

## Evaluation of two core-shells ( $\text{Ag}_2\text{S}@-$ and $\text{Bi}_2\text{S}_3@-$ ) based on metal-organic framework ( $\text{NH}_2\text{-MIL-125-Ti}$ )/polyaniline for the electroanalysis of uric acid in urine samples.

Gullit Deffo<sup>ab\*</sup>, Cyrille Ghislain Fotsop<sup>ac\*</sup>, Marcel Cédric Deussi Ngaha<sup>ad</sup>, Sengor Gabou Fogang<sup>a</sup>, Lionel Averie Vomo<sup>a</sup>, Bibiane Wandji Nkuigoua<sup>a</sup>, Calmette Akenmo Shella<sup>a</sup>, Alex Vincent Somba<sup>a</sup>, Thierry Flavien Nde Tene<sup>a</sup>, Ida Kouam Tchummegne<sup>a,e</sup>, Evangeline Njanja<sup>a</sup>, Ignas Kenfack Tonlé<sup>a</sup>, Panchanan Puzari<sup>b</sup>, Emmanuel Ngameni<sup>f</sup>.

<sup>a</sup> *Electrochemistry and Chemistry of Materials, Department of Chemistry, Faculty of Science, University of Dschang, P.O. Box 67, Dschang, Cameroon.*

<sup>b</sup> *Department of Chemical Sciences, Tezpur University, Tezpur, Assam 784028, India.*

<sup>c</sup> *Institute of Chemistry, Faculty of Process and Systems Engineering, Universitätsplatz 2, 39106 Magdeburg, Germany.*

<sup>d</sup> *Department of Chemistry, Higher Teacher Training College, University of Bamenda, Bambili P.O.Box. 39, Cameroon.*

<sup>e</sup> *University of Yaoundé 1, Faculty of Science, Department of Chemistry, Laboratory of Analytical Chemistry, P.O. Box 812, Yaoundé, Cameroon.*

<sup>f</sup> *Center for the Environment, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India*

\* Corresponding author. E-mail address: [gullitdeffo@gmail.com](mailto:gullitdeffo@gmail.com); [fotsopcyril@yahoo.fr](mailto:fotsopcyril@yahoo.fr)

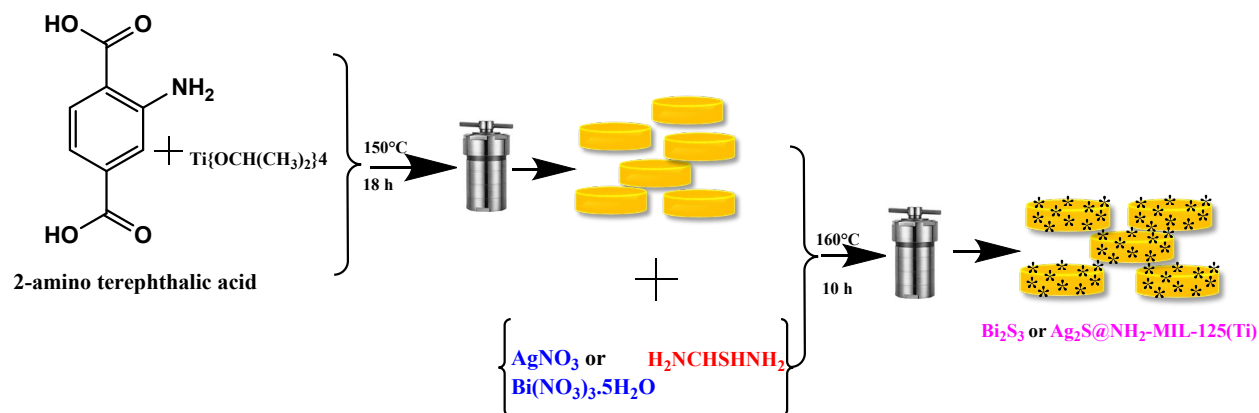
### Supporting information

#### **SI-1. Synthesis of $\text{NH}_2\text{-MIL-125(Ti)}$**

$\text{NH}_2\text{-MIL-125(Ti)}$  was synthesized by the solvothermal method as previously described<sup>43-44</sup> with modifications. Briefly a solution of 4 mmol of titanium isopropoxide and 8 mmol of 2-amino terephthalic acid were mixed in 60 mL of DMF/methanol mixture (1:1, v/v). The solution was stirred at room temperature for 2 h. After dissolution, the homogenous mixture was transferred to a 120 mL Teflon-lined autoclave and heated in a convection oven at 150°C for 18 h. After cooling to room temperature, the yellow product recovered by filtration was washed three times with 20 mL DMF and twice with 20 mL methanol, then dispersed in DMF at room temperature for 24 h. The final material, coded  $\text{NH}_2\text{-MIL-125(Ti)}$  was recovered by centrifugation (9000 rpm, 10 min) and dried at 75°C overnight.

#### **SI-2. Synthesis of $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125(Ti)}$ and $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125(Ti)}$**

This synthesis is adapted the one proposed<sup>45,46</sup> with slight modifications. 0.5 g of the above  $\text{NH}_2\text{-MIL-125(Ti)}$  was mixed with 0.25 g  $\text{AgNO}_3$  or  $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 0.3 g thiourea in 60 mL DMF and stirred for 3 h at room temperature, then transferred to a 120 mL Teflon-lined autoclave and heated in a convection oven at 160°C for 10 h. After cooling to room temperature, the resulting product was washed twice with DMF and five times with absolute methanol, and finally dried at 50°C overnight. The resulting product was named  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125(Ti)}$  and  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125(Ti)}$ . For comparison,  $\text{Ag}_2\text{S}$  and  $\text{Bi}_2\text{S}_3$  nanosheets were also synthesized using the same procedure without adding  $\text{NH}_2\text{-MIL-125(Ti)}$ . Fig. SI-1 shows the experimental process of the synthesis of  $\text{NH}_2\text{-MIL-125(Ti)}$ ,  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125(Ti)}$  and  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125(Ti)}$ .

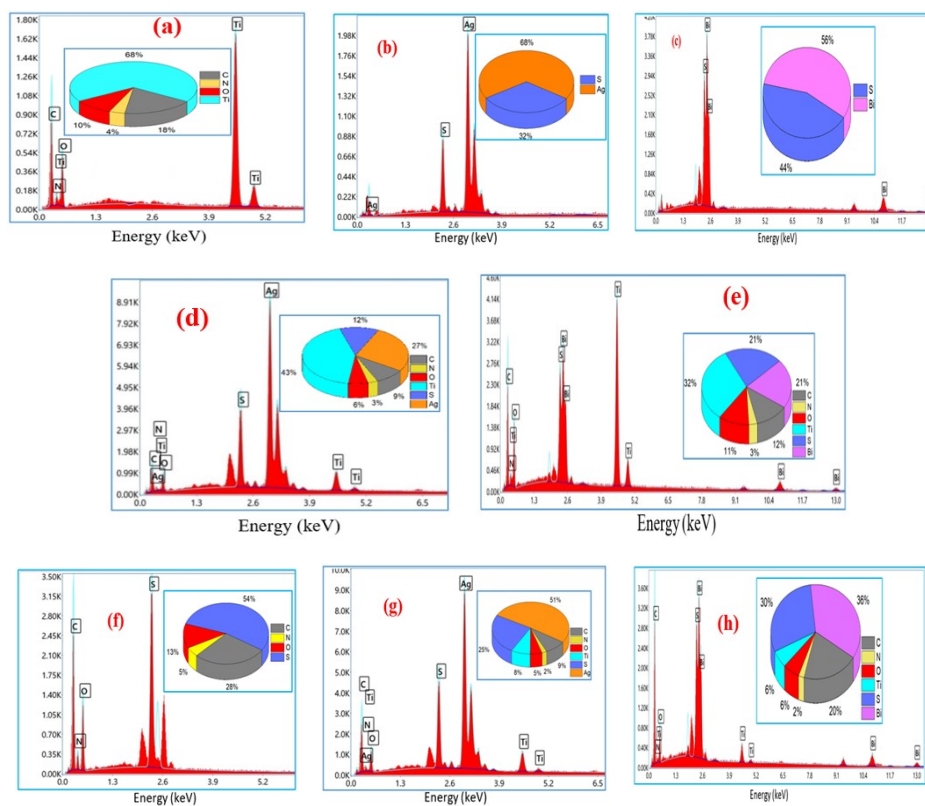


**Fig. SI-1.** Experimental process of the synthesis of MIL-125-Ti-NH<sub>2</sub>, Ag<sub>2</sub>S@MIL-125-Ti-NH<sub>2</sub> and Bi<sub>2</sub>S<sub>3</sub>@MIL-125-Ti-NH<sub>2</sub>.

### SI-3. Synthesis of polyaniline

Polyaniline (PANI) was synthesized using the method described.<sup>32</sup> Properly, 1.86 g (0.02 mol) of aniline was added to 20 g of 1 M HCl solution and the pH was adjusted to 1. Under constant stirring of aniline hydrochloride at temperature 0-5°C, 5.705g (0.125 mol) of ammonium peroxydisulfate in 10.3 g of water was added to it. After 1 h stirring, the reaction was stopped and allowed to stay for 24 h and to polymerize. The next day, polyaniline (PANI) precipitates were collected on a whatman filter paper, washed several times with distilled water followed by 0.2 M HCl and acetone. Finally, the PANI precipitate was dried in vacuum oven at 60°C for 24 h to obtain the dark green powder of PANI and kept in pendorf for further use.

### SI-4. EDX spectra



**Fig. SI-2.** EDX spectrum of (a) NH<sub>2</sub>-MIL-125(Ti), (b) Ag<sub>2</sub>S, (c) Bi<sub>2</sub>S<sub>3</sub>, (d) Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti), (e) Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti), (f) PANI, (g) Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti)/PANI, and (h) Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI.

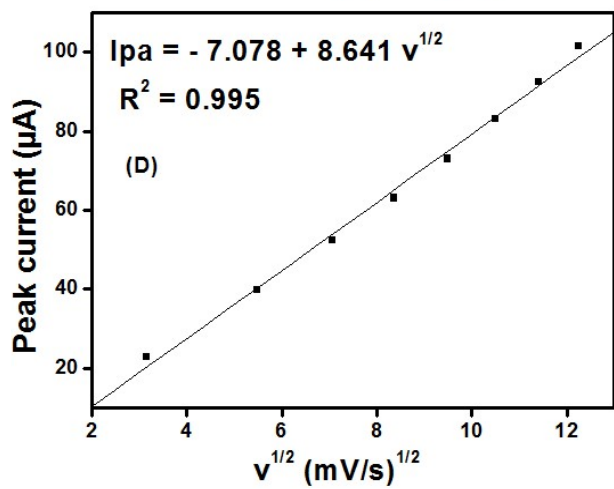
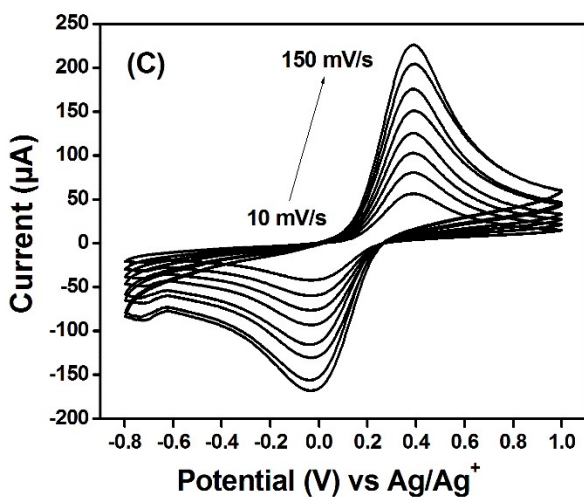
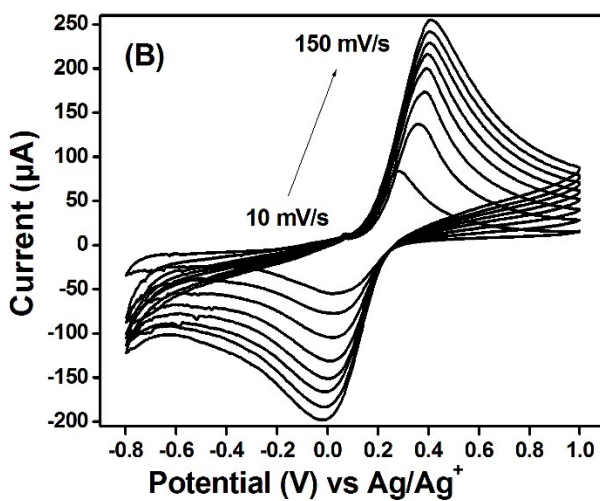
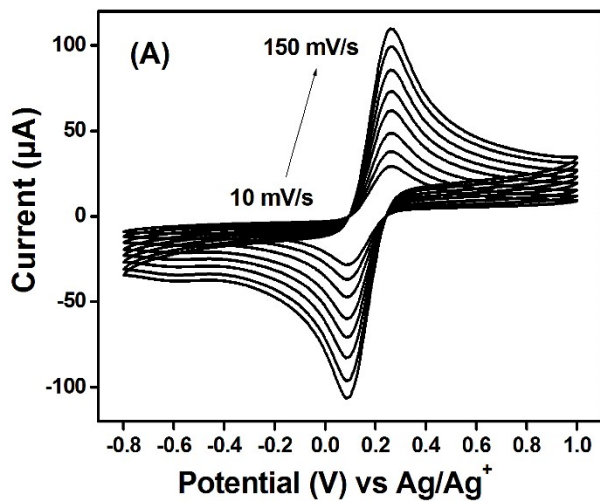
### SI-5. N<sub>2</sub> adsorption-desorption characterization

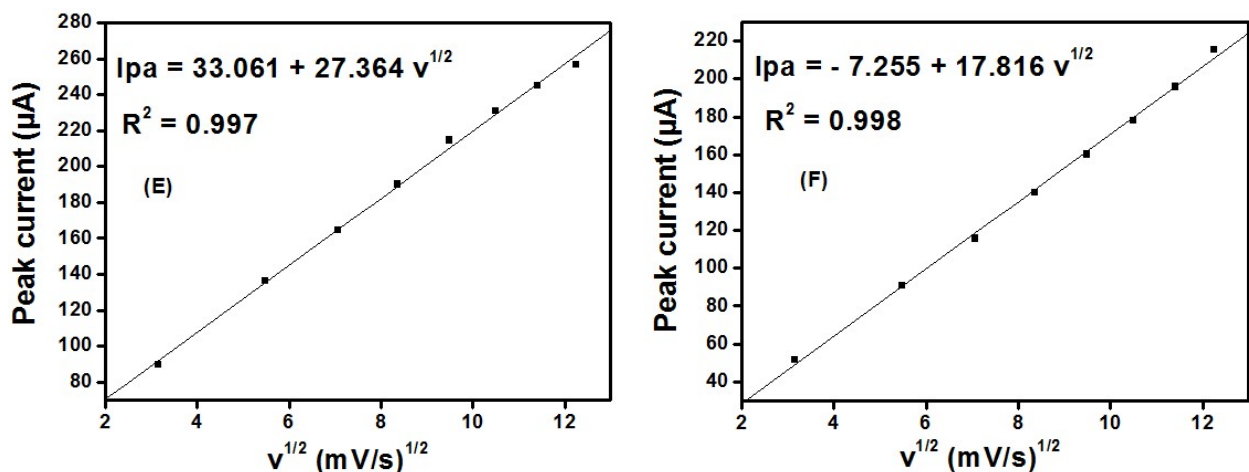
**Table SI-1.** BET surface area and textural characteristics of NH<sub>2</sub>-MIL-125(Ti), Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti) and Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)

Sample	BET (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Micropore area (m <sup>2</sup> g <sup>-1</sup> )	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )
NH <sub>2</sub> -MIL-125(Ti)	1085.27	0.7826	700.34	0.3603
Ag <sub>2</sub> S@NH <sub>2</sub> -MIL-125(Ti)	415.82	0.4806	310.15	0.2087
Bi <sub>2</sub> S <sub>3</sub> @NH <sub>2</sub> -MIL-125(Ti)	372.52	0.3201	260.15	0.1827

### SI-6. Active surfaces

The determination of the microscopic active surface area of the different electrodes bare GCE (a), Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (b), and Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (c) have been performed in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> (0.10 M KCl, pH 7) at different scan rate from 10 to 150 mV/s and the obtained voltammograms are shown by Fig. SI-3A, B and C. The plotting of the peak current versus the root of the scan rate are shown by Fig. SI-3D, E and F, where by using the Randles Sevcik equation ( $I_{pc} = K n^{3/2} A D^{1/2} C v^{1/2}$ , with the constant  $K = 2.09 \times 10^5$ , the number of electron exchanged  $n = 1$ , the concentration of the analyte  $C = 5$  mM, the real surface ( $cm^2$ )  $A$ , the scan rate  $v$  and the diffusion coefficient  $D = 7.6 \times 10^{-6} cm^2 s^{-1}$ ),<sup>32,36,57</sup> it has been possible to determine the active surfaces as 0.0029 cm<sup>2</sup> for (a), 0.0095 for (b), and 0.0062 for (c). This result suggests that the modification of the bare GCE with Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti)/PANI and Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI increases the surface area to be respectively 3.28 and 2.14 times higher than bare GCE. Therefore, will surely increase the sensitivity of the electrodes.

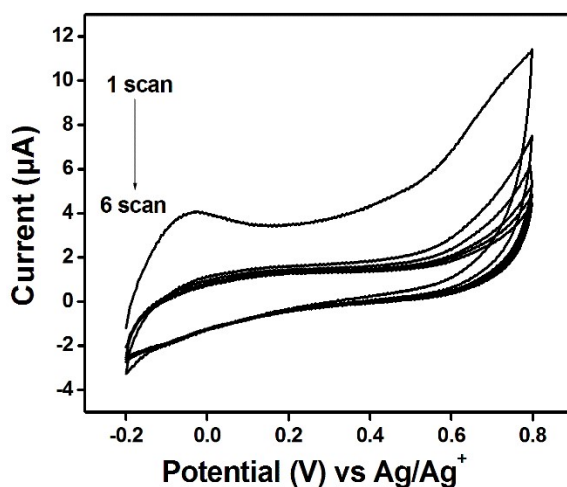




**Fig. SI-3.** Cyclic voltammograms of 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (0.10 M KCl, pH 7) recorded on (A) bare GCE, (B)  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$ , and (C)  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$  at different scan rate. (D, E, and F) are the corresponding peak currents in function of the root square of the scan rate respectively.

#### SI-7. Stabilization of the modified GCE

Prior to use each fabricated electrode for the electroanalysis of uric acid (UA), they were stabilized in a solution of 0.10 M phosphate buffer at pH 7.0, by running multicyclic voltammograms and it was found that only 6 cycles show by Fig. SI-4 were sufficient to stabilize the working electrode  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$  made with polyaniline, as the oxidation of PANI take place around 0.0 V.<sup>32</sup> Same result not shown was obtained with  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$ .



**Fig. SI-4.** Multicyclic voltammograms of  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$  recorded in phosphate buffer solution (0.1 M, pH 7) at scan rate of 100 mV/s.

#### SI-8. Influence of scan rate and kinetic studies

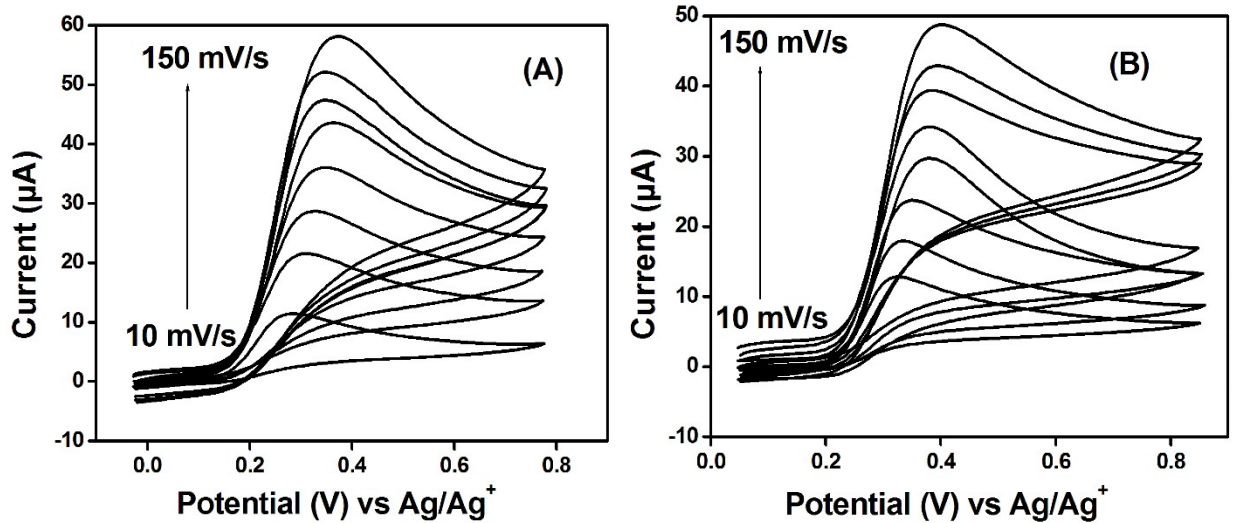
In order to determine which phenomena is responsible for the transfer of electrons/particles at the surface of electrodes, the influence of scan rate was investigated in the scanning range from 10 to 150 mV/s show by Fig. SI-5A and B respectively with  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$ , and

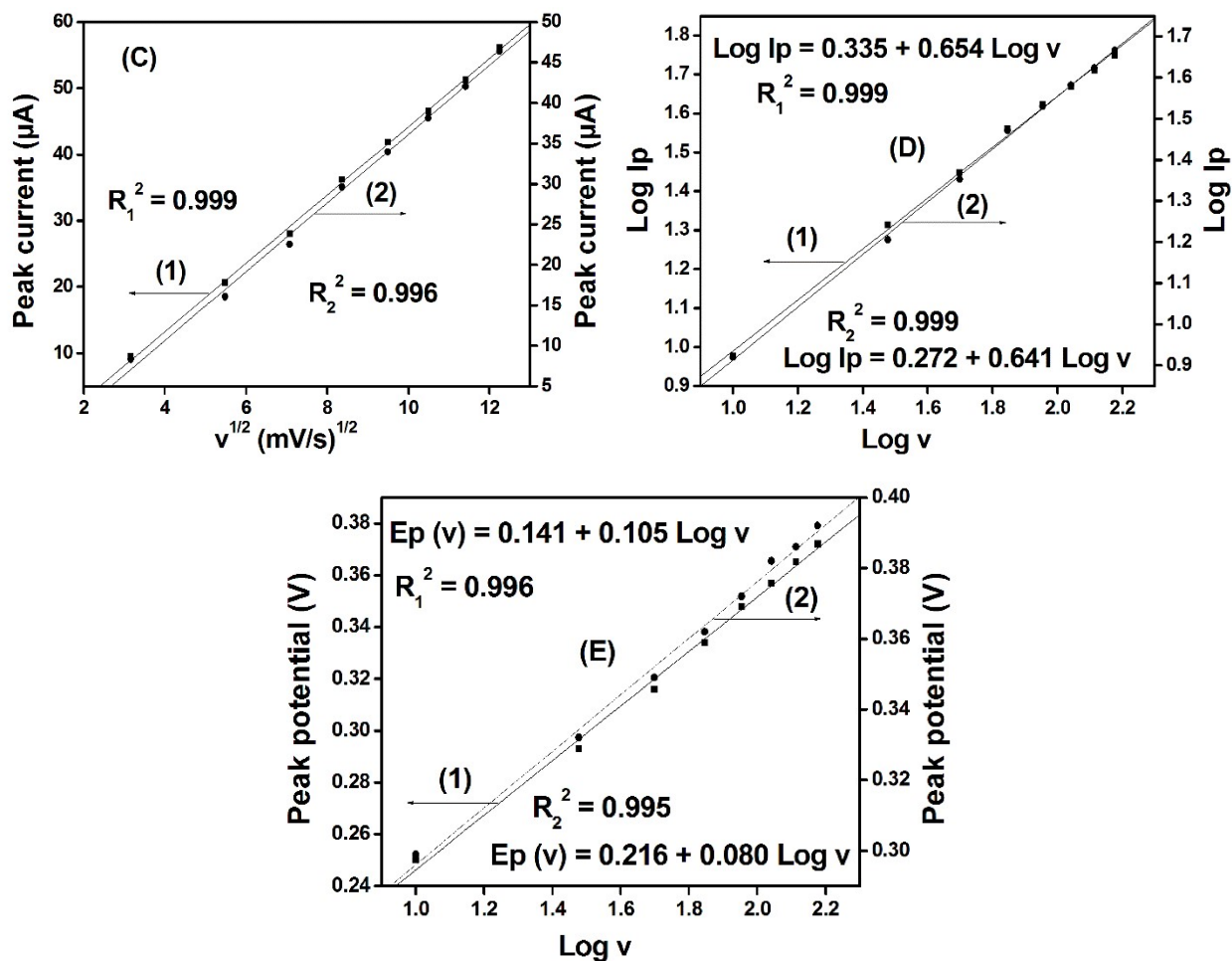
Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE. The plotting of peak current versus the root square of the scan rate (Fig. SI-5C) shows from the correlation coefficient values (0.999 for Ag<sub>2</sub>S@- and 0.996 for Bi<sub>2</sub>S<sub>3</sub>@-) closed to 1, that diffusion is the phenomena that govern the transfer of particles at the surface of electrodes. By plotting log(I<sub>p</sub>) versus log(v) given by Fig. SI-5D, the slope values (0.654 for Ag<sub>2</sub>S@- and 0.651 for Bi<sub>2</sub>S<sub>3</sub>@-) obtained closed to the reference value (0.5) confirmed the diffusion process in this work.<sup>32</sup> By plotting E<sub>p</sub> = f (Log v) given by Fig. 11E, the values of the slopes obtained from the Laviron equation<sup>59,60</sup> (Eq. 1) for irreversible process are 105 mV/decade for Ag<sub>2</sub>S@- and 80 mV/decade for Bi<sub>2</sub>S<sub>3</sub>@- which are included in the normal range of 30 to 120 mV/decade.

$$E_p = E^0 + \left(\frac{2,303 RT}{\alpha nF}\right) \log\left(\frac{RTK^0}{\alpha nF}\right) + \left(\frac{2,303 RT}{\alpha nF}\right) \log(v) \quad (1).$$

Where  $\alpha = 0.50$ , represents the transfer coefficient<sup>61</sup>;  $n$ , the number of electrons exchanged;  $v$ , the scan rate;  $K^0$ , the heterogeneous rate constant;  $T = 298$  K, the temperature;  $R = 8.314$  J. mol. K<sup>-1</sup>, the gas constant; and  $E^0$ , the standard potential obtained by extrapolation on the potential axis when  $v = 0$  mV/s.

From this equation 1, we obtained  $\alpha n = 0.563$ ;  $n = 1.024 \approx 1$  for Ag<sub>2</sub>S@- and  $\alpha n = 0.738$ ;  $n = 1.342 \approx 1$  for Bi<sub>2</sub>S<sub>3</sub>@-, which suggests the use of one electron for the oxidation process. Moreover, the number of electron exchange here is 1 instead of 2 as it was reported,<sup>61,62</sup> showing the partial oxidation of UA, may be assigned to its solubility.

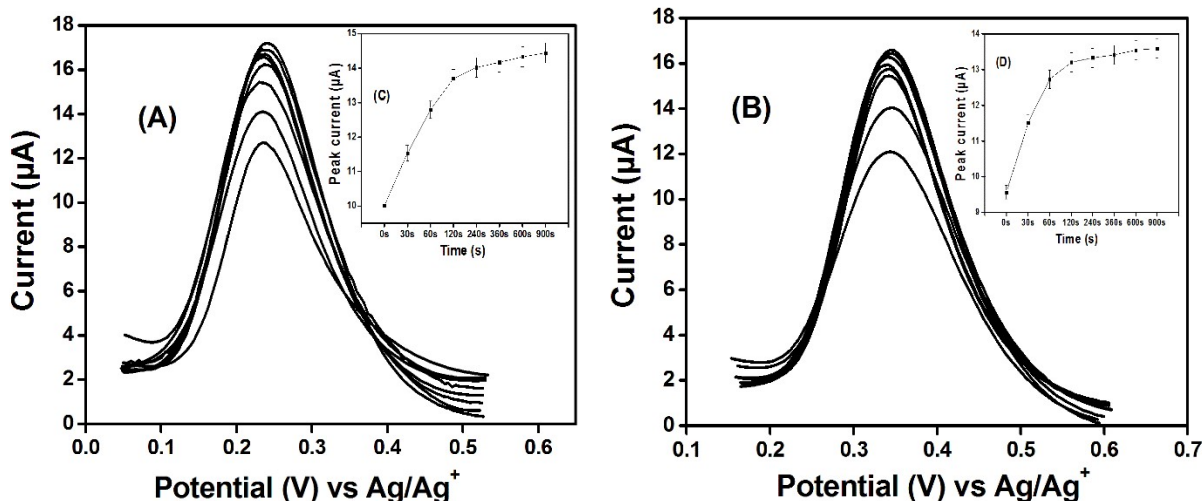




**Fig. SI-5.** Cyclic voltammograms of uric acid (1 mM, pH 7.0) in PB recorded on  $\text{Ag}_2\text{S}@NH_2\text{-MIL-125(Ti)/PANI/GCE}$  (A) and  $\text{Bi}_2\text{S}_3@NH_2\text{-MIL-125(Ti)/PANI/GCE}$  (B) at scan rate 10 to 150 mV/s. (C-1 and C-2) shows the variation of peak  $I_p = f(v^{1/2})$ . (D-1 and D-2) shows  $\text{Log } I_p = f(\text{Log } v)$  and (E-1 and E-2) shows  $E_p = f(\text{Log } v)$ , obtained respectively with the two electrodes.

### SI-9. Influence of accumulation time

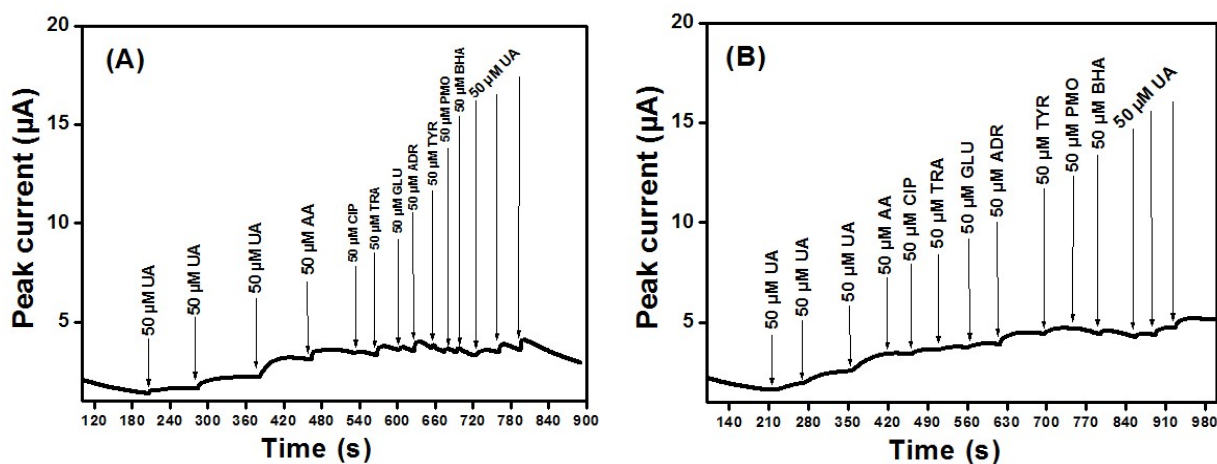
The influence of accumulation has been evaluated from 0 to 15 min and the voltammograms obtained with the modified electrodes  $\text{Ag}_2\text{S}@NH_2\text{-MIL-125(Ti)/PANI/GCE}$  and  $\text{Bi}_2\text{S}_3@NH_2\text{-MIL-125(Ti)/PANI/GCE}$  are given by Fig. SI-6A and B respectively. It is clearly seen that the peak current rapidly increasing with the accumulation time up to 2 min where it is stabilized (Fig. SI-6C and D for  $\text{Ag}_2\text{S}@$ - and  $\text{Bi}_2\text{S}_3@$ - respectively). This saturation indicates that the fixation sites of elaborated electrodes after two minutes of accumulation are almost all occupied. This equilibrium time of 2 min was then used for the study of the influence of concentration.



**Fig. SI-6.** Differential pulse voltammograms of UA obtained with Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (A) and Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (B) in the accumulation time from 0 to 15 min. The insets (C and D) show the corresponding peak currents. Experimental conditions: 50 μM UA in 0.1 M PB at pH 7. Experiments were triplicate.

### SI-10. Interference study

Several potential interfering organic compounds generally present in the same medium like with UA such as ascorbic acid (AA), ciprofloxacin (CIP), tartrazine (TRA), glucose (GLU), adrenaline (ADR), tyrosine (TYR), promazine (PMO), butylated hydroxyanisole (BHA), have been recorded and the results are given in the Fig. SI-7. It can be seen that AA, TRA and ADR can interfere with the signal of UA when using Ag<sub>2</sub>S@- and ADR, TYR, and BHA can interfere with the signal of UA when using Bi<sub>2</sub>S<sub>3</sub>@-.

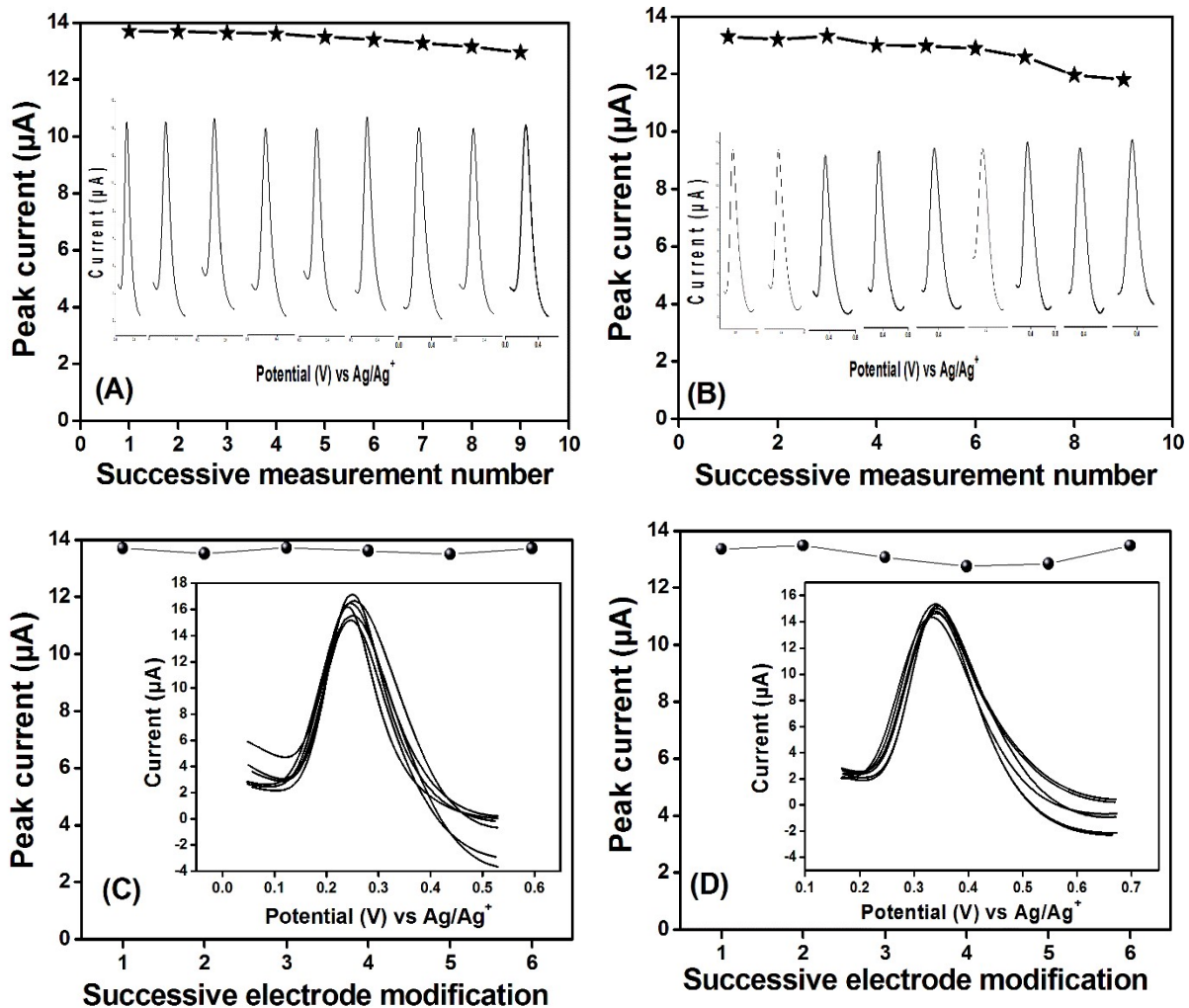


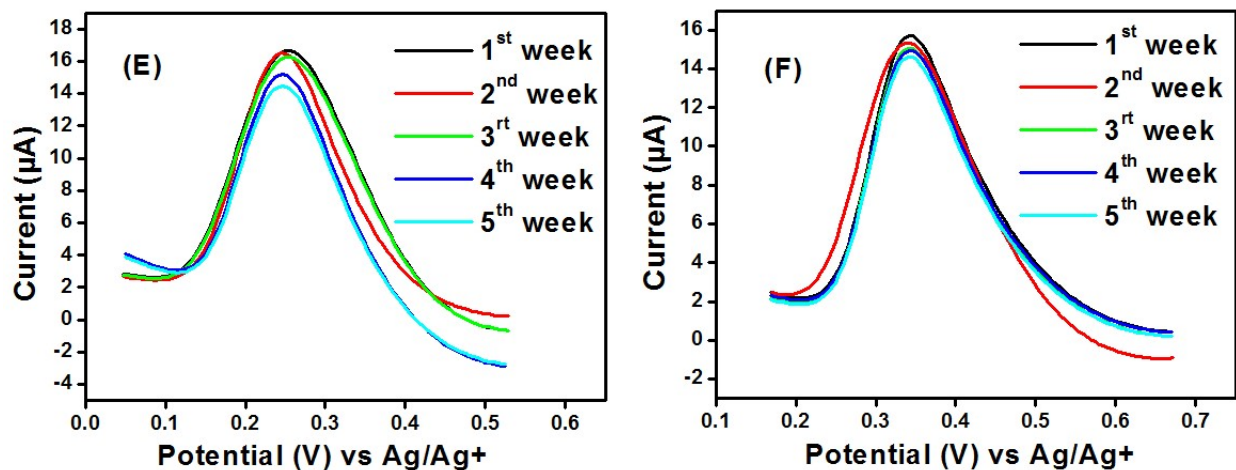
**Fig. SI-7.** Chronoamperometric responses of Ag<sub>2</sub>S@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (A) and Bi<sub>2</sub>S<sub>3</sub>@NH<sub>2</sub>-MIL-125(Ti)/PANI/GCE (B) towards addition of 50 μM interfering agents in presence of 50 μM UA, in phosphate buffer solution (0.10 M, pH 7.0).

### SI-11. Reproducibility and repeatability of the modified electrode

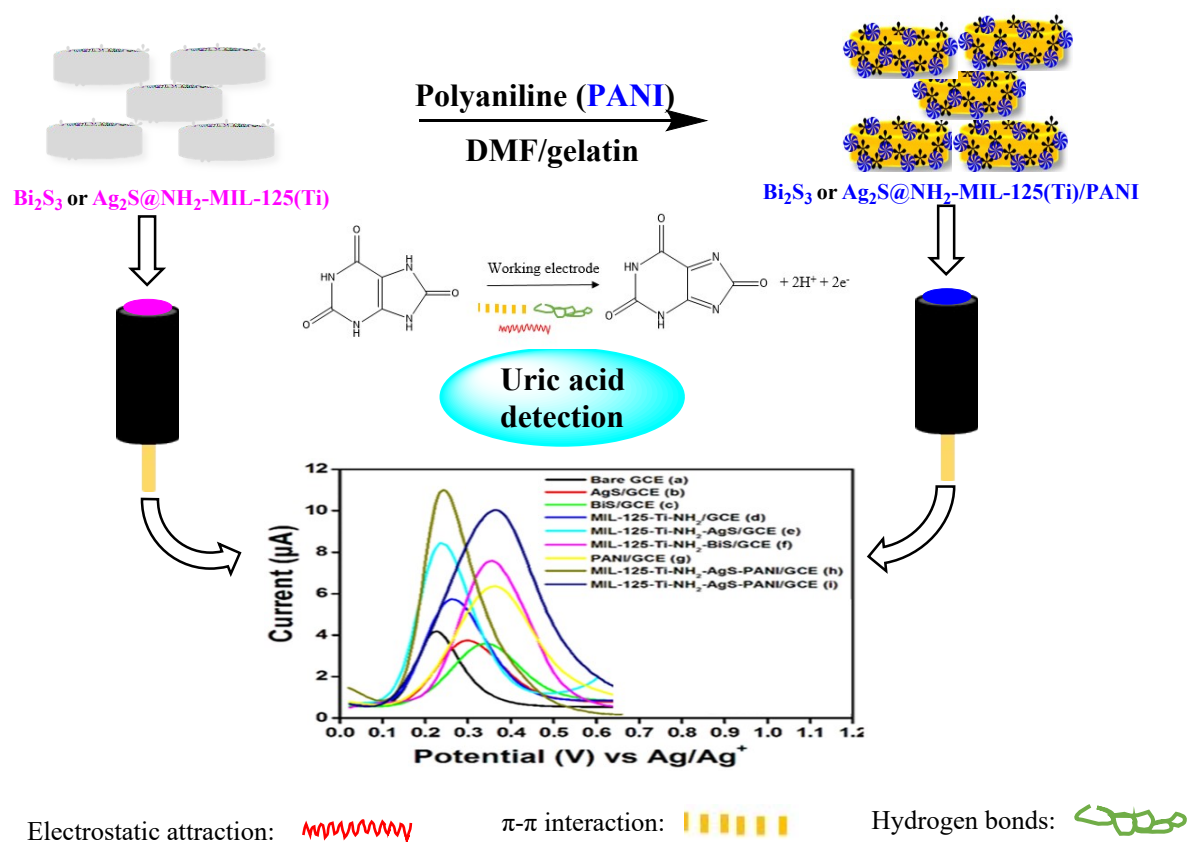


The reproducibility of the sensors has been evaluated by recording nine successive measurements on the same films and the DPV responses are given by Fig. 16A and B, while the repeatability was done by recording the signal of nine successive film preparations and the results are given by Fig. 16C and D respectively for  $\text{Ag}_2\text{S}@-\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$  and  $\text{Bi}_2\text{S}_3@-\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{PANI}/\text{GCE}$ . The plotting of peak current in function of the successive measurement number and in function of the successive electrode modification shows that the prepared sensors have good reproducibility (recovery of  $98.512 \pm 0.951$  and  $95.761 \pm 2.101$ ) and repeatability (recovery of  $100.053 \pm 0.077$  and  $96.563 \pm 1.763$ ) respectively for the  $\text{Ag}_2\text{S}@-$  and  $\text{Bi}_2\text{S}_3@-$ . The storage stability was evaluated by recording the DPV signal of the prepared electrodes once per week during five weeks (Fig. 16 E and F), with the storage at room temperature. The electrodes after recording in  $50 \mu\text{M}$  UA  $0.10 \text{ M}$  PB at  $\text{pH} = 7.0$  were rinsed inside distilled water before being kept for the next measurement the next week. The recovery of  $97.268 \pm 0.109$  and  $99.198 \pm 0.003$  were obtained respectively for  $\text{Ag}_2\text{S}@-$  and  $\text{Bi}_2\text{S}_3@-$ . This indicates that the prepared sensors have acceptable stabilities up to five weeks.





**Fig. SI-8.** (A and B) Successive peaks current recorded on the same films preparation showing the reproducibility, (C, D) peak current recorded on the different films preparation showing the repeatability, and (E and F) peak current recorded after each week showing the stability respectively for  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125(Ti)/PANI/GCE}$  and  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125(Ti)/PANI/GCE}$



**Scheme SI-1.** Proposed mechanism of interaction between  $\text{Ag}_2\text{S}@/\text{NH}_2\text{-MIL-125(Ti)/PANI/GCE}$  and  $\text{Bi}_2\text{S}_3@/\text{NH}_2\text{-MIL-125(Ti)/PANI/GCE}$  and the uric acid analyte.

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