Current-dependent formation of Bechgaard salt nanocrystals using nanoscale electrocrystallization for the fabrication of organic nanodevices

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Abstract

Herein, the nanocrystal formation of tetramethyltetraselenafulvalene (TMTSF)-based nanocrystals based on nanoscale electrocrystallization is reported. Whereas direct current electrolysis produced nanocrystals over the entire anode surface, nanocrystals were only formed in the gap between the two electrodes using alternating current (AC) electrolysis. Consequently, a two-terminal device where nanocrystals bridge the source and drain electrodes was simply prepared via this one-step electrolysis process. The prepared nanocrystal had the same structure as the bulk crystal of $(\text{TMTSF})_2\cdot\text{ClO}_4$, which is known as a superconducting Bechgaard salt. Although the nanocrystal

exhibited a metallic nature, weak gate-voltage-dependent characteristics were observed in the current–voltage characteristics measurements. Facile fabrication of organic nanodevices was thus enabled using this AC electrolysis method.

1. Introduction

Nanofabrication is a fundamental technology for next-generation electronics, and excellent nanofabrication technologies based on silicon devices are already available. However, these fabrication technologies generally consume a large amount of energy under high-vacuum and/or high-temperature conditions. To protect the global environment, energy-saving nanofabrication technologies are needed in the near future, and organic materials appear to be promising candidates for such eco-friendly nanofabrication [1–4]. These materials can be applied to energy-saving processes such as spin-coating methods, self-assembled monolayers, and printing techniques [4,5], and great efforts have thus been dedicated to fabrication using organic devices. The novel nanofabrication of organic devices based on bottom-up technology has also actively been performed to minimize the device sizes for integrated devices [6,7]. The simple,

well-controlled, and eco-friendly fabrication of highly oriented organic material is expected to yield practical organic nanoscale devices.

To achieve well-controlled and eco-friendly nanodevice fabrication, electrochemical techniques are one of the most applicable methods for the following reasons. First, site-selective fabrication is possible as material deposition is generally limited to the electrode surface because an electrochemical reaction occurs on the electrode. Second, the product amount is controllable and generally proportional to the quantity of electricity. Third, selection of materials is possible because each organic material has a different redox potential, which is controllable based on the molecular design. Finally, the electrochemical technique can occur at room temperature under ambient conditions, and there is no need for high-energy-consumption instruments. Accordingly, various nanofabrication techniques based on electrochemical methods have been developed [8–10].

We previously developed a technique called *nanoscale electrocrystallization*, which is a highly promising nanofabrication approach based on *bulk* electrocrystallization [11–13] that is used for the synthesis of organic conducting bulk crystals [14]. When DC

electrolysis is used for site-selective fabrication, the electrodes must be modified because the DC electrolysis yields products over the entire electrode surface. To date, some fabrication techniques for organic nanocrystals based on DC electrocrystallization have been reported [8,15–17]. Unlike these methods, our nanoscale electrocrystallization does not require modification of the electrodes to site-selectively form nanocrystals. Nanoscale electrocrystallization based on alternating current (AC) electrolysis enables us to site-selectively grow nanocrystals in the gap between the two electrodes on the substrate, eventually forming a bridge between the two electrodes. The nanoscale electrocrystallization yields nanocrystals with three types of electronic states through the electrochemical reaction. In our previous reports, we demonstrated the site-selective fabrication of partially π -electron oxidized and completely one- π -electron oxidized nanocrystals using phthalocyanine derivatives [11–13,18,19]. In addition, non- π -electron oxidized nanocrystals can be obtained using some types of metal complexes. We also reported the first example of negative giant magnetoresistance in an organic nanocrystal [20] as well as the field-effect characteristics of the nanocrystal [21–23] using site-selectively as-grown nanocrystals as devices. Thus, the nanoscale

electrocrystallization can potentially be applied to various organic conductors because it is based on *bulk* electrocrystallization.

In this paper, the first attempt of site-selective growth of tetramethyltetraselenafulvalene [TMTSF, Fig. 1(a)][24] -based nanocrystals using nanoscale electrocrystallization as well as the application of bridged as-grown nanocrystals in an electronic device are reported. TMTSF is a well-known component of the first organic superconductor [25–27]. Bechgaard *et al.* developed a TMTSF-based superconductor via heavy atom substitution of tetrathiafulvalene (TTF)-based compounds. Bulk electrocrystallization of TMTSF and tetrabutylammonium perchlorate in trichloroethane yielded a $(\text{TMTSF})_2 \cdot \text{ClO}_4$ crystal [25], which exhibited superconductivity below 1.4 K at ambient pressure [27]. Perruchas *et al.* also reported a new polymorph of μ'' -(TMTSF) $_2 \cdot \text{ClO}_4$ in 2005 [28]. The special electronic properties are modulated by minimization of the material and through external fields such as electric fields. Fine nanocrystals based on TMTSF were also reported [29–32]; thus, minimization of this material is gaining much attention. Accordingly, TMTSF was applied to nanoscale electrocrystallization to discover novel properties for future device application.

2. Results and Discussion

2.1. Nanocrystal growth

The TMTSF-based nanocrystals were first site-selectively synthesized using nanoscale electrocrystallization without any modification of the electrode surface. The original single compartment glass cell with a multi-tip electrode substrate shown in Fig. 1(b) was used for electrolysis [33]. The crystal growth in electrocrystallization primarily occurs on the electrode where the electrochemical reaction occurs. For donor molecules, which include TMTSF molecules, crystals generally grow on the anode surface. This situation was also observed in the nanocrystals when tetrabutylammonium perchlorate was used as the supporting electrolyte. Fig. 2(a) shows the $(\text{TMTSF})_2\cdot\text{ClO}_4$ nanocrystal formed using DC electrolysis (1.0 V, 5 min.). The nanocrystals were formed over the entire anode surface.

However, when AC was used for the electrolysis, the nanocrystals were formed only in the gap between the two electrodes. Fig. 2(b) shows the $(\text{TMTSF})_2\cdot\text{ClO}_4$ nanocrystal formed using AC electrolysis (1.25 V, 5 kHz, square waveform, 5 s, 10 times with 15-s pause between each step). The nanocrystals of both electrochemical conditions appear

morphologically similar even though the growth patterns are different. Therefore, this noteworthy phenomenon of site-selective crystal growth is not an electrophoresis but an electrochemical reaction. As discussed in previous papers [13,20–23], the reasons behind the site-selectivity of the nanowire-formation process are considered to be the following: the concentration of the oxidized species around the gap is higher than that in the other areas, and the slope of the electric field is the steepest in the gap area.

Furthermore, the site-selective fabrication of this material was refined by adjusting the electrochemical conditions. As observed in Fig. 2(b), nanocrystals were grown mainly in the narrowest area of the gap when an AC was applied. In particular, an AC voltage of 1.25 V at 2.0 kHz with a square waveform applied for 5 min enables more controlled nanocrystal formation [Fig. 2(c)], and a nanocrystal bridge structure between the two electrodes was ultimately obtained. Overall, for this nanoscale electrocrystallization, the typical nanocrystals ranged from 100 nm to approximately 3 μm in width and were less than 50 μm in length, and the sizes of the crystals depended on the electrolysis condition. The growth manner and amount of the nanocrystals depended on the electrolysis conditions. The amount of nanocrystals depended on the current and period

of electrolysis because the amount of product produced by the electrochemical process is generally proportional to the current and time [14]. In addition, the growth manner of the nanocrystals also depends on the frequency in AC electrolysis. Lower frequency electrolysis results in a wider growth area.

In addition to the ClO_4 salt, when tetrabutylammonium nitrate was used as the supporting electrolyte, $(\text{TMTSF})_2\cdot\text{NO}_3$ nanocrystals were also obtained in the same manner. Fig. 2(d) shows the site-selectively formed nanocrystal of $(\text{TMTSF})_2\cdot\text{NO}_3$ using AC electrolysis (2.0 V, 5.0 kHz, square waveform, 20 s). The nanocrystals were also formed in the gap between the two electrodes.

2.2. Structure of nanocrystals

The crystal morphologies of these materials are the same as those of bulk crystals indicated as $(\text{TMTSF})_2\cdot X$. The structure was investigated using a $(\text{TMTSF})_2\cdot\text{ClO}_4$ nanocrystal using selected area electron diffraction (SAED). A transmission electron microscopy (TEM) image and corresponding SAED pattern are presented in Figs. 3(a) and (b), respectively. Although the sample nanocrystals were slightly damaged during the transfer process onto the mesh, the diffraction pattern was obtained and resolved

using a lattice parameter of the bulk crystal [25] with an error of less than 1.9 %. This type of nanocrystal was observed to have the same structure as the partially oxidized crystal $(\text{TMTSF})_2\cdot\text{ClO}_4$. The crystal structure is shown in **Figure 3(d)**.

2.3. Electronic properties of $(\text{TMTSF})_2\cdot\text{ClO}_4$ nanocrystals

The field-effect characteristics of the nanocrystals showed weak n-type-like behavior that was also observed in the TTF-based nanocrystal [23]. The nanoscale electrocrystallization also produced a two-terminal device by reusing the two electrochemical electrodes as source and drain electrodes. A bottom-gate-type field-effect transistor structure could also be obtained when the two-terminal device was fabricated on a silicon substrate with an oxide layer as shown in Fig. 4(a). Therefore, the electrical properties were measured using the as-grown nanowires that bridged the two electrodes. To avoid the effect of impurities during electrolysis, the substrate was rinsed with pure methanol and dried before measurements. The linear behavior of the I - V characteristics in Fig. 4(b) suggests that the contact between electrodes and nanocrystals is ohmic. The $I_{\text{ds}}-V_{\text{ds}}$ plots become steeper with increasing gate voltage as observed in n-type semiconductors. Because the band structure of this crystal comprised of partially

oxidized TMTSF molecules is considered metallic, this result might appear inconsistent.

In addition to probable causes such as the gate-dependent contact resistance and/or charge injection barriers of the interface, the bias of the counter anions in the crystal was also considered a probable cause of this phenomena in the TTF-based nanocrystals [23]. Based on the SAED structure analysis, the chemical composition of this material is as the same as the $(\text{TMTSF})_2 \cdot \text{ClO}_4$ crystal, which includes disordered ClO_4^- anions.

Therefore, the anomalous $I_{\text{ds}}-V_{\text{ds}}$ characteristics may be also due to the bias of the orientation of ClO_4^- anions in the crystal in addition to the aforementioned causes. In TMTSF cation radical salts, it is known that metal–insulator transition due to disorder of the anion occurs [14]. Therefore, order/disorder of the anions has a great effect on the properties of the crystal. If the anomalous behavior here is due to the anion ordering by an electric field, new devices with the unusual properties will be developed. Further investigations of the electrical properties of the nanocrystals based on organic radical salts will open new possibilities for device development.

3. Summary

In summary, TMTSF-based nanocrystals were first prepared using nanoscale electrocrystallization based on AC electrolysis, and the applicability of this technique was successfully enhanced. These nanocrystals were only formed in the gap between the two electrodes and eventually formed a nanocrystal bridge between the two electrodes when perchlorate and nitrate anions were used as counter ions. Therefore, a two-terminal device was easily prepared when two electrochemical electrodes were used as the source and drain electrodes. SAED structural analysis first revealed that the structure of the nanocrystal was identical to that of the bulk crystal. The electronic characteristics of $(\text{TMTSF})_2 \cdot \text{ClO}_4$ indicated a weak n-type-like character even though this material has a metallic band structure. Considering the crystal structure of this nanocrystal, the bias of the orientation of ClO_4^- anions caused by the electric field could also be responsible for this anomalous behavior. This method has the potential to be extended to various organic molecules, and the enhancement of this method will enable us to prepare various desired devices by merely selecting an appropriate molecule with the desired properties. The semiconductor industry generally uses high-energy-consumption processes such as ultrahigh vacuum techniques and sputtering.

Thus, nanoscale electrocrystallization could be potentially useful for eco-friendly nanofabrication processes in the next generation.

4. Material and Methods

Electrochemical preparation of TMTSF-based nanocrystals: Nanocrystal growth was performed following a previously reported procedure for nanoscale electrocrystallization [11–13]. Tetrahydrofuran (THF, anhydrate, no stabilizer, purest grade, Wako Pure Chemical Industries, Ltd.) was used as a solvent. TMTSF (Aldrich) and an excess amount of an appropriate counter anion salt [tetrabutylammonium perchlorate (Strem Chemicals Inc.), tetrabutylammonium nitrate (Wako Pure Chemical Industries, Ltd.)] were dissolved in the THF. The solution was placed in a one-compartment electrochemical cell [Figure 1(b)][\[33\]](#) using a syringe filter (Sartorius Minisart RC15). To grow nanocrystals, an electrode substrate was then dipped into the solution. The electrode substrate consisted of two electrodes and was used for both electrolysis and electronic property measurements. Two electrodes were made from platinum using a conventional lift-off photolithography technique. The gap between the two electrodes was 5 μm . Alternating voltage in the form of a square waveform was

applied between the electrodes at room temperature where the amplitudes ranged from 1.0 to 3.0 V and the frequencies ranged from 1.5 to 2.0 kHz. The electrolysis lasted from 2 to 30 min. Similar to the previous report [23], pauses were also introduced during the electrolysis in some batches to examine the effect of diffusion of the reactants. Afterward, the substrates were dipped into pure THF to prevent recrystallization of the starting material.

Electron microscopy: The morphology of the nanocrystals was characterized using a JEOL JSM-6700F field-emission scanning electron microscope at an acceleration voltage of 5.0 kV. TEM and SAED analyses were performed using a JEOL JEM-1400 transmission electron microscope at an acceleration voltage of 120 kV. The sample was prepared by the transfer method using an acetyl cellulose film. The camera constant (λL) was 9.83 cm·Å.

Electronic property measurements: A homemade electrical transport measurement apparatus equipped with an ADC 8252 digital electrometer/source, ADC 6243 voltage/current source, and Keithley 2636A dual-channel system source meter was used. These instruments were controlled by custom-written software. All the measurements

were performed at room temperature under vacuum conditions. The transport measurements were performed in several batches, and the transport properties were confirmed to be qualitatively reproducible.

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References

- [1] H. Klauk (Ed.), Organic Electronics: Materials, Manufacturing, and Applications, Wiley-VCH: Weinheim, 2006.
- [2] M. Köhler, W. Fritzsche, Nanotechnology 2nd, Completely Revised Ed., Wiley-VCH: Weinheim, 2007, Ch. 5.
- [3] W.S. Wong, A. Salleo (Eds.), Flexible Electronics: Materials and Applications, Springer Science+Business Media , New York, 2009.
- [4] E. Cantatore (Ed.), Applications of Organic and Printed Electronics: A Technology-Enabled Revolution, Springer Science+Business Media , New York, 2013.
- [5] I.M. Hutchings, G.D. Martin (Eds.), Inkjet Technology for Digital Fabrication, Wiley-VCH: Weinheim, 2012.
- [6] J. Ramsden, Nanotechnology: An Introduction, Elsevier, Oxford, 2011, Ch. 8.
- [7] H.-G. Rubahn, Basics of Nanotechnology; Wiley-VCH, Weinheim, 2008.

- [8] F. Favier, H. Liu, R.M. Penner, Size-Selective Growth of Nanoscale Tetrathiafulvalene Bromide Crystallites on Platinum Particles, *Adv. Mater.* 13 (2001) 1567–1570.
- [9] M. Matsuda, N. Kinoshita, M. Fujishima, S. Tanaka, H. Tajima, H. Hasegawa, Electrochemically Fabricated Phthalocyanine-Based Molecular Conductor Films and Their Potential Use in Organic Electronic Devices, *Appl. Phys. Express* 6 (2013) 021602.
- [10] M. Matsuda, M. Nishi, S. Koga, M. Fujishima, N. Hoshino, T. Akutagawa, H. Hasegawa, Novel Method for the Fabrication of a Charge-Transfer Complex Crystal by Photoirradiation, *Chem. Eur. J.* 20 (2014) 11318–11321.
- [11] H. Hasegawa, T. Kubota, S. Mashiko, Fabrication of Molecular Nanowire Using an Electrochemical Method, *Thin Solid Films* 438–439 (2003) 352–355.
- [12] H. Hasegawa, T. Kubota, S. Mashiko, An Electrochemical Fabrication of Nanowire Comprised of Phthalocyanine, *Synth. Met.* 135–136 (2003) 763–764.

- [13] H. Hasegawa, T. Kubota, S. Mashiko, Site-selective Fabrication of Conducting Molecular Nanowires Based on Electrocrystallization, *Electrochim. Acta* 50 (2005) 3029–3032.
- [14] T. Ishiguro, K. Yamaji, G. Saito, *Organic Superconductors*, 2nd ed.; Springer-Verlag: Berlin, Germany 1998, Ch. 11.
- [15] J.-P. Savy, D. de Caro, C. Faulmann, L. Valade, M. Almeida, T. Koike, H. Fujiwara, T. Sugimoto, J. Fraxedas, T. Ondarçuhuf, C. Pasquier, Nanowires of Molecule-based Charge-transfer Salts, *New J. Chem.* 31 (2007) 519–527.
- [16] K. Kobayashi, H. Koyama, K. Ishikura, T. Mitsui, Growth and Observation of Micro-organic Crystals in Two-dimensional Glass Nanovolume Cell, *Appl. Phys. Lett.* 93 (2008) 143114.
- [17] L. Ren, X. Xian, K. Yan, L. Fu, Y. Liu, S. Chen, Z. Liu, A General Electrochemical Strategy for Synthesizing Charge-Transfer Complex Micro/Nanowires, *Adv. Funct. Mater.* 20 (2010) 1209–1223.

- [18] H. Hasegawa, R. Ueda, T. Kubota, S. Mashiko, Multiple Simultaneous Fabrication of Molecular Nanowires Using Nanoscale Electrocrystallization, *Thin Solid Films* 499 (2006) 289–292.
- [19] H. Hasegawa, Y. Noguchi, R. Ueda, T. Kubota, S. Mashiko, Organic Mott insulator-based nanowire formed by using the Nanoscale-electrocrystallization, *Thin Solid Films* 516 (2008) 2491–2494.
- [20] H. Hasegawa, M. Matsuda, H. Tajima, Giant negative magnetoresistance in an organic nanocrystal: site-selective device fabrication by nanoscale electrocrystallization, *J. Mater. Chem. C* 1 (2013) 6416–6421.
- [21] H. Hasegawa, Fabrication of sodium phthalocyanine nanocrystals using nanoscale electrocrystallization, *New J. Chem.* 37 (2013) 2271–2274.
- [22] H. Hasegawa, Site-Selective Electrochemical Fabrication of Lithium Phthalocyanine Nanocrystals, *Sci. Adv. Mater.* 6 (2014) 1548–1552.
- [23] H. Hasegawa, Tetrathiafulvalene-based Nanocrystals: Site-selective Formation, Device Fabrication, and Electrical Properties, *J. Mater. Chem. C* 3 (2015) 8986–8991.

[24] K. Bechgaard, C.S. Jacobsen, K. Mortensen, H.J. Pedersen, N. Thorup, The Properties of Five Highly Conducting Salts: $(\text{TMTSF})_2\text{X}$, $\text{X} = \text{PF}_6^-$, AsF_6^- , SbF_6^- , BF_4^- and NO_3^- , Derived from Tetramethyltetraselenafulvalene (TMTSF), Solid State Commun. 33 (1980) 1119–1125.

[25] K. Bechgaard, K. Carneiro, F.B. Rasmussen, and M. Olsen, Superconductivity in an Organic Solid. Synthesis, Structure, and Conductivity of Bis(tetramethyltetraselenafulvalenium) Perchlorate, $(\text{TMTSF})_2\text{ClO}_4$, J. Am. Chem. Soc. 103 (1981) 2440–2442.

[26] K. Bechgaard, K. Carneiro, M. Olsen, F.B. Rasmussen, C.S. Jacobsen, Zero-Pressure Organic Superconductor: Di-(Tetramethyltetraselenafulvalenium)-Perchlorate $[(\text{TMTSF})_2\text{ClO}_4]$, Phys. Rev. Lett. 103 (1981) 2440–2442.

[27] S.S.P. Parkin, M. Ribault, D. Jérôme, K. Bechgaard, Superconductivity in the Family of Organic Salts Based on the Tetramethyltetraselenafulvalene(TMTSF) Molecule: $(\text{TMTSF})_2\text{X}$ ($\text{X} = \text{ClO}_4$, PF_6 , AsF_6 , SbF_6 , TaF_6), J. Phys. C 14 (1981) 5305–5326.

[28] S. Perruchas, J. Fraxedas, E. Canadell, P.A-Senzier, P. Batail, Monoclinic

Polymorphs of Bechgaard and Fabre Salts, *Adv. Mater.* 17 (2005) 209–212.

[29] Y. J. Jung, Y. Kim, G. T. Kim, W. Kang, D.-Y. Noh, Electrochemical

Fabrication of (TMTSF)₂X (X = PF₆, BF₄, ClO₄) Nanowires, *J. Nanosci. Nanotechnol.*

12 (2012) 5397–5401.

[30] D. de Caro, K. Jacob, C. Faulmann, L. Valade, First Nanoparticles of

Bechgaard Salts, *C. R. Chimie* 16 (2013) 629–633.

[31] D. de Caro, L. Valade, C. Faulmann, K. Jacob, D. V. Dorselaer, I. Chtioui, L.

Salmon, A. Sabbar, S. E. Hajjaji, E. Pérez, S. Franceschi, J. Fraxedas, Nanoparticles of

Molecule-based Conductors, *New J. Chem.* 37 (2013) 3331–3336.

[32] D. de Caro, C. Faulmann, L. Valade, K. Jacob, I. Chtioui, S. Foulal, P. de

Caro, M. Bergez-Lacoste, J. Fraxedas, B. Ballesteros, J. S. Brooks, E. Steven, L. E.

Winter, Four Molecular Superconductors Isolated as Nanoparticles, *Eur. J. Inorg. Chem.*

(2014) 4010–4016.

[33] Commercially available from *Iwata Glass Industrial Co., Ltd.* as *Nanowire*

Fabrication Kit, <http://www.iwataglass.com>.

Figure 1. (a) Structure of TMTSF. (b) Electrochemical cell for nanoscale electrocrystallization. The cell consisted of the following components: (1) substrate holder, (2) electric terminal, (3) electrode, (4) substrate, (5) starting material solution, and (6) gaps.

Figure 2. (a) Formation of $(\text{TMTSF})_2 \cdot \text{ClO}_4$ nanocrystals using a DC voltage of 1.0 V applied for 5 min. Nanocrystals were grown over the entire anode surface. (b) The formation of $(\text{TMTSF})_2 \cdot \text{ClO}_4$ nanocrystals using AC electrolysis. Nanocrystals were

grown only around the gap between the two electrodes. (c) Site-selective fabrication of a $(\text{TMTSF})_2\cdot\text{ClO}_4$ nanocrystal using an AC voltage of 1.25 V at 2.0 kHz with a square waveform applied for 5 min. A nanocrystal was grown in the gap between the two electrodes. (d) The $(\text{TMTSF})_2\cdot\text{NO}_3$ nanocrystal formed in the gap using a AC voltage of 2.0 V at 5.0 kHz with a square waveform applied for 20 s. The nanocrystals also formed a bridge between the two electrodes.

Figure 3. (a) TEM image of nanocrystals transferred onto a mesh and (b) corresponding SAED pattern. (c) Crystal structure of $(\text{TMTSF})_2\cdot\text{ClO}_4$ crystal.

Figure 4. (a) Schematic of electrical properties measurements using the two electrochemical electrodes as source and drain electrodes. (b) The current–voltage (I_{ds} – V_{ds}) characteristics of phthalocyanine neutral radical nanocrystals for various gate voltages.

Graphical abstract