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Brief communication

Colorimetric Detection of Hg(II) Sensor Based on MoS_2 Nanosheets Acting as Peroxidase Mimics

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ABSTRACT

This paper presents colorimetric determination of Hg(II) based on MoS_2 nanosheets with peroxidase mimics activity. The structure of this sensor by the peroxidase mimic activity material of MoS_2 nanosheets with TMB (Tetramethylbenzidine) solution, the colorimetric detection target of Hg(II) is determined by on-off mechanism using biomolecule of cysteine. The MoS_2 nanosheets evaluated by X-ray diffraction, FT-IR and SEM image, confirms the formation of a flower like structure. Our results shows that a simple colorimetric detection using peroxidase mimic mechanism can be used to MoS_2 nanosheets and determine the Hg(II) in aqueous solution with high sensitivity (10 nM) comparable to those of other nanomaterials. The result suggests that MoS_2 nanosheets is a promising new and simple colorimetric sensor for applications in environmental and biological applications.

Keywords: MoS_2 nanosheets, Colorimetric sensor, Peroxidase, Hg (II) and TMB.

INTRODUCTION

Now a days heavy metals are the major pollutants in food and environment. Out of different metal ions present, mercury ion is the most toxic.[1-3] It will enter into the food chain and the ecological system which will affect the animal and human beings.[4-7] Thus, development of sensitive and simple method for detection of mercury ions is highly challengeable. Recently, researchers were developed numerous detection method for mercury ions like atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), fluorometric, colorimetric, surface plasma resonance and electrochemical methods.[8-15] For all these techniques, peroxidase mimic activity-based assay is the best tool for the detection of mercury ions due to its facile and compatibility mode of detection. Furthermore, peroxidase mimic activity-based assays were mainly fabricated on MoS_2 nanosheets having high peroxidase mimic activity with TMB molecules to improve the sensitivity.[16-19]

However, the previously reported peroxidase mimic activity assays are very low sensitivity and affect the selectivity study. Therefore, development of highly sensitive and selective to peroxidase mimic mechanism would be greatly preferred[20-26].

In this study,we have developed a novel and facile method of determination of mercury ions based on peroxidase mimic activity MoS_2 nanosheets. The MoS_2 nanosheets possess intrinsic catalytic active to TMB molecules in presence of H_2O_2 at optimized time. Peroxidase mimic activity of MoS_2 nanosheets catalyze the oxidation of TMB to formation of blue colour in presence of H_2O_2. and the addition of L-cystinetinetine molecules in the above sensing system eliminate the blue colour in the solution due to L-Cystine molecule captures the electrons. Addition of mercury ions in the solution regains the blue colour due to the complex formation on mercury ions with L-Cystine molecules. Based on the above strategy, we have developed new colorimetric sensor used detection of mercury ions.

EXPERIMENTAL

Sodium molybdate ($Na_2MoO_4.2H_2O$), thioacetamide (C_2H_5NS), mercury(II)nitrate, Lead nitrate, iron(II) chloride hexahydrate, calciumchloride, copper(II) chloride dehydrate, cobalt(II) chloride hexahydrate, nickel(II) chloride, cadmium (II) chloride hydrate, magnesium chloride, manganese(II) chloride tetra hydrate and other standard chemicals were purchased from Sisco Research Laboratories PVT. Ltd (India) and Sigma-Aldrich. The stock solution of mercury (II) was prepared by purified water and used as a further experiment.

Preparation of MoS_2 nanosheets

MoS_2 nanosheets were synthesized by hydrothermal method[27]. In this typical synthesis, 30 g of sodium molybdate was mixed with 60 g of thioacetamide and make the solution with 20 mL distilled water. The solution is magnetically stirred at ambient temperature for 60 minutes. The obtained clear solution is transferred into Teflon-lined autoclave heated for 24 h at 200°C. Finally, the MoS_2 nanosheets obtained was taken out and washed with deionsed water and dried in a hot air oven for further use.

Colorimetric detection experiments

The UV-Visible absorption spectrum was evaluated with different concentration range on mercury ions in aqueous solution. Different concentration range on mercury ions were added in the solution containing MoS_2 nanosheets (0.02 mg/mL). H_2O_2 (5mm), L-Cystine (10mm) and 7.2 pH acetate buffer (50 mM). All the mixed sample were incubated at 25°C for 15 minutes. After the incubation period UV-Visible absorption spectrum were measured at 650 nm for all the samples.

RESULTS AND DISCUSSION

Characterization

The MoS_2 nanosheets were analyzed by SEM, TEM, XRD and FT-IR. The scanning electron microscopy (SEM) studies were reported by prepared materials (Fig.1a). The MoS_2 nanosheets synthesized by hydrothermal method are self-possessed aggregated with flower-like morphology. Fig.1b is that the XRD patterns were performed to explore the samples. The characteristic peaks for MoS_2 could be located at 33.6, 35.55 and 58.55, which are associated with the 002, 100 and 110 (JCPDS No. 37-1492). Fig. 1c shows the FT-IR spectra of MoS_2 nanosheets, the peaks observed at 480 cm^{-1} and 900 cm^{-1} were the characteristic peaks attributed to the Mo-S and S-S bond. The stretching vibration of hydroxyl groups and Mo-O vibrations are present in 3431 cm^{-1} and 1650 cm^{-1}.

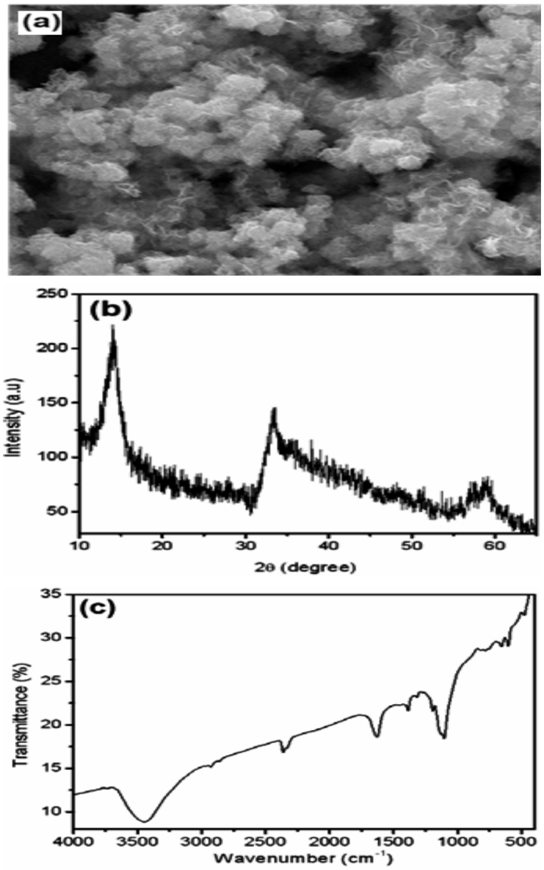
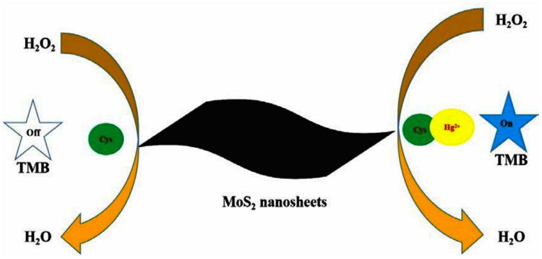


Fig.1. (a) SEM (b) XRD and (c) FT-IR spectra of MoS_2 nanosheets

Colorimetric sensing mechanism



Scheme 1. Schematic diagram of MoS_2 nanosheets based colorimetric sensor for detection of mercury

The mechanism of the proposed sensor is depicted in Scheme 1. The mechanism follows the switch off/on state of the system. When MoS_2 nanosheets was added in the TMB-H_2O_2 solution, the sensor was switched "on" with appearance of intense blue colour due to formation of TMB radical cation by oxidation of TMB by MoS_2 nanosheets. Addition of L-Cystine in the solution, switched "off" the blue colour due to strong restoration of cation radicals by the thiol functionality of Cystine. The inclusion of Hg^{2+} in the system switch on the blue colour in the solution due to the development of mercury- thiol complex.

Sensitivity and Selectivity

Sensitivity of the proposed sensing system was investigated under optimized condition with different concentration range of mercury from 5-25 nM, the change in absorbance value at UV-Visible spectra at 652 nm were plotted in the graph shown in Fig. 2a. The intensity of the absorption increases as the concentration of the mercury increases in the solution with the change in colour of from pale blue to intense blue. The reason is, as the concentration of the mercury increase, the degree of mercury-Cystine complex also increases in the solution which may leads to oxidize more TMB into its radical ions in the solution.

Figure 2b shows the graphical representation of absorbance intensity with respect to the concentrations of Hg^{2+}. The graph shown in Fig. 2c indicates the linear correlation coefficient of $R^2 = 0.990$ exist in the range of 5-25nM concentration of mercury with the limit of detection value of 5nM calculated by 3σ method. Selectivity of 5 μM mercury ions in the solution by MoS_2 nanosheets was determined along with the other metal ions such as calcium, silver, copper, zinc, nickel, cadmium, cobalt, magnesium, manganese, iron, lead of same concentration. The Fig. 2d indicates that only sample containing mercury shows maximum relative activity as compared with the samples of other metal ions. The colour of mercury solution turns into blue colour by TMB/MoS_2 nanosheets/Cystine sensing system. This is due to the stronger affinity of mercury ions with the thiol moiety of Cystine. This clearly shows that the recommended sensor is highly selective to mercury ions in aqueous solution.

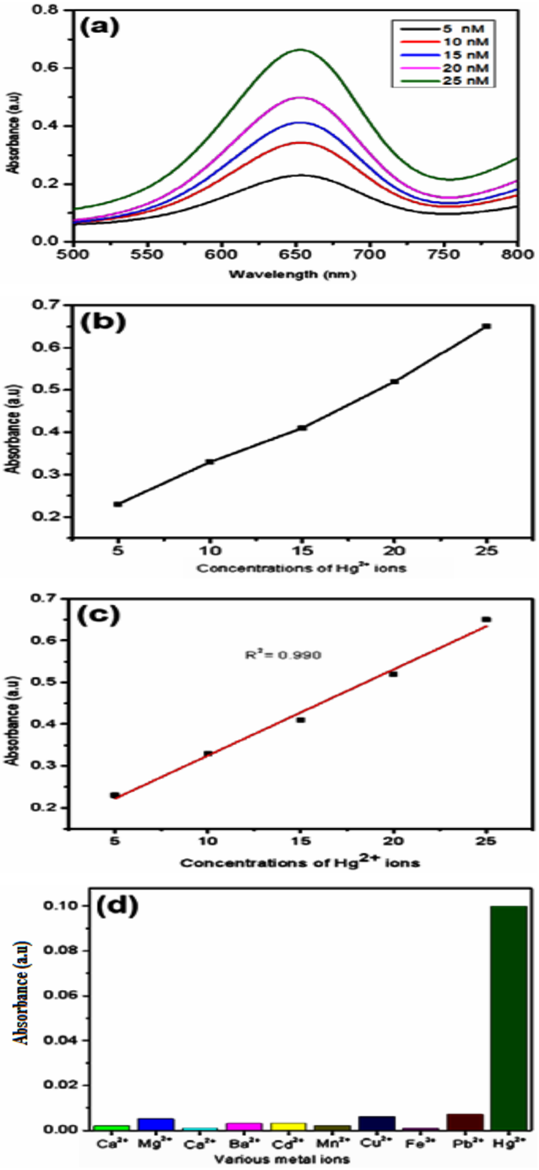


Fig. 2. (a) UV-Vis spectra of Hg (II) ions of concentration range (5-20 nM) in TMB/MoS_2nanosheets/Cys sensing system. (b) Graph of absorbance Vs concentration of Hg (II), (c) The linear calibration plot of the sensing system, (d) Selectivity of Hg (II) ion by the sensing system with respect to the counter metal ions

Detection of real water samples for mercury ions

The practical utilization of proposed colorimetric sensing system in environmental application for the investigation of mercury contamination was done. Water samples were collected from lake near MDT Hindu College, Tirunelveli. The suspended impurities were removed and pH of solution was adjusted to 3.5 and known concentration of Hg^{2+} ion was spiked followed by the addition of proposed sensor in optimized condition. Each sample were measured thrice. The obtained result were tabulated in Table 1.

Table 1: Determination real water samples for mercury ions

Sample	Spiked (mm)	Detected ± sd	Recovery (%)
Lake Water	5	4.697 ± 1.0	93.94
	10	9.755 ± 1.015	97.55
	20	19.776 ± 1.11	98.88

CONCLUSION

A novel colorimetric sensing system was designed for Hg (II) determination based on the peroxidase like activity of MoS_2 nanosheets. MoS_2 nanosheets oxidize the TMB molecule in presence of H_2O_2 and develop the intense blue colour in the solution. Introduction of Cystine quenched the blue colour whereas incorporation of Hg (II) ion reagain the blue colour in the solution. Based on this strategy highly sensitive and selective colorimetric sensor was developed for mercury with good detection limit of 5 nM and the linear relationship of $R^2 = 0.990$ were achieved. The above strategy was successfully applied for environmental samples with good results.

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Conflict of interest

The authors do not have any conflict of interest.

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