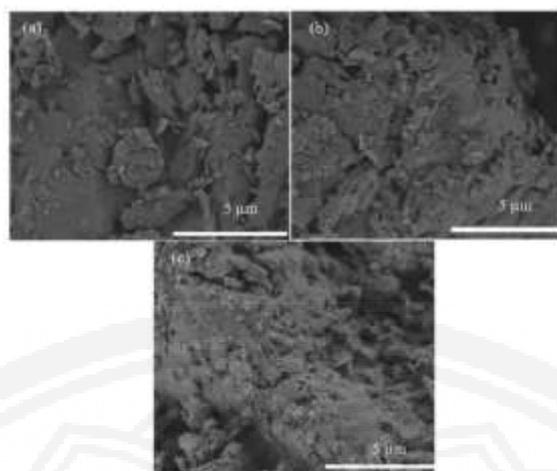


**Figure 4** FT-IR spectra of Na<sup>+</sup>-Cloisite (black), Cd-MMT (red) and CdS-MMT (blue)

Figure 4 shows IR spectra of Na<sup>+</sup>-Cloisite (black), Cd-MMT (red) and CdS-MMT (blue) respectively. The characteristic vibration peak of Na<sup>+</sup>-Cloisite is shown in Figure 4. The most intense band at 1,001 cm<sup>-1</sup> and band at 1,115 cm<sup>-1</sup> are attributed to Si-O-Si stretching vibration of the tetrahedral layer. The broad bands at 3,391 and 1,637 cm<sup>-1</sup> correspond to OH stretching and bending vibrations of adsorbed water molecules in the interlayer of montmorillonite. The band at 3,623 cm<sup>-1</sup> is assigned to OH stretching of Al-OH and Si-OH in octahedral layer and Al-OH bending vibration band is at 915 cm<sup>-1</sup> (Mallakpour & Barati, 2012). The bending vibration of Si-O-Al appears at 515 cm<sup>-1</sup>. After ion exchange and solid-solid reactions, the Si-O-Si stretching vibration peaks are slightly shifted to 1,005 cm<sup>-1</sup> and 1,000 cm<sup>-1</sup> and the intensity of peak at 1,000 cm<sup>-1</sup> is significantly changed. This could be assumed that CdS exhibited in the montmorillonite structure.

#### FE-SEM EDX analysis

FE-SEM images of Na<sup>+</sup>-Cloisite, Cd-MMT and CdS-MMT are shown in Figure 5 (a), (b) and (c) respectively, which exhibit that shape of Na<sup>+</sup>-Cloisite clay crystals are flake like and resemble pillar structure. The clay crystal shape does not change after ion exchange and solid-solid reactions.



**Figure 5** FE-SEM images of Na<sup>+</sup>-Cloisite (a), Cd-MMT (b) and CdS-MMT (c)

Energy dispersive X-ray (EDX) analysis results of Na<sup>+</sup>-Cloisite and CdS-MMT are shown in Table 1 and 2. EDX quantitative data exhibit atomic (%) of Si, Al and O atoms at 24.80%, 11.06% and 57.32 % which are the main compositions of montmorillonite and the atomic (%) of Na was found 2.91 %. After ion exchange and solid-solid reactions, the atomic (%) of Na in montmorillonite is significantly decreased from 2.91 to 0.43 % and the amount of cadmium ion is found 7.64%. In basically, the amount of cadmium ion was 46.25 mmol with respect to the CEC (92.6 meq/100g) if cadmium ion completely exchanged with sodium ion in intercalated layer of montmorillonite. After ion exchange reaction, the amount of cadmium ion is higher than sodium ion which is indicated that the exchange of sodium ion by cadmium ion was successfully completed. The atomic (%) compositions of Cd and S were found to be 7.64 and 5.23 % respectively and the ratio of sulfur and cadmium (S/Cd) was 0.68. The results indicated that CdS was presented in montmorillonite and the molar ratio of sulphur and cadmium (S/Cd) is closed to 1:1.

**Table 1** EDS quantitative result of Na<sup>+</sup>-Cloisite

Element line	Weight (%)	Atomic (%)
OK	42.62	57.32
FeL	6.41	2.47
NaK	3.11	2.91
MgK	1.64	1.45
AlK	13.86	11.06
SiK	32.37	24.80

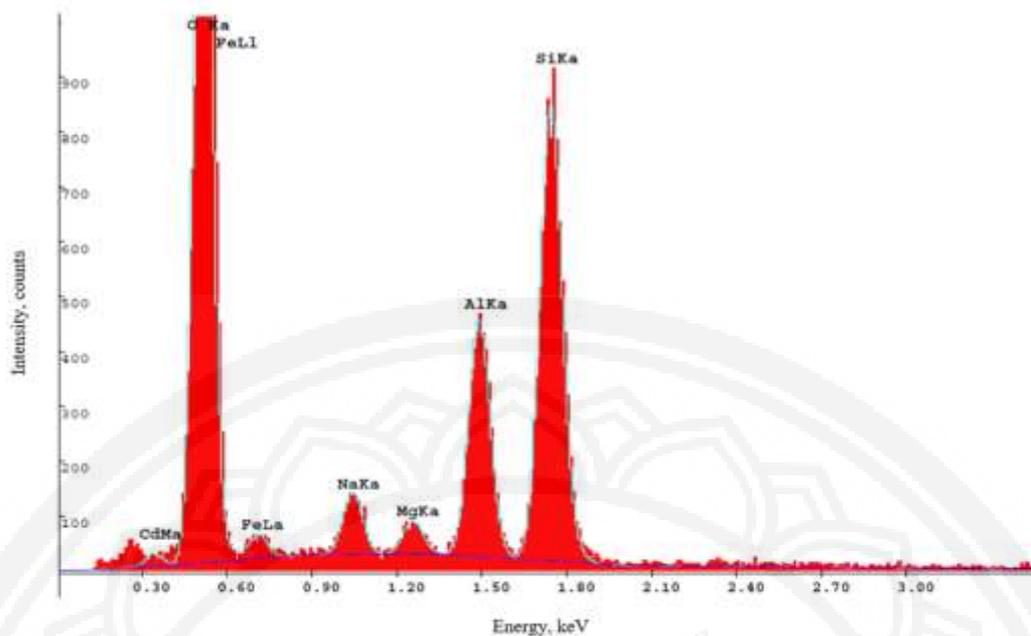
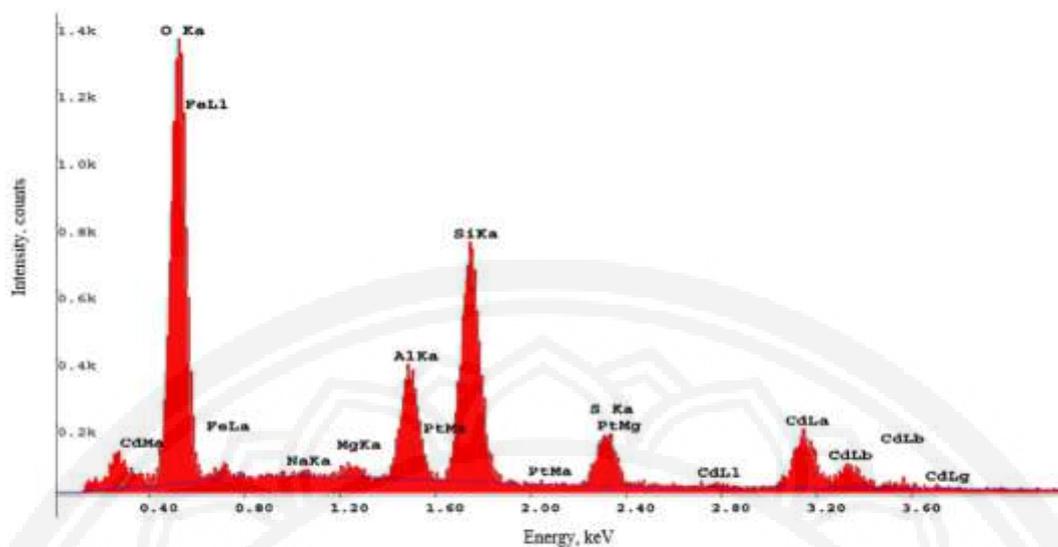


Figure 6 EDX spectrum of Na<sup>+</sup>-Cloisite

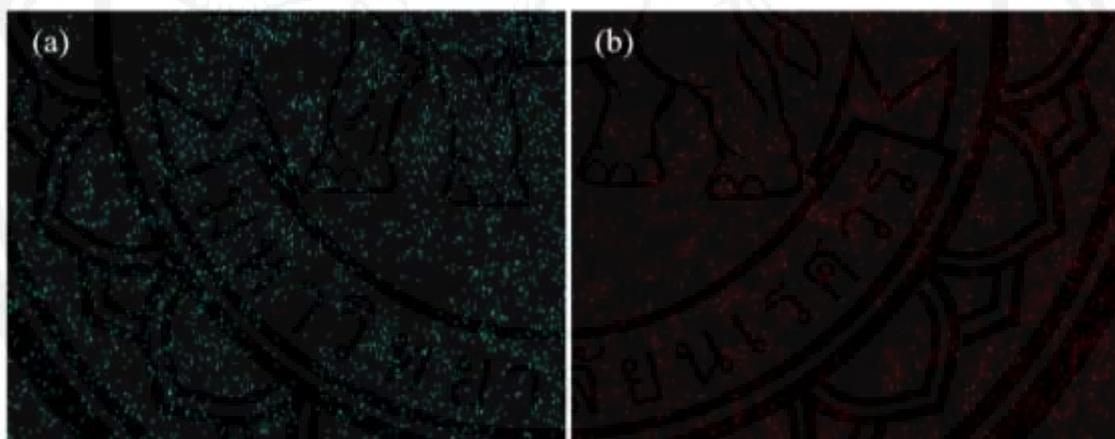
Table 2 EDS quantitative result of Cds-MMT

Element line	Weight (%)	Atomic (%)
OK	32.56	57.56
FeL	4.55	2.30
NaK	0.35	0.43
MgK	0.76	0.88
AlK	7.43	7.78
SiK	18.05	18.17
PtM	0.00	0.00
SK	5.93	5.23
CdL	30.37	7.64



**Figure 7** EDX spectrum of CdS-MMT

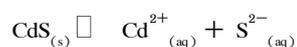
FE-SEM-EDX was also used to perform elemental mapping analysis. The results indicated that CdS exhibited the most homogeneous and uniform on  $\text{Na}^+$ -Cloisite surface as seen in Figure 8 (a) for cadmium and 8 (b) for sulfide distribution respectively.



**Figure 8** Elemental mapping of Cd (a) and S (b) on sodium montmorillonite surface

#### Applications for potentiometric sensor

In this study, we constructed a potentiometric electrode to determine cadmium and sulfide ion in solution as explained in the experimental procedure. The measurement was performed in cadmium and sulfide solutions with different concentrations. The propose of electrochemical performance of electrode could be responded both of cadmium and sulfide ions due to equilibrium of CdS in montmorillonite structure as following equation;





The potentiometric measurement results are shown in Figure 9– 14 and also comparison of slope and linear concentration range are shown in Table 3.

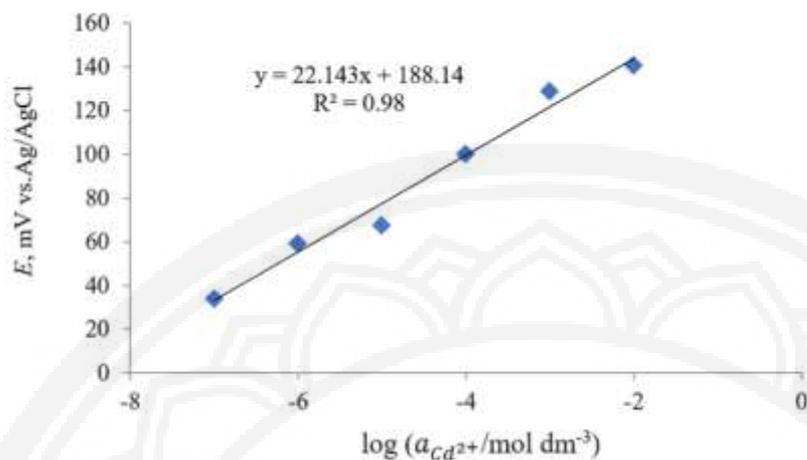


Figure 9 Plot of potential and  $\log (a_{Cd^{2+}} / \text{mol dm}^{-3})$  of electrode composition 1

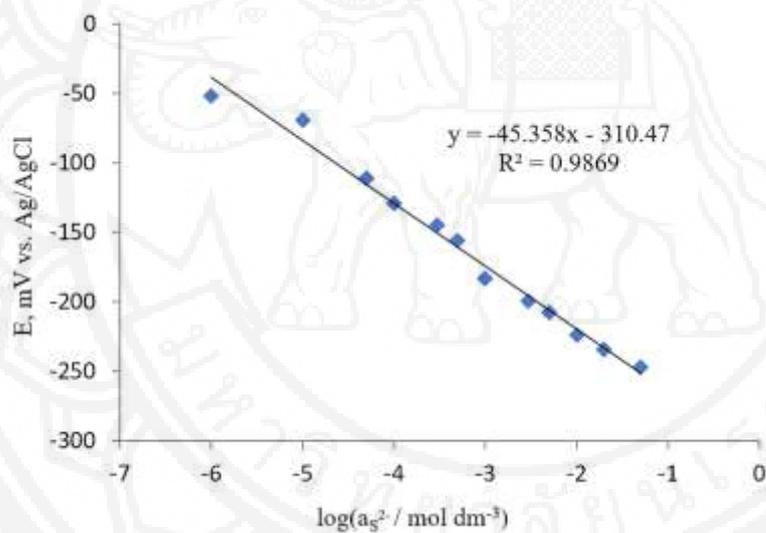


Figure 10 Plot of potential and  $\log (a_{S^{2-}} / \text{mol dm}^{-3})$  of electrode composition 1

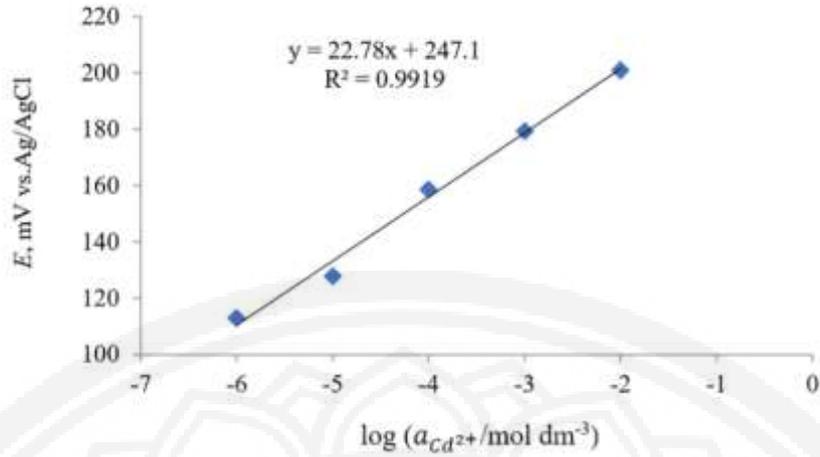


Figure 11 Plot of potential and  $\log(a_{Cd^{2+}} / \text{mol dm}^{-3})$  of electrode composition 2

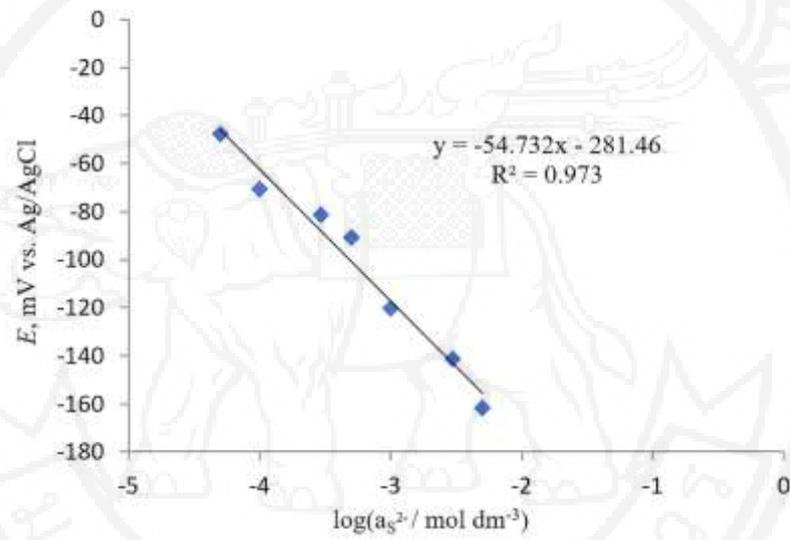


Figure 12 Plot of potential and  $\log(a_{S^{2-}} / \text{mol dm}^{-3})$  of electrode composition 2

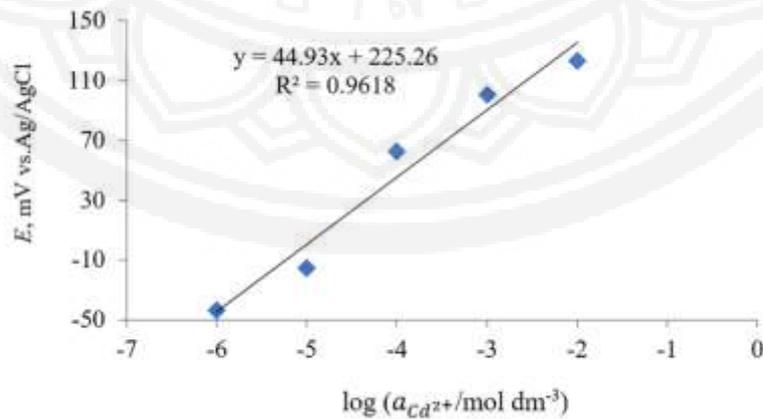


Figure 13 Plot of potential and  $\log(a_{Cd^{2+}} / \text{mol dm}^{-3})$  of electrode composition 3

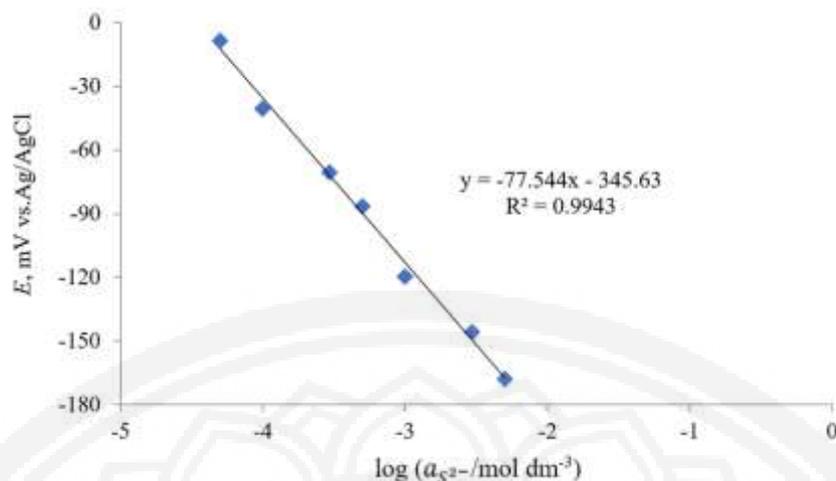


Figure 14 Plot of potential and  $\log(a_{S^{2-}} / \text{mol dm}^{-3})$  of electrode composition 3

Table 3 Slope and linear concentration range of CdS intercalated montmorillonite (CdS-MMT) electrode

Composition of materials: CdS-MMT:carbon:paraffin oil (g)	Slope			Linear concentration range ( $\text{mol L}^{-1}$ )		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
<b>Measured in cadmium ion solution</b>						
Composition 1 (0.05:0.25:0.23)	22.14	nd	nd	$10^{-7}$ – $10^{-2}$	nd	nd
Composition 2 (0.1:0.13:0.1)	15.39	22.78	nd	$10^{-7}$ – $10^{-2}$	$10^{-6}$ – $10^{-2}$	nd
Composition 3 (0.15:0.15:0.2)	44.93	nd	nd	$10^{-6}$ – $10^{-2}$	nd	nd
<b>Measured in sulfide ion solution</b>						
Composition 1 (0.05:0.25:0.23)	-51.74	-45.36	nd	$10^{-5}$ – $10^{-2}$	$10^{-6}$ – $5 \times 10^{-2}$	nd
Composition 2 (0.1:0.13:0.1)	-	-86.83	-54.73	$10^{-4}$ – $10^{-2}$	$10^{-4}$ – $10^{-2}$	$5 \times 10^{-5}$ – $5 \times 10^{-3}$
Composition 3 (0.15:0.15:0.2)	104.45 -77.54	nd	nd	$5 \times 10^{-5}$ – $5 \times 10^{-3}$	nd	nd

nd = not detected

Results exhibited that electrode composition 1 responded to cadmium and sulfide ions with slope 22.14 and -45.36, linear concentration range  $10^{-7}$ – $10^{-2}$  and  $10^{-6}$ – $10^{-2}$  M respectively. It gave better results than electrode compositions 2 and 3 due to appropriate containing of electroactive materials (CdS-MMT) and showed the most quantity of graphite which could be improved the electrochemical performance of electrode. Although the result did not give good repeatability, wide linear concentration range and slopes were far from theoretical value of 29.5 and -29.5 for cadmium and sulfide ions as from Nernst equation:  $E_{\text{cell}} = K \pm (0.059/n) \log a$ . Moreover, the intercalated material has been swelling and loose from the electrode while electrochemical measuring was performed which could be due to the properties of sodium montmorillonite. However, we could



fix this problem by using a polymer-based binder in order to prevent CdS-MMT falls off due to its swelling behavior for further studies.

Furthermore, CdS precipitate (without montmorillonite) was used to construct as potentiometric electrode with same composition of electrode composition 1 which contained amount of CdS-MMT:carbon:paraffin oil of 0.05:0.25:0.23 g in order to compare the result with CdS-MMT. Results found that the electrochemical performance of CdS precipitate potentiometric electrode not responded to cadmium and sulfide ions. The relation between potential and  $\log(a)$  did not give good linear and slope value cannot determine. This could be suggested that cation exchange property of montmorillonite enhance the selectivity and electrochemical performance of electrode when measured potential in cadmium and sulfide ions which gave the result better than CdS precipitate carbon paste electrode.

### Conclusion

CdS-intercalated montmorillonite was successfully prepared by an *in situ* solid-solid reaction with  $\text{Na}_2\text{S}$ . Characterizations of the intercalation compounds were confirmed by using XRD, FT-IR and FE-SEM-EDX. XRD patterns of CdS-MMT showed that the basal spacing of  $\text{Na}^+$ -Cloisite montmorillonite has increased from 1.13 nm to 1.82 nm after ion exchange and solid-solid reactions. FT-IR analysis exhibited the most intense band at  $1,001 \text{ cm}^{-1}$  which corresponded to Si-O-Si stretching vibration showed intensity changed when CdS presented in  $\text{Na}^+$ -Cloisite structure. FE-SEM images showed that clay crystal has flake like structure and also EDX results indicated that the atomic (%) of Na in montmorillonite was decreased from 2.91 to 0.43, the amount of cadmium ion was found 7.64% after ion exchange reaction, the molar ratio of sulfur and cadmium (S/Cd) was found 0.68 which closed to 1:1 as in the CdS formula. This could be concluded that CdS has been completely intercalated in the interlayer space of  $\text{Na}^+$ -Cloisite after ion exchange reaction and solid-solid reaction. It was found that after using CdS intercalated montmorillonite potentiometric sensor,  $\text{Na}^+$ -Cloisite was swelling and the intercalated material loose from the electrode while measuring ions in solution, which gave not good results. This might be because paraffin oil is not appropriate to use as a binder in this work. Finding of a more appropriate binding materials is needed for further studies of this sensor construction.

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