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Magnetless Device for Conducting Three-Dimensional Spin-Specific Electrochemistry Experiments

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Abstract:

Electron spin states play an important role in many chemical processes. Most of the spin state studies require the application of a magnetic field. Recently it was found that the transport of electrons through chiral molecules also depends on their spin states and that it may also play a role in enantio-recognition. Electrochemistry has been an important tool both in studying spin-specific processes as well as for enantio-separation of chiral molecules. Here we present a new device that serves as the working electrode in electrochemical cells and is capable of providing information on the correlation of spin selectivity and the electrochemical process. The device is based on the Hall effect and it eliminates the need to apply an external magnetic field. We demonstrate the ability to monitor the spin-selective electron transfer through chiral molecules and the relationship between the enantio-recognition process and the electron's spin.

The control of chemical reactions by spin effects is a well-established field^{1,2} that has been investigated by applying photochemistry³ as well as various magnetic and electrochemical methods.^{4,5} In recent years, a new aspect regarding the role of the electron spin in chemistry was found to be related to the spin-selective electron transport through chiral molecules. This phenomenon is known as the chiral-induced spin selectivity (CISS) effect.^{6,7} It has also been proven that when chiral molecules are polarized by applying an electric field, the charge reorganization is accompanied by the electrons' spin polarization.¹⁷ The actual chirality of the enantiomer defines which spin direction is associated with which electric pole.

In recent years, the CISS effect has been utilized for conducting spin-specific electrochemistry experiments.^{8,9} In those studies, a magnetized substrate was coated with chiral molecules that transmit one preferred spin direction. By flipping the magnetic field, it was possible to define which spin orientation is the preferred one. Electrodes coated with chiral molecules were also used in the past for enantio-selective electrochemistry studies, mainly aimed at developing enantio-selective electrochemical sensors.¹⁰⁻¹⁵ As is generally accepted, the enantio-selectivity of chiral-coated electrodes results from the stereo-specific interaction of the electrode with two enantiomers in the solution, indicated by the higher current for the stronger interacting one. This notion is consistent with the assumption that, in general, stereo effects like the “lock and key” model¹⁶ are responsible for chiral recognition. However, recently it has been suggested that enantio-selectivity also involves an electronic term that relates to the electrons' correlation energy; hence, it is affected by the electrons' spin.¹⁷ This term affects the repulsion part of the interacting potential, so that for the homochiral system the repulsion is “softer” than for a hetero-chiral system.

Here we present “three-dimensional (3D) spin-electrochemistry” methodology, based on Hall potential measurements;¹⁸ this enables us to conduct electrochemical studies while monitoring the spin polarization of the current. This method provides *simultaneously*, in operando, a three-way source of information about the applied voltage, the resulting electrochemical current, and spin injection; the latter is probed via the Hall potential measurements. This device is based on the AlGaIn/GaN high electron mobility transistor (HEMT).¹⁹ This device serves two purposes: it is the working electrode as in a conventional electrochemical cell and, simultaneously, it measures the spin polarization of the current, as presented schematically in Figure 1. A regular CV electrochemical measurement is conducted by varying the voltage between the GaN working electrode and a counter electrode, and a constant current flows in the channel between the source

and drain electrodes on the GaN. The Hall potential is monitored between electrodes located perpendicular to the current (Figure 1). The Hall potential stems from the spin-polarized electrons injected into (or out from) the GaN device. The accumulated spins in GaN produce a magnetic field perpendicular to the device's surface.

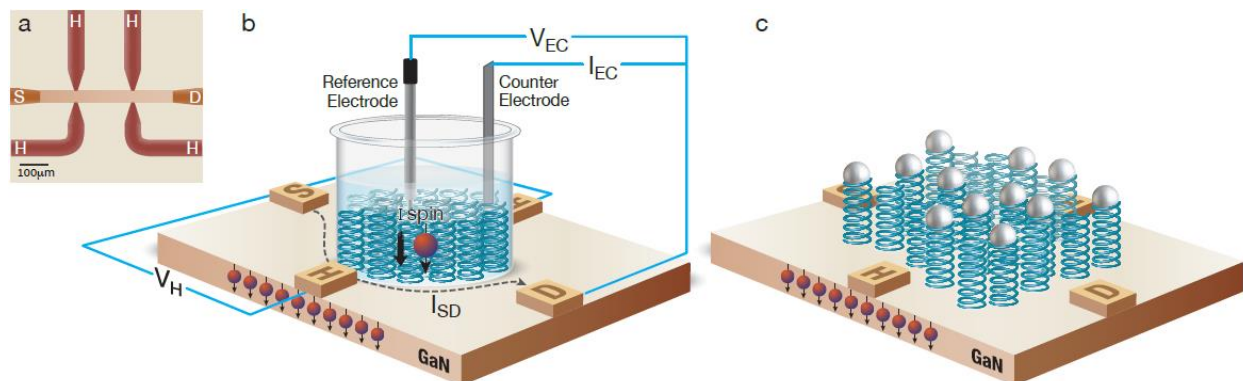


Figure 1: The scheme of the experimental set-up: (a) Optical microscope image of the GaN-based Hall device. S and D are the source and drain electrodes, respectively, and H denotes the electrodes used for Hall measurements. (b) The scheme of the combined electrochemical/Hall-device apparatus. (c) A scheme of the working electrode with silver nanoparticles (AgNPs) attached to the adsorbed oligopeptides. The AgNPs serve as the redox probe.

This experimental method eliminates the need to use magnetic electrodes or a magnetic field for studying the spin-dependent effects in electrochemistry. This is important since it is known that magnetic fields introduce various effects that may influence the electrochemical process, even if there is no spin-dependent reaction.²⁰⁻²⁴ In addition, it directly correlates the electrochemical process at various potentials and the spin selectivity as expressed by the magnitude of the Hall potential (See Fig. S4).

In the present work, we present an example of the ability of the new method by probing the spin selectivity of electrons transmitted through a monolayer of chiral molecules of various lengths that are adsorbed on the GaN device. In addition, the chiral GaN-based working electrode is applied for conducting an enantio-specific electrochemical process. We found that the enantio-selectivity correlates with the spin polarization. Hence, we further validate that chiral recognition occurs not only via stereo-selectivity but a spin-related interaction contributes very significantly to the recognition process.¹⁷

Figure 2 presents the results obtained when the GaN device is coated with a self-assembled monolayer of achiral molecules (MPA: 3-mercaptopropanoic acid) or with chiral α -

helical oligopeptides of variable length L-SHCH₂CH₂CO- $\{Ala-Aib\}_n$ -COOH, where n=5,7,9 for AL-5, AL-7, and AL-9, respectively. The α -helical oligopeptides are covalently bound to the surface via the carboxylic group and to silver clusters (15-20 nm in diameter, see Fig. S1) through the thiol group at the other end (see Figure 1C for a schematic representation, See Figures S2, S3).

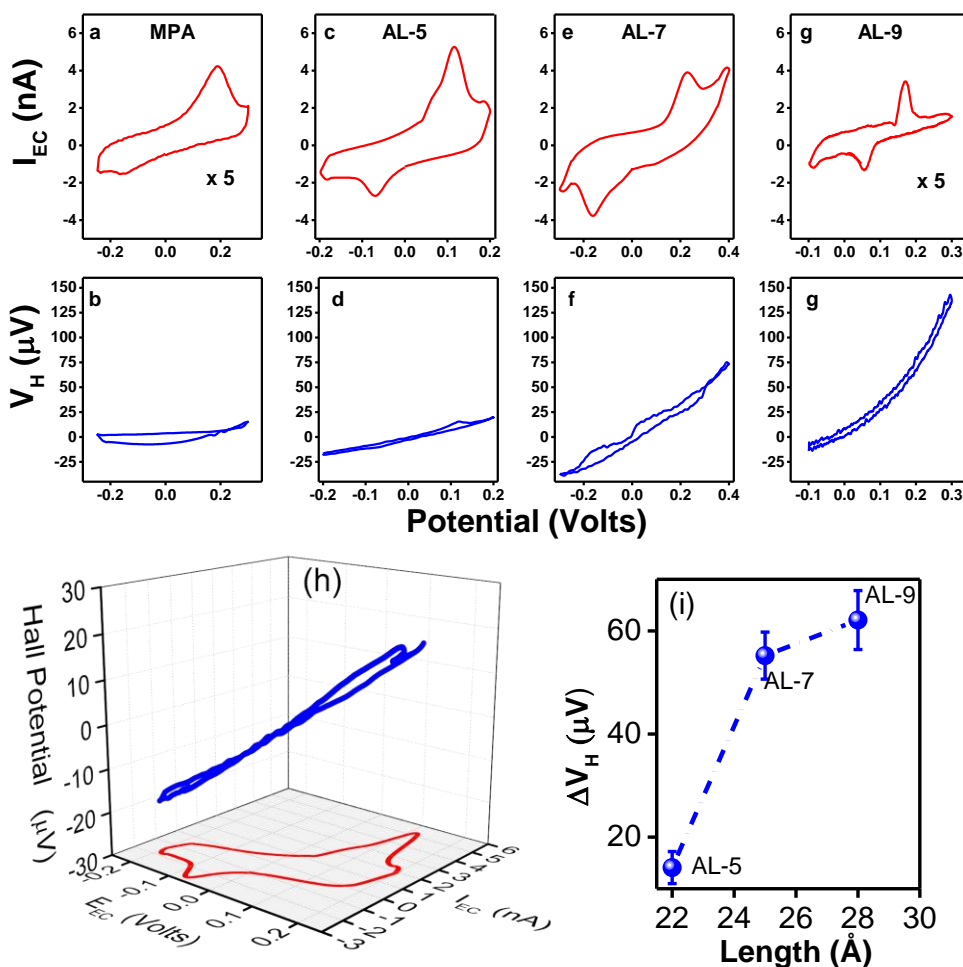


Figure 2: a-g) The current/potential characteristic curve (in red) and the Hall potential, V_H , (in blue) for achiral 3-mercapto propanoic acid (MPA), for the chiral oligopeptides L-SHCH₂CH₂CO- $\{Ala-Aib\}_n$ -COOH when AL-5, AL-7, and AL-9 refer to n= 5,7,9, respectively. h) The three-dimensional presentation of the results shown in panels (c) and (d). i) Hall potential difference, $\Delta V_H = V_{H(\text{ox peak})} - V_{H(\text{red peak})}$, as a function of the molecular length, when $V_{H(\text{ox peak})}$ is the Hall potential measured at the potential corresponding to the peak of the current in the oxidation regime and $V_{H(\text{red peak})}$ is the Hall potential measured at the potential corresponding to the peak in the current in the reduction regime. The peaks appear in the curves c, e, and g.

Note that the oxidation/reduction peaks in the CV curves are not expressed in the Hall potential measurements, indicating that the reduction and oxidation processes of the silver nanoparticles are not spin selective and that the spin selectivity arises from the electrons' conduction

through the adsorbed chiral monolayer. Another interesting observation is that despite the fact that the current in the CV process is almost constant for all molecules and even decreases somewhat for AL-9, the relevant measured Hall potential increases with the length of the adsorbed molecules. This observation is consistent with former studies of the CISS effect indicating that the spin polarization scales almost linearly with the length of the chiral molecules.⁸ Hence, Figure 2 clearly shows that by combining a Hall device with the electrochemical set-up, one can directly measure the spin polarization in the electrochemical process, without the need to apply magnetic fields or magnetic substrates.⁹

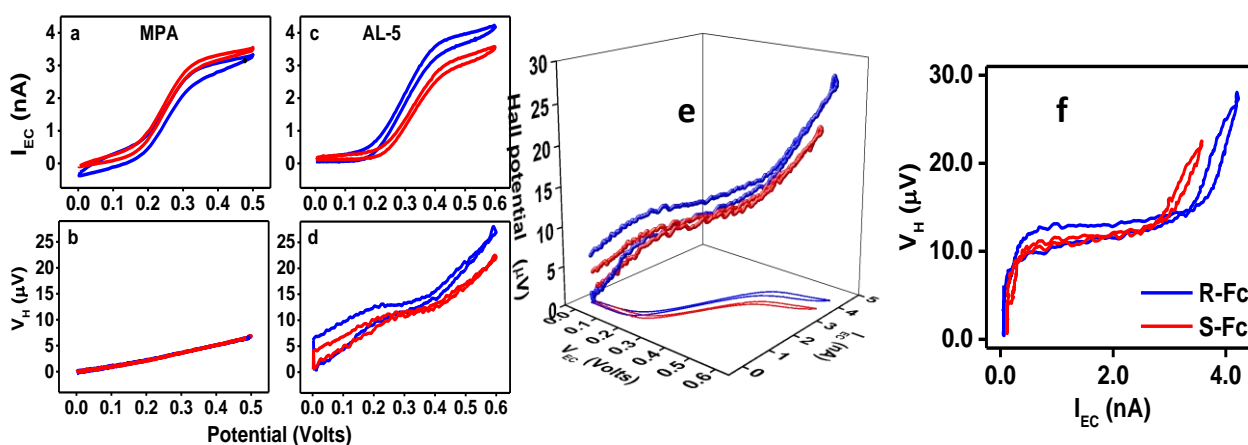


Figure 3: The enantio-selectivity data for devices coated with achiral molecules (a,b) and with chiral AL-5 (c,d) with R- and S-ferrocene (blue and red curves, respectively). e) The 3D presentation of the results of c,d. f) The variation of the Hall potential as a function of the current for a device coated with AL-5.

Once the properties of the 3D electrochemical device were established, we applied it for verifying the role of the electron spin in enantio-recognition. For verifying the role of spin polarization in the enantio-selectivity process, the device was coated with AL-5 and the redox couple was either (S)-(-)-N,N-Dimethyl-1-ferrocenylethylamine or (R)-(+)-N,N-Dimethyl-1-ferrocenylethylamine (S and R Ferrocene, respectively) dissolved in phosphate buffer (pH ~ 7). Since the device has a small surface area, it is not expected to observe the redox peaks in this type of experiments.²⁵⁻²⁷ Owing to the chiral working electrode, we observed enhanced current in the CV curve with R-ferrocene, as shown in Fig. 3. This observation is consistent with results obtained when chiral electrodes are used with a chiral redox couple. However, with the present set-up, we were also able to observe enhanced spin polarization with R-ferrocene (Fig. 3f).

If the spin polarization would result only from the polarization induced by the chiral monolayer, one would expect to observe a linear relation between the Hall signal and the current in the CV curve. A non-linear dependence of the Hall potential on this current indicates an additional spin-dependent process, namely, a spin-selective interaction between the chiral electrode and the chiral redox partner.

As shown in Fig. 3f, the Hall potential measured is not simply linear with the current. This is an indication that indeed, with the correct enantiomer (R-Ferrocene) the higher current is more spin polarized. This finding supports the proposed model that relates the enantio-recognition mechanism to an exchange energy term that is influenced by the spin polarization in chiral molecules. This observation is also consistent with previous studies that found a relation between spin-selective electron interaction with molecules and the electron-induced dissociation in those molecules.²⁸

Here we presented a new 3D spin electrochemistry method and demonstrated that the new device enables measuring spin-specific processes in electrochemical cells without a magnetic field or magnetic substrate. This method provides new insight into the role played by spin polarization in the interaction between two chiral molecular systems, here the adsorbed chiral (L)- α -helical oligopeptides and the chiral ferrocene derivatives. It indicates that indeed, spin polarization is a parameter that strongly affects the enantio-recognition process.

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