



Article

Asymmetric Magnetoelectrochemistry: An Efficient Method to Grow Enantiopure Self-Assemble Monolayer

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Abstract: In this work, we are presenting magnetic field dependent electrochemical method to grow enantiopure monolayer. Thiol gold monolayer formation by redox reaction is studied on gold coated ferromagnetic surface. Infrared and photoemission spectroscopies are used to probe the quality of the monolayers, grown using different direction of magnetization of surface. Commercially available chiral molecules, L-cysteine along with dsDNA are used as control molecules for the measurements. Since it is established by aligning the electron spin within the surface, it helps to adsorb specific enantiomer of molecules, we have shown how direction of the magnet helps to grow good quality monolayer. Potential application of this work is in improving quality of monolayer and chiral separation.

Keywords: monolayer; CISS; asymmetric reaction; chiral separation

1. Introduction

In the last decade, it was discovered that electron spin during its transfer can be controlled by chiral molecules which is also known as Chiral Induced Spin Selectivity (CISS), recently it is also established, charge distribution within chiral molecules is spin specific phenomena, which is known as spin polarization [1–5]. In the past there were many efforts to correlated electronics spin and its role in chiral recognition. It is believed that the enantiospecific interaction between ferromagnetic surface with chiral molecule is a combined effect of dipole electric field and exchange interaction. There are many experimental evidences like, electrochemistry, crystallization or independent adsorption which shows electronic spin enables asymmetric reaction [6–12].

During the electrochemistry, when molecule reach at the electrode surface, charge reorganization occurs within the molecule, and when it comes to chiral molecules, this charge polarization is spin dependent. By external perturbation, spin accumulated on either of the terminal of the molecule depends on the handedness of chiral molecule. During the reaction when these spin polarized charged molecules come in contact with spin-aligned working electrode, formation of singlet and triplet states at the interface occurs [13]. The interaction between the surface and spin polarized molecules is not only electrostatic, but also exchange-interaction. In these interactions, unpaired electrons of specific spin, plays vital role in selection of handedness of the molecules. Figure 1 shows pictorial representation of enantiospecific adsorption of chiral molecule on the ferromagnetic surface. This concept becomes more significant when it comes to the electrochemical method, where the electric field not only helps to polarize the molecule, but also drives them toward the surface.

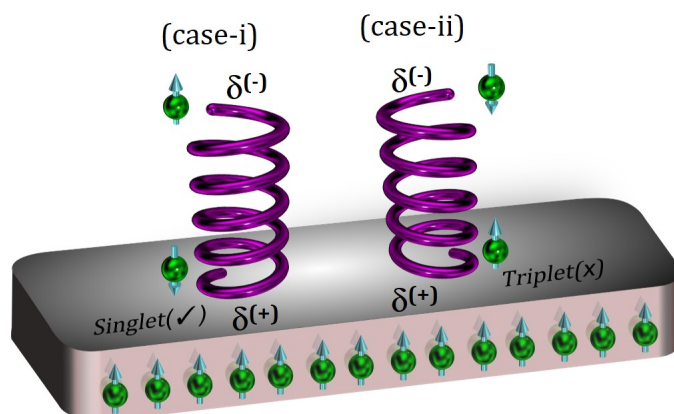


Figure 1. Scheme shows interaction of chiral molecules and ferromagnetic surface. In the first case where spin polarized molecule comes in contact with spin aligned ferromagnet and singlet state forms, where probability of molecule to get adsorbed on the surface is higher. In the second case, spin of the unpaired electron is parallel to the spins in the FM forms triplet state and have lower chance to get adsorbed. δ : charge.

The above presented model is the core theme of present work, where electrochemistry used as a tool to grow the monolayer of thiolated molecules. In addition to this, the magnetic field on the ferromagnetic surface works as catalyst and help in enantiospecific recognition of molecules and improve their adsorption. The magnetic field aligns the spin in the working electrode in either direction. We compare the quality of the monolayer of enantiomer by switching the spin of the working electrode, showing a change in the IR and X-ray photoemission spectra.

2. Experimental Section

A special setup for electrochemical measurement is used, where a magnet underneath a working electrode arranges in such a way that it applies the maximum field. A neodymium magnet of strength 0.35 T oriented perpendicular to the working electrode is used for magnetization. A AgCl_{sat} coated silver wire and Pt wire are used as reference and counter electrode, respectively. Both of these electrodes are used as fine needles, so they can be in contact with drop electrolytes and at the same time avoid touching each other. Au protected Ni bottom surface with an area of 1 cm^2 is used as working electrode. Two sets of thiolated molecules L-cysteine along with double helix DNA (dsDNA) are used to grow monolayers. Enantiopure L-cysteine bought from Sigma Aldrich and dsDNA is from IDT. An electrolytic solution in case of cysteine (20 mM) and DNA (30 μM) was prepared in 0.4M PBS buffer as electrolyte with maintain pH-7. PalmSens potentiostats is used for all the electrochemical measurements where PStrace is used to record the data. Polarization modulation-infrared reflection-absorption spectroscopy (PM-IRAS), Nicolet 6700 FTIR equipped with a PEM-90 photoelastic modulator made by Hinds Instruments, Hillsboro, OR. Silicon <100>, p-type wafer used for the surface, on which Ni-120nm and Au-10nm grown by e-beam evaporation. XPS are measurements performed on Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) operating at a power of 75 W.

3. Results

Electrochemical reaction is used for growing monolayer of the given molecules, a small drop of electrolyte is placed on surface. The advantage of using this setup is to keep the working surface at the center and closet proximity of the magnet and using very small amount of electrolyte solution of the molecules (Figure 2A). Cyclic voltammetry (CV) response recorded during the adsorption of the molecule on the working electrode shown in Figure 2B. Figure S1 in Supporting Information (SI) shows schematic presentation of L-cysteine, self assemble monolayer (SAM) on ferromagnetic-gold

surface. The CV curve shows oxidation and reduction peak of the gold surface with 0.4 volt maximum voltage. It takes around 15 to 20 cycles to grow homogeneous and densely packed monolayer. AFM measurement in Figure S2 of SI is performed to check the quality of the monolayer. The CV response shows continues increase of the area under curve which is due to formation ionic layers at the surface–electrolyte interface, where the most-near to surface molecules participate in monolayer formation. These surfaces were cleaned with a buffer solution and dried with a N₂ gun before further characterization.

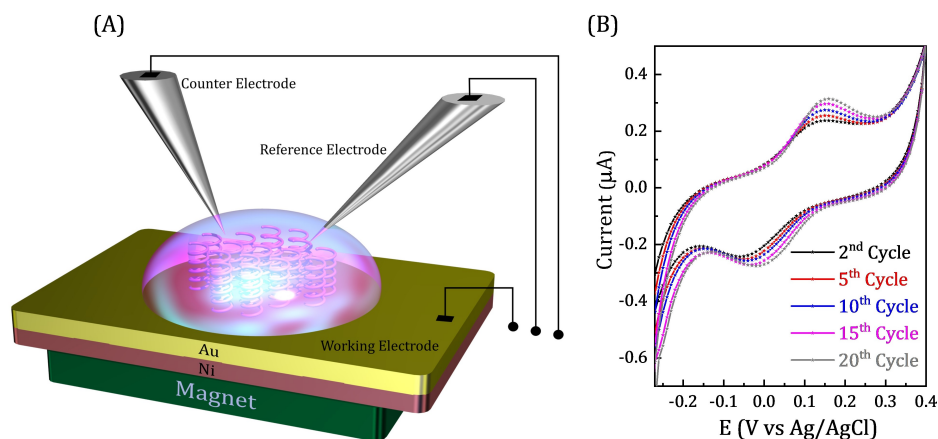


Figure 2. (A) Schematic presentation of drop magneto-electrochemistry for the deposition of enantiospecific adsorption. (B) Cyclic voltammetry recorded during the L-cysteine monolayer preparation. Note: scan rate 100mV/sec was maintained during each scan with total 20 cycles.

In this study, we used L-cysteine and double helix DNA, two sample each with the magnet's north pole in the UP and DOWN direction. We compare the quality of the monolayer by recording the reflection mode infrared (IR) and X-ray photoemission (XPS) spectra of the monolayers, given in Figures 3 and 4. In IR, during the study, we have compared the quality of the monolayer by intensity of the peak positioned at 1589 nm and 1650 nm, which correspond to amine (asymmetric) and carboxylate (C=O) stretch respectively. It is observed, when the magnetic north pole is pointing toward the surface, it is in the UP direction, L-cysteine shows high intensity response compare to the magnet in the DOWN position. Percentage changes in the study of the both peaks are around 44% to 50%.

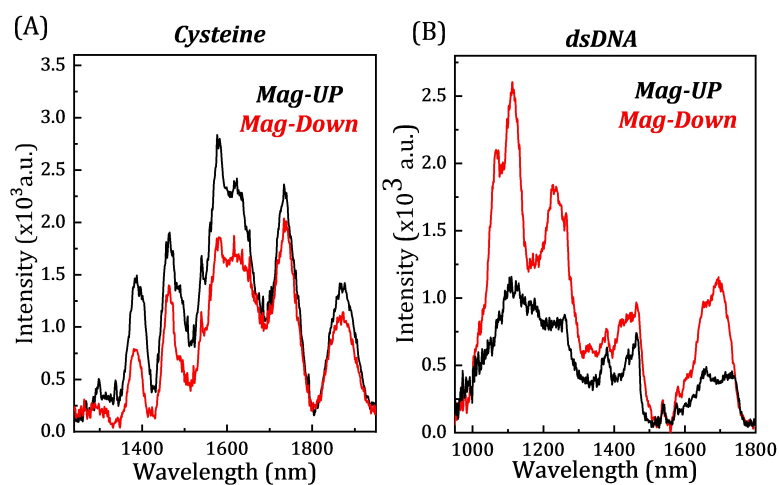


Figure 3. IR spectra of the adsorbed monolayer on the gold surface recorded in reflection mode using PMIRAS spectroscopy in magnet up (black) and magnet down (red) (A) L-cysteine, (B) dsDNA.

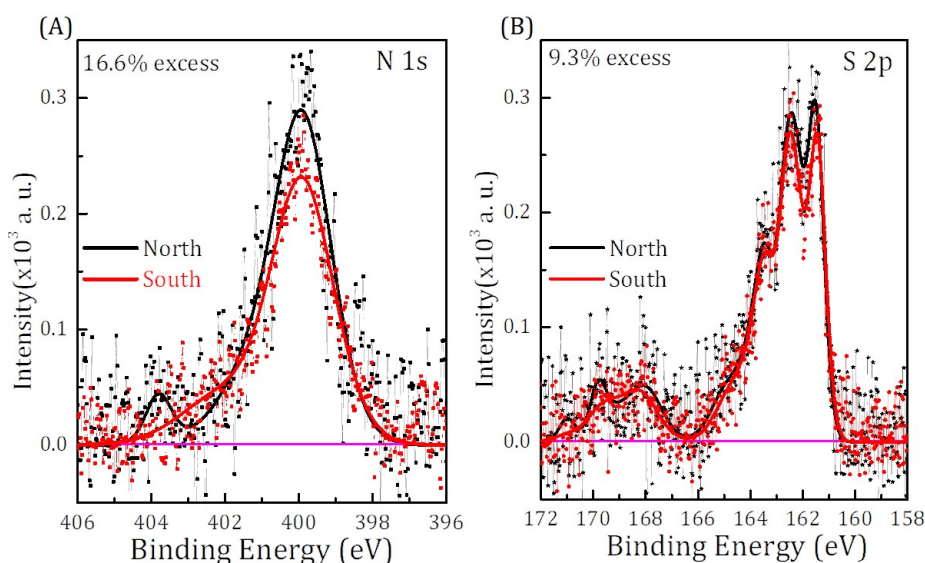


Figure 4. XPS spectra recorded on L-cysteine monolayer, where (A) nitrogen- N_{1s} with north up (black) and south up (red), similarly (B) for sulfur- S_{2p} .

To check this effect on the other system, we chose biomolecules, which are dextrorotational in nature, double helix, thiol terminated dsDNA. Interestingly, in case of DNA adsorption we also observed the effect of magnet during monolayer growth. We found the reverse effect of the magnet in case of DNA compare to cysteine, which is due to their opposite handedness as we observed it in past [3,6]. Difference in the quality of the monolayer is again measured by intensity of the peak positioned at 1087 nm and 1240 nm, corresponds to symmetric and asymmetric stretching of phosphodiester present in base pairs. When the magnet is pointed UP, it gives lower IR response compare to when the magnet is pointed DOWN. This shows, the south pole pointing up is the preferred interaction of the dsDNA with electron spin. We observed around 55% percent lower-quality monolayer by switching magnet direction.

Here, we would also like to emphasize that, during IR spectra measurement, the intensity of reflecting IR light depends upon how samples are placed. In this specific case, we always use two beams one on the sample and other one is probe to cross verify the effect of sample alignment. In order to further support our claim, we have performed X-ray photoemission spectra (given in Figure 4) on the cysteine samples. Sulfur and nitrogen signal which arise from cysteine molecules were compared between the two monolayers grown using two opposite magnetic polarization. We have found there is around a 17% higher content of N_{1s} and 10% of S_{2p} for magnet UP polarization, which shows specific direction of the magnet facilitate adsorption of enantiopure monolayer.

4. Conclusions

From this study, it is found that electron spin plays a significant role in the enantiospecific adsorption of chiral molecules. During the electrochemistry, the magnetic field helps to align the spin of working electrode which overall drive the selective electrochemical reaction. In the past, there have been studies to grow the monolayer from electrochemistry, but from this study we established that the magnetic field helps in the case of ferromagnetic working electrodes compared with randomize spin electrodes to grow good quality monolayers.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2312-7481/6/3/37/s1>, Schematic presentation of cysteine thiol gold monolayer along with AFM image of dsDNA.

Author Contributions: Conceptualization, methodology, formal analysis, investigation, S.M.; data curation, S.M. & D.B.; writing—original draft preparation, S.M.; writing—review and editing, S.M. & D.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Göhler, B.; Hamelbeck, V.; Markus, T.Z.; Kettner, M.; Hanne, G.F.; Vager, Z.; Naaman, R.; Zacharias, H. Spin Selectivity in Electron Transmission Through Self-Assembled Monolayers of Double-Stranded DNA. *Science* **2011**, *331*, 894–897. [[CrossRef](#)] [[PubMed](#)]
2. Naaman, R.; Waldeck, D.H. Chiral-Induced Spin Selectivity Effect. *J. Phys. Chem. Lett.* **2012**, *3*, 2178–2187. [[CrossRef](#)] [[PubMed](#)]
3. Mishra, S.; Mondal, A.K.; Pal, S.; Das, T.K.; Smolinsky, E.Z.B.; Siligardi, G.; Naaman, R. Length-Dependent Electron Spin Polarization in Oligopeptides and DNA. *J. Phys. Chem. C* **2020**, *124*, 10776–10782. [[CrossRef](#)]
4. Mishra, S.; Pirbadian, S.; Mondal, A.K.; El-Naggar, M.Y.; Naaman, R. Spin-Dependent Electron Transport through Bacterial Cell Surface Multiheme Electron Conduits. *J. Am. Chem. Soc.* **2019**, *141*, 19198–19202. [[CrossRef](#)] [[PubMed](#)]
5. Mishra, S.; Poonia, V.S.; Fontanesi, C.; Naaman, R.; Fleming, A.M.; Burrows, C.J. Effect of Oxidative Damage on Charge and Spin Transport in DNA. *J. Am. Chem. Soc.* **2019**, *141*, 123–126. [[CrossRef](#)] [[PubMed](#)]
6. Ghosh, S.; Mishra, S.; Avigad, E.; Bloom, B.P.; Baczewski, L.T.; Yochelis, S.; Paltiel, Y.; Naaman, R.; Waldeck, D.H. Effect of Chiral Molecules on the Electron's Spin Wavefunction at Interfaces. *J. Phys. Chem. Lett.* **2020**, *11*, 1550–1557. [[CrossRef](#)] [[PubMed](#)]
7. Naaman, R.; Paltiel, Y.; Waldeck, D.H. Chiral molecules and the electron spin. *Nat. Rev. Chem.* **2019**, *3*, 250–260. [[CrossRef](#)]
8. Banerjee-Ghosh, K.; Dor, O.B.; Tassinari, F.; Capua, E.; Yochelis, S.; Capua, A.; Yang, S.-H.; Parkin, S.S.P.; Sarkar, S.; Kronik, L.; et al. Separation of enantiomers by their enantiospecific interaction with achiral magnetic substrates. *Science* **2018**, *360*, 1331–1334. [[CrossRef](#)]
9. Metzger, T.S.; Mishra, S.; Bloom, B.P.; Goren, N.; Neubauer, A.; Shmul, G.; Wei, J.; Yochelis, S.; Tassinari, F.; Fontanesi, C.; et al. The Electron Spin as a Chiral Reagent. *Angew. Chem. Int. Ed.* **2020**, *59*, 1653–1658. [[CrossRef](#)]
10. Mishra, S.; Marzio, M.D.; Giovanardi, R.; Tassinari, F. Magnetochemistry and Asymmetric Electrochemical Reactions. *Magnetochemistry* **2020**, *6*, 1. [[CrossRef](#)]
11. Mondal, P.C.; Fontanesi, C.; Waldeck, D.H.; Naaman, R. Field and Chirality Effects on Electrochemical Charge Transfer Rates: Spin Dependent Electrochemistry. *ACS Nano* **2015**, *9*, 3377–3384. [[CrossRef](#)] [[PubMed](#)]
12. Gazzotti, M.; Arnaboldi, S.; Grecchi, S.; Giovanardi, R.; Cannio, M.; Pasquali, L.; Giacomino, A.; Abollino, O.; Fontanesi, C. Spin-dependent electrochemistry: Enantio-selectivity driven by chiral-induced spin selectivity effect. *Electrochim. Acta* **2019**, *286*, 271–278. [[CrossRef](#)]
13. Kumar, A.; Capua, E.; Kesharwani, M.K.; Martin, J.M.; Sitbon, E.; Waldeck, D.H.; Naaman, R. Chirality-induced spin polarization places symmetry constraints on biomolecular interactions. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 2474–2478. [[CrossRef](#)] [[PubMed](#)]



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