SCIENTIFIC
REPORTS

OPEN

SUBJECT AREAS:
ELECTROCATALYSIS
ASYMMETRIC CATALYSIS
METAL-ORGANIC FRAMEWORKS
MAGNETOSPHERIC PHYSICS

Received
13 February 2013

Accepted
15 August 2013

Published
3 September 2013

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Surface chirality induced by rotational electrodeposition in magnetic fields

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The surfaces of minerals could serve important catalytic roles in the prebiotic syntheses of organic molecules, such as amino acids. Thus, the surface chirality is responsible for the asymmetric syntheses of biomolecules. Here, we show induction of the surface chirality of copper metal film by electrodeposition via electrochemical cell rotation in magnetic fields. Such copper film electrodes exhibit chiral behaviour in the electrochemical reaction of alanine enantiomers, and the rotating direction allows control of the chiral sign. These findings are discussed in connection with the asymmetric influence of the system rotation on the magnetohydrodynamic micro-vortices around the electrode surfaces.

Many types of chiral molecules exist in biochemical systems, in which one enantiomer is active and the other is inactive. These differences in activity depending on the chirality of biomolecules are related to the origin of life on Earth and are one of the most attractive mysteries in the life sciences. A number of reports have proposed[1] mechanisms of homochirality, such as those for circularly polarised light[2,3], magneto-chiral fields[4], vortex and stirring conditions[5–9], and nonlinear autocatalysis[10–12]. However, a final conclusion regarding a universal homochirality mechanism has not yet been reached.

Regarding the molecular evolution of life, the surfaces of minerals, *e.g.* iron sulfide, are likely to have catalysed prebiotic reactions to produce biomolecules such as amino acids in the oceans on early Earth[13,14]. If such catalytic surfaces were chiral, then one biomolecule enantiomer would be rich and another would be poor. Thus, the chiral formations on metal or metal compound surfaces could be a key processes in the origin of the homochirality in biomolecules. One of the most probable symmetry-breaking inductions is the vortex motion of fluids for deposition and crystal growth in the oceans. Ribo *et al.*[5] demonstrated the chiral sign induction in the aggregation of achiral porphyrins in aqueous solutions through vortices. Tsujimoto *et al.*[9] reported that DNA molecules could align helically in a vortex generated by mechanical stirring. Thus, even macroscopic vortices have an asymmetric influence on supramolecular formation and alignment at the nanometer scale. Here, we report the chirality induction in metal electrodeposits through the magnetohydrodynamic micro-vortex motion of fluids.

Aogaki showed that electrolysis in a magnetic field (magnetoelectrolysis) causes vortices on electrode surfaces[15]. Similarly, we previously reported that magnetoelectrodeposition produces chiral surfaces on silver[16,17] and copper[18,19] metal thin films. When a magnetic field is imposed on an electrochemical cell, the Lorentz force acting on the faradaic currents generates convections around the electrodes in the electrolytic solutions[20,21]. This phenomenon is well known as the MHD (magnetohydrodynamic) effect. Figure 1a shows two types of MHD effects on an electrodeposition process where the magnetic field is perpendicular to the surface of a working disc electrode. Electrodeposition is a non-equilibrium phenomenon; thus, non-equilibrium fluctuations produce multiple humps on the deposit surfaces. The Lorentz force acting on the currents around the humps causes micro-vortices near the surface (No. 3 in Figure 1a). This process is termed the micro-MHD effect[15]. Micro-MHD vortices have been indirectly observed as circular structures[15] or network structures[18,22] of the electrodeposits. Another MHD effect produces a macroscopic flow around the electrode edge, where the current direction is not parallel to the magnetic field, causing the macroscopic flow to grow into a tornado-like rotating stream over the electrode surface. This phenomenon is termed the vertical MHD effect[15,23].

If the micro-MHD vortices are nanometer or sub-micrometer scale, they could produce chiral defects, such as screw dislocations, on the electrodeposit surfaces. In the micro-MHD effect, both clockwise and anticlockwise vortices must coexist on the electrode surface such that the adjoining flows never conflict with each other. As a result, a self-organised state is formed for the micro-MHD vortices, leading to the network structures of the electrodeposits. The coexistence of clockwise and anticlockwise vortices produces both right- and left-handed

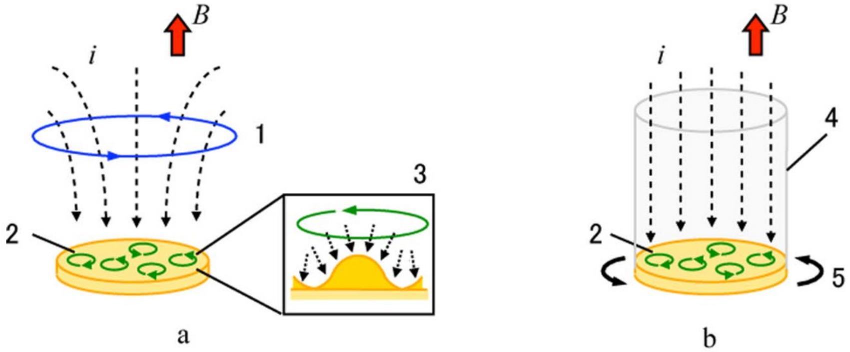

Figure 1 | **Two methods for symmetry breaking in the micro-MHD vortices.** (a) the influence of the vertical MHD flow and (b) the influence of the system rotation on symmetry breaking. The magnetic field *B* is perpendicular to the electrode surface and antiparallel to the faradaic current *i*. 1; vertical MHD flow around the electrode edge, 2; micro-MHD vortices, 3; schematic of the micro-MHD vortex around the non-equilibrium fluctuations (humps) on the deposit surface, 4; wall surrounding the electrode to suppress the vertical MHD flow, and 5; system (cell) rotation by an actuator.

chiral sites on the electrodeposits, and if the numbers of both chiral sites are equal, a racemic, or achiral, state is obtained.

Studies of vortices in astrophysical hydrodynamics have suggested symmetry breaking in the micro-MHD vortices. Sommeria *et al.*[24] studied vortices in a rotating annulus as a model experiment of Jupiter's Great Red Spot, and Marcus[25] attempted to numerically simulate the vortices in the Jovian atomosphere. According to their results, a stable vortex forms if the vorticity has the same sign as the surrounding azimuthal flow, whereas anticyclonic vortices become unstable and short-lived. These results suggest that the symmetry breaking of the inner small vortices is caused by the influence of the system's rotation or the surrounding rotating flow.

Aogaki and Morimoto proposed two methods to break the symmetry of the micro-MHD vortices[23]. The first method considers the influence of the vertical MHD flow on the micro-MHD vortices, as shown in Figure 1a. When micro-MHD vortices are excited within a macroscopic vertical MHD flow, the vertical MHD flow influences the micro-MHD vortices through the Coriolis force. The direction of the vertical MHD flow is anticlockwise in the configuration of Figure 1a, which is determined by the magnetic field vector and the faradaic current vector. Considering the results of the Jovian vortex studies, the cyclonic anticlockwise micro-MHD vortices would be stable, and the clockwise vortices would become unstable, resulting in the different relative amounts of right- and left-handed chiral sites on the deposit surfaces. Another method is a system rotation, which is the rotation of an electrolytic cell in magnetic fields that are perpendicular to the electrode surface, as shown in Figure 1b. System rotation also causes the Coriolis force to act on the vortex flow, and thus might induce chirality on the surface of the electrodeposits.

We attempted to explore the chiral surfaces of electrodeposited metal films in the configuration of Figure 1a, and we found chiral behaviour in the magnetoelectrodeposited (MED) Ag and Cu films[16–19]. The MED films were employed as electrodes, and the electrochemical reactions of chiral organic molecules, such as glucose[16,17], amino acids[18,19], and tartaric acid[26], were examined using voltammetry. The chiral behaviour of the MED film electrodes appeared as the reaction yield differences between the enantiomers, and the chiral signs in the voltammograms depend on the polarity of the magnetic fields during the electrodeposition. The latter data indicate that the surface chirality is determined by the direction of the vertical MHD flow. The chiral behaviours of the MED films depend on the preparation conditions of the magnetoelectrodeposition, including the magnetic field, electrodeposition potential, film thickness, and electrode diameters[17–19]. However, in most cases, the enantiomeric excesses of the reaction yields were not sufficiently large, approximately 0.03–0.1. In the configuration of Figure 1a, the homogeneous influence of the vertical MHD flow on the micro-MHD vortices over the entire electrode surface is difficult to predict. Thus, we have explored the high enantioselectivity of MED Cu films through the system rotation in magnetic fields, as shown in Figure 1b. Here, we present our experimental rotational magnetoelectrodeposition technique and the chiral electrochemical behaviours of such MED films.

Results

Figure 2 shows the experimental scheme of the magnetoelectrodeposition with the rotation of the electrolytic cell. The cylindrical cell (No. 4) is placed in a cryocooled superconducting magnet (No. 3) and is rotated by a non-magnetic ultrasonic motor (No. 1) located on the outside of the magnet. In the electrolytic cell, the rotating axis is on the centre of the working Cu disc electrode (WE; No. 6). The electrode is embedded in a sheath (No. 9) filled with the electrolytic solution to suppress the influence of the vertical MHD flow. The imposed magnetic field ***B*** is parallel to the rotational axis, antiparallel to the faradic current ***i***, and perpendicular to the electrode surface. This configuration satisfies the experimental conditions of Figure 1b.

The magnetoelectrodeposition of Cu films was conducted in a magnetic field of 5 T. The electrolytic cell was rotated during the electrodeposition with a frequency of 2 Hz in a clockwise (CW) or

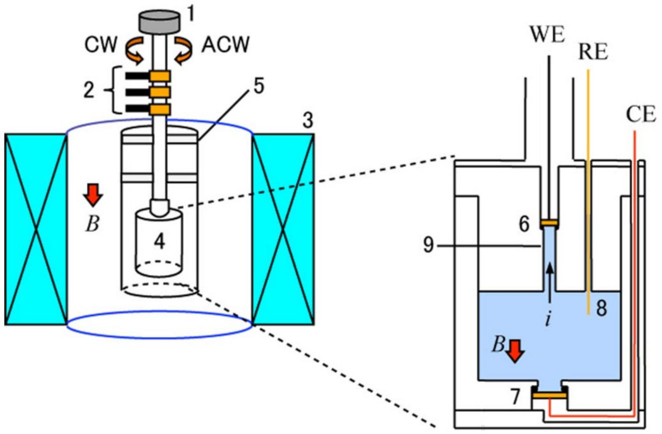

Figure 2 | **A schematic representing rotational electrodeposition in magnetic fields.** (1); an actuator (non-magnetic ultrasonic motor) to rotate the electrolytic cell in a clockwise (CW) or anticlockwise (ACW) sense (viewed from the bottom), (2); metal brushes for electric contacts, (3); a cryocooled superconducting magnet, (4); an electrolytic cell, (5); non-magnetic bearings, (6); a working electrode (WE), (7); a counter electrode (CE), (8); a reference electrode (RE), and (9); a sheath to suppress the vertical MHD flow.

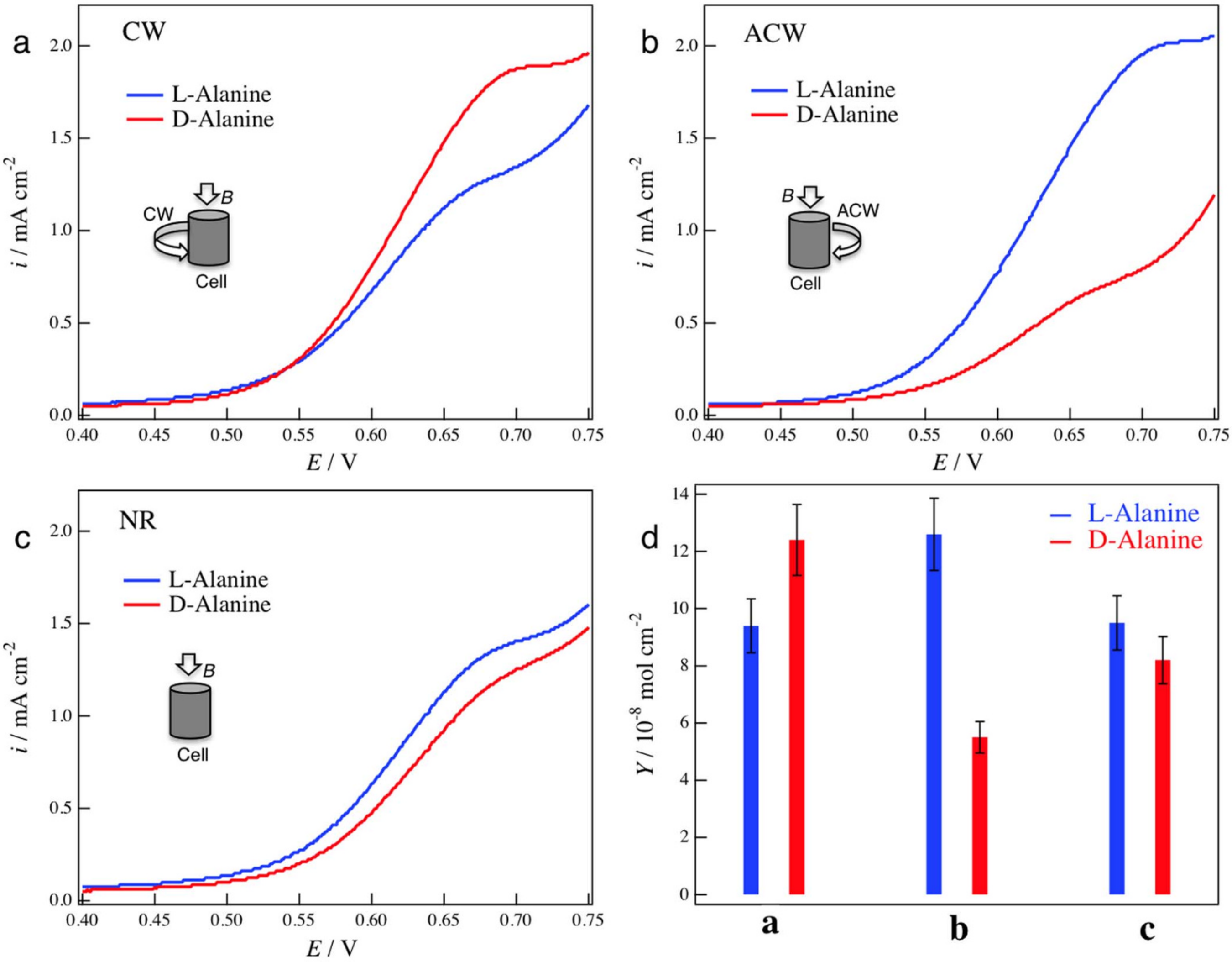

Figure 3 | **Chiral electrochemical behaviours in the voltammograms of alanine enantiomers on the MED Cu film electrodes.** (a) MED-CW film electrode, (b) MED-ACW film electrode, (c) MED-NR film electrode, and (d) reaction yield *Y* of alanine enantiomers using the three MED film electrodes are represented. The insets in (a)–(c) show the rotation configurations during the MED film preparation. The voltammograms represent the faradaic current *i* against the sweeping potential *E* of the working electrode. The voltammogram data were recorded using the following parameters: 20 mM alanine, 0.1 M NaOH aqueous solution, and a linear potential sweep rate of 10 mV s^{-1}. The reaction yields are estimated from the integration of the currents of each voltammogram in (a) – (c). The error bars in (d) reflect the reaction yields of multiple rotational magnetoelectrodeposition experiments for each condition.

anticlockwise (ACW) direction (viewed from the bottom of cell). In this study, the MED films with the CW and ACW rotations and with no rotation are termed MED-CW, MED-ACW, and MED-NR films, respectively.

The MED Cu films were used as electrodes after oxidising the surface from Cu to CuO, as described below (in the Methods section). The chiral behaviours of the MED film electrodes were examined using the voltammetric measurements of alanine (an amino acids). Voltammetry measures the *i* of electrode reactions with the linear potential (*E*) sweep of a working electrode. Figures 3a–3c present the voltammograms of alanine enantiomers with the MED-CW, MED-ACW and MED-NR film electrodes, respectively. The voltammograms exhibit a current increase at approximately 0.55–0.7 V, which corresponds to the oxidation currents of alanine. Figure 3d lists the reaction yields of the alanine enantiomers on the three MED film electrodes; the reaction yield represents the proportion (mol number) of alanine reacting on the electrode surface during the voltammetric sampling period.

Obvious chiral behaviour is observed in the voltammograms and in the reaction yields from the MED-CW and MED-ACW film electrodes. The oxidation current and reaction yield of D-alanine are greater than those of L-alanine on the MED-CW film electrode. However, the current and yield of L-alanine are greater than those of D-alanine on the MED-ACW film electrode. The MED-NR film electrode shows minimal chiral behaviour, as shown in Figure 3c. The oxidation current of L-alanine is slightly larger than that of D-alanine. The enantiomeric excess (*ee*) ratio in the reaction yields of the enantiomers can be defined as $ee = (Y_L - Y_D)/(Y_L + Y_D)$, where Y_L and Y_D represent the reaction yields of L- and D-alanines, respectively. Whereas the *ee* ratio is –0.13 on the MED-CW film electrode, it is considerably larger, 0.39, on the MED-ACW film electrode. The *ee* ratio is only 0.07 on the MED-NR film electrode.

Discussion

The minimal chiral behaviour of the MED-NR film electrodes indicates that both CW and ACW micro-MHD vortices coexist on the electrode surface and that the symmetry primarily remains in the self-organised configuration for both vortices. The slight current difference might be due to the influence of the vertical MHD flows from the outer edge of the sheath. In contrast, the clear chiral behaviours of the MED-CW and MED-ACW film electrodes demonstrate that the combination of magnetoelectrodeposition with mechanical cell rotation induces chirality on the surfaces of electrodeposited films and that the rotation direction controls the surface chirality. These results imply that cell rotation results in the difference between the motions of the CW and ACW micro-MHD vortices, and thereby inducing symmetry breaking in the micro-MHD vortices. Assuming that the Jovian vortex studies are applicable to the present case, the cyclonic micro-MHD vortices become stable and contribute to the formation of the chiral site, whereas the anticyclonic micro-MHD vortices become unstable and only minimally contribute to the chirality. Furthermore, the *ee* ratios in the reaction yields are quite large (approximately 0.1–0.4) compared to the 0.03–0.1 for the combination of the vertical MHD flows and the micro-MHD vortices as shown in Figure 1a. These data suggest that the influence of the cell rotation is more homogeneous and effective than that of the vertical MHD flow.

The chiral behaviours of the MED-CW and MED-ACW films depended on the magnetic field strength during magnetoelectrodeposition. Both MED film electrodes prepared in a magnetic field of 1 T showed no chiral behaviour. This magnetic field strength is too small for the self-organised state of the micro-MHD vortices to form on the electrode surface[19]. Both of the MED film electrodes prepared in an 8 T magnetic field also exhibited relatively little chiral behaviour. The *ee* ratios were 0.1 for the MED-CW films and 0.03 for the MED-ACW films. This result suggests that the magnetic field of 8 T is too strong to synchronise the micro-MHD vortices with a 2 Hz rotation. If the chiral behaviour depends on the rotation frequency, then an optimal combination of frequency and magnetic field could be found to obtain high enantioselectivity. Exploring such experimental conditions is the next stage of this research.

The possible chiral sites on the MED Cu films are interesting. Switzer *et al.*[27] reported the chiral electrodeposition of CuO (111) faces on Au (001) substrates in the presence of a chiral tartrate ion in an electrolytic solution. These authors showed that chirality exists in the crystal structure of the CuO (111) faces. In our experiments, both the substrate electrode and the MED films were polycrystalline, and the electrolytic solutions did not contain any chiral species during the magnetoelectrodeposition and pre-treatment. Furthermore, the origin of chirality is attributed to the micro-MHD vortices; Aogaki and Morimoto[23] suggested the formation of screw dislocations on a deposit surface from the micro-MHD vortices. Hence, the most probable chiral site is a screw dislocation on the film surface. Such a singularity on an electrode surface could be an electrochemically active site on which the specific adsorption and the electron-transfer reaction occur preferentially[28]. In the present case with the Cu film and alanine, ACW rotation promotes the formation of L-active sites, while CW rotation promotes D-active sites. Examination of the general relationship between the surface chirality and the rotating direction is a priority for our future research.

We have demonstrated that magnetoelectrodeposition with cell rotation induces chirality on Cu film surfaces and that the direction of the rotation controls the chirality. The chiral structures on the electrodeposit surfaces can be controlled by the macroscopic cell rotation. This fact arises from the interference effect of the cell rotation on the micro-MHD vortices near the electrode. This method can be applied to the preparation of chiral catalytic surfaces without chiral chemicals, which is favourable from the viewpoint of green chemistry.

Methods

In the electrodeposition experiments, a conventional three-electrode system was employed: a polycrystalline Cu disc working electrode with a diameter of 3.2 mm, a Cu plate counter electrode, and a Cu wire reference electrode. The Cu films were formed on the Cu working electrode via the potentiostatic electrodeposition at a potential of −0.45 V (vs. Cu) in a 50 mM $CuSO_4$ aqueous solution containing 0.5 M H_2SO_4. To minimise the influence of the vertical MHD flows at the outer edge of the sheath, a pulse electrodeposition technique was employed with a pulse width of 5 s. The total passing charge was 0.4 C cm^{-2}, and the film thickness was approximately 150 nm. In the voltammetric measurements of alanine, three electrodes were employed: a MED Cu film working electrode, a Pt wire counter electrode, and a Ag | AgCl | 3 M NaCl reference electrode. Because Cu metal is more easily oxidised than alanine in an alkaline solution, the Cu film electrodes underwent a potential sweep pre-treatment (−0.3–0.4 V) in a 0.1 M NaOH aqueous solution, forming a stable oxide film of CuO on the surface[18]. The voltammetric conditions were the following: 20 mM alanine, a 0.1 M NaOH aqueous solution, and a linear potential sweep rate of 10 mV s^{-1}.

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Acknowledgments

This research was partially supported by the High Field Laboratory for Superconducting Materials (HFLSM) of IMR Tohoku University. The authors thank the staff members of HFLSM for the use of their cryocooled superconducting magnet.

Author contributions

I.M. and K.W. initiated the chirality research using the magnetoelectrodeposition. R.M. and R.A. proposed the idea of chirality induction via the rotational electrodeposition in magnetic fields and prepared the handmade apparatus used in this work. I.M., R.M. and R.A. conducted the rotational magnetoelectrodeposition and the voltammetric measurements to examine the chiral behaviours of the MED films. K.W. provided a cryocooled superconducting magnet to perform the magnetoelectrodeposition. I.M. wrote the manuscript with advice and assistance from R.A. and R.M.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Mogi, I., Morimoto, R., Aogaki, R. & Watanabe, K. Surface chirality induced by rotational electrodeposition in magnetic fields. *Sci. Rep.* **3**, 2574; DOI:10.1038/srep02574 (2013).