Supplementary Information for

Reversible Anionic Redox in Na₃RuO₄ Cathode: A Prototype Na-Rich

Layered Oxide

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Materials and Methods

1. Chemicals and Electrolyte

Propylene Carbonate (PC, Sigma Aldrich, 99%) solvent was dried over freshly activated 4 Å molecular sieves for several days. Sodium perchlorate salt (NaClO₄, purity of >98 %, Wako Chemicals) was dried by heating under vacuum at 80 °C oven overnight. Electrolytes with 1.0 M NaClO₄ in PC (with 2 vol% fluorinated ethylene carbonateethylene (FEC) additive) was prepared and stored in a glove box under Ar atmosphere. The water concentration in the electrolyte measured by Karl Fischer titration was below 75 ppm. Other chemicals employed for synthesis and spectrum assignment were purchased from Wako Chemicals Co. Inc. (Osaka, Japan).

2. Na₃RuO₄ Cathode Preparation

(a) <u>Na₃RuO₄ powder</u>: Single-phase Na₃RuO₄ was synthesized according to the previous report.¹ In brief, powder samples of Na₃RuO₄ were prepared by solid-state reactions from stoichiometric amounts of NaOH and RuO₂. The starting stoichiometric mixture was initially ground together and then held at 500 °C for 20 h under an O₂ atmosphere. After re-grinding, the powder was heated to 650 °C for another 20 h, again under an O₂ atmosphere. The resulting dark gray powder was reground and carefully checked for impurity phases using x-ray diffraction. If any impurity phases were evident, the powder was refired and the process repeated.

(b) <u>Na₃RuO₄ cathode</u>: the Na₃RuO₄ cathode film composed of Na₃RuO₄ powder, Ketjen black (KB, Type EC600JD, Lion Co. Ltd.) and polytetrafluoroethylene (PTFE) (A dispersion of 15 wt%, Du Pont-Mitsui Fluorochemicals Co. Ltd.) with a ratio of 85:10:5 wt% was rolled with a glass rod. The cathode film was pressed onto a smooth aluminum mesh substrate (0.11*100*100 mm, 100 mesh, No. 018100, Nilaco Co. Ltd.). After pressing, the Na₃RuO₄-loaded substrate was dried at 80 °C in an air oven for 1 hour, and final cathode plates (7 mm in diameter) were punched out to form the dried KB-loaded carbon paper. The punched cathodes were placed in separated glass bottles and further dried in vacuum at 100 °C for 10 hours, and then transferred to a glove box under Ar atmosphere. The final Na₃RuO₄ loading per cathode plate was ~2.5 mg/cm².

3. Cells Assembly

The typical assembly process of the 2032 coin-type cell was the same as our previous report.² The in-situ Raman cell herein (the photo and schematic of the cell is shown in Fig. S1) has been designed and modified based on the typical in-situ Raman cell for Li-ion battery (Hohsen Corp., Osaka, Japan). In detail, a thin quartz window (thickness, 0.5 mm) has been fixed on the top of the cell as a sight window. Gold nanoparticles (NPs) approximately 40 nm in diameter with a SiO₂ coating shell (~5 nm) were synthesized as in previous reports.³⁻⁵ The washed and dried Au@SiO₂ NPs were dripped onto the specific cathode surface and dried before assembly. The cathode was assembled at the bottom of the cell with the active material-face upward. On the top of the cathode, 50-100 μ L of electrolyte was homogeneously dropped onto the glassy fiber filter separator (GF/A, Whatman). As a standard two-electrode configuration cell, lithium foil (thickness, 0.4 mm) was assembled at the top as the reference and counter electrode. Note that, a small hole was punched on the center of both the separator and Li foil, through which the laser and Raman signals can fluidly cross. Note that the assembly of the cell was conducted in an Ar-filled glove box that has a dew point of around -90 °C and O₂ content below 5 ppm.

4. Electrochemical Measurements

For the in-situ Raman test, the electrochemical experiments were carried out under control of a potentiostat (Potentiostat/Galvanostat PGSTAT30, Autolab Co. Ltd., Netherlands) at room temperature. The current and potential outputs from the potentiostat were recorded by a multifunction data acquisition module/amplifier (PGSTAT30 Differential Electrometer, Autolab), which was controlled by General Purpose Electrochemical Software (GPES). Typically, the galvanostatic control was carried out at a current of 5 or 10 uA, and the linaer sweep mode was controlled at a sweeping rate of 10 mV s⁻¹. For the cathode assembled into the pouch cell, the electrochemical measurements were carried out under potential control using the battery tester system HJ1001SD8 (Hokuto Denko) at 25 °C. Typically, the characterizations of the cell were carried out under galvanostatic control at a current density of 50 mA g⁻¹ (based on the load mass of Na₃RuO₄) from OCP unless other noted. The potential limits were selected between 1.5 and 4.0 V in the study. The cell was kept on open circuit for 10 h. The OCP was approximately 3.0 V in most cases in the study. All of the potentials in this study were referenced to Na/Na⁺.

5. Raman Measurements

The Raman spectra were recorded using a JASCO microscope spectrometer (NRS-1000DT). The excitation light of an air-cooled He–Ne laser at 632.8 nm wavelength was focused on the electrode surface through a 50×long working distance lens (Olympus America Inc.). The confocal slit was adjusted to be 4.0 μ m to minimize the band broadening effect due to the contribution of non-confocal signal. The scattered light was collected in a backscattering geometry along the same optical path as the pumping laser. The power of laser beam delivered to the electrode surface was roughly 10% of the maximum 30 mW laser intensity, unless specified, to avoid degradation to the products and/or cathode. The Raman spectrum acquisition time varied from 600~800 s with 2 accumulations. At least 3 different places on the electrode surface at each cathode plate were checked to ensure the Raman spectra were credible and reproducible. The spectral resolution of the Raman spectra in the study was fixed at ca. 1.0 cm⁻¹.

6. Other Characterizations

X-ray photoelectron spectroscopy (XPS) was performed using a VG scientific ESCALAB 250 spectrometer with monochromic Al K α excitation. For the pretreatment of the XPS samples, the cycled cells were transferred into an Ar glove box once the discharge (or charge) finished, and the cathodes were extracted from the cell and placed in a glass bottle. The cathodes were twice rinsed by dimethoxyethane (DME, Sigma Aldrich, 99%) to wash off the electrolyte salt and the residual solvent, and then evaporated in a vacuum chamber, connected to the glove box, for ~15 min. The Scanning Electron Microscopy (SEM) measurements were performed on a LEO Gemini Supra 35 system, and images were obtained at an electron current of 50 pA with an accelerating voltage of 5 kV. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advanced diffractometer fitted with Cu-K α X-rays ($\lambda = 1.5406$ Å) radiation at a scan rate of 0.016 °/s. A JEOL-2100F STEM equipped with a double aberration-corrector for both probe-forming and imaging lenses is used to perform HAADF and ABF imaging, which was operated at 200 KV. The convergence angle was 25 mrad and the angular range of collected electrons for HAADF imaging is about 60-250 mrad. X-ray absorption near edge structure (XANES) experiments on Ru K-edge were carried out in transmission mode at Beamline 20-BM-B of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL).

Table S1	. Refinement	results	of Na ₃ RuO ₄ .
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Refinement results of NRO samples				
Phase	Na ₃ RuO ₄			
Space Group	C 2/m			
	a (Å)	11.1051 (5)		
	b (Å)	12.9016 (4)		
	c (Å)	5.7362 (2)		
Cell parameters	a (°)	90.000 (0)		
	β (°)	109.850 (3)		
	γ (°)	90.000 (0)		
	Volume (Å3)	773.023 (39)		
	Rwp (%)	8.30		
Agreement factors	Rp (%)	6.53		
	χ2	1.023		

Figure S1. Photo and schematic of in-situ Raman cell employed in this study.







Figure S3. Li-O₂ electrochemistry in PC-based electrolyte. (a) Cathodic sweep at 10 mV/s; (b) Corresponding in-situ Raman spectra collected on SERS gold substrate.



In order to exemplify the Raman assignment (and also the production) of superoxide and related PC decomposition production during nucleophilic attack, in-situ Raman spectroscopy has been operated on SERS gold cathode in Li-O₂ cell with same PC-based electrolyte system employed in this study.⁶ The oxygen reduction reaction (ORR) process occurs upon cathodic linear sweeping. During initial process (point-A), O-O stretch in adsorbed superoxide anion can be observed around 1100 cm^{-1.6-8} Subsequently (point-B), superoxide anion would attack PC solvent molecule, resulting in the observation of relevant peak in ring-opening decomposition products (highlighted by green frame in Figure S3-b). The metastable intermediate product(s) would be further reduced into carbonate species, which is consistent with the observation of CO₃-related peak at 1080 cm^{-1.9} Although the well-known decomposition of carbonate solvent (PC, DMC, etc.) in aprotic Li-O₂ battery technology has been reported,¹⁰ the production of superoxide intermediate and related ring-opening by-products have been firstly introduced herein, which is very help for us to confirm the production of superoxide and PC decomposition products during initial charging process on specific Na₃RuO₄ cathode material in Na-ion battery technology (as shown in Figure 2 in the main text).

Figure S4. (a) Potentiostatic Intermittent Titration Technique (PITT) characterization on Na_3RuO_4 cathode with 50 mV step. Corresponding in-situ Raman spectra obtained during: (b) 3.0 to 3.3 V (vs. Na/Na⁺) various potential plateaus/steps; (c) 3.75 V single potential plateau/step.



decomposition pro**Bacter**(Shiffh@rin⁴tial charging) present quite^Rettinteide^{if}(Mfff⁻¹the phenomena reveals in Figure 2. Herein, on different voltage plateau, the position of O-O stretch in superoxide anion gradually shift with the potenital movement, which present as a unique feature of adsorption species.^{6, 8} This shift has no relationship with the adsorbing capacity/amount, but only potential dependent (as summarized inset Figure S4-b). However, the O-O stretch in peroxo-species observed at high voltage region (3.75 V step, green frame, Figure S4-c) shift with its total quantity/amount on a certain voltage plateau, which indicates that peroxo-species is not a adsorption.





Raman Shift (cm⁻¹) The in-situ Raman spectra collected on various charging states (3.7 and 4.0 V, respectively) are listed above for comparison. Besides of the related stretching modes in Na2O and Na2CO3, the O-O stretch, which is attributed to peroxo-like species observed in the related in-situ Raman spectrum, are precisely within the region of O-O stretching in peroxide species (Li₂O₂, Na₂O₂ and H₂O₂ aqueous solution). Thus, the assignment of peroxo-related O-O stretch formed during relevant anionic redox process has been further confirmed.

Figure S6. Comparision between the in-situ collected Raman spectra and corresponding spectra collected after rinsing and drying treatments: (b) initial stage of charging; (c) end of charge process.



Typically, the **adamptiShiftpeni** and soluble products **Ramin Shift fixed** have, especially after continuously vacuum drying procedure. In this case, with the disappearance of the related Raman peaks in superoxide anion and PC decomposition products (blue frame, Figure S6-b), we can further confirm that the superoxide species is not a stable product, but an adsorption (as proved in Figure S4 above). On the contrary, both the CO_3 stretch in carbonate and O-O stretch in peroxo-related species still remain after rinsing and drying treatment, which indicates that the preoxo-related product is not an trace amount of adsorption, but a stable product inside the crystal lattice (intracell).

Figure S7. Fitting and assignment results of specific region (Ru-O stretching mode region) in in-situ Raman spectra collected duing charging process on Na_3RuO_4 cathode. The original spectra have already shown in Figure 2c. All of the spectra are fitted by Gaussian-Lorentzian distribution functions.



(a) Blue Frame: The Ru-O stretch in typical RuO₆ octahedron structure can be fitted out. During charging, the blue shift of the Ru-O stretch indicates the shorten of Ru-O bond upon Na extraction.

(b) Orange Frame: The production of Na₂O and related assignment has been revealed in both Figure 2 and Figure S5. The disappearance of Na₂O can be rationally attributed to its decomposition upon relatively high voltage plateau.

(c) Green Frame: Sharing the same increasing trend with O-O stretch in peroxo-related products, another pair of Ru-O stretches can be clearly observed after fitting. This indicates the formation of $\text{Ru-O}_2^{2^-}$ structure during related charging stage. Besides, the opposite shift direction also demonstrate the shorten of O-O bond and the lengthen of Ru-O bond(s) in newly-produced peroxo-related structure (Ru-O₂²⁻).

Figure S8. Ru $3d_{5/2}$ and Ru 3p ($3p_{1/2}$ and $3p_{3/2}$) XPS spectra collected from Na₃RuO₄ cathodes at the initial charged state. Related etching procedures have been conducted on the cathode for clarity.



For both of the 3d and 3p spectra, an abnormal negative/reverse shift in binding energy during anionic redox-related charging process can be clearly observed, which was ascribed to "a significant modification of the Ru environment (for example, distortion) inducing strong electronic redistributions along the Ru–O bonds" by Tarascon and co-workers in their previous studies.^{11, 12}

We commonly believe that the binding energy of core ion (redox active) would shift to a positive site during charging. In this case, the reverse shift of the redox insert Ru ion during anionic redox-related charging process present unexpected. Actually, the binding energy shift(s) is assigned to the effective charge of the core-ionized atom. Based on Tarascon and co-workers, if the ionized atom carries a positive/negative charge (compared with its reference/pristine state), it will lead to an increase/decrease of the binding energy. Thus, the Δ binding energy $\leftrightarrow \Delta$ charge (Q) relationship can be regarded as an oversimplification mode. In fact, from our point of view, there exist several number of other factors, which can also impact the shift/position of binding energy (eV), for example: changes in coordination (herein, Ru-O and Ru-Ru bonds) around the ionized atoms, or any variation in the mean bond distance that changes both the environmental charge density and the chemical bonding between the atom and its neighbors.^{12, 13}

In the case of Na₃RuO₄ cathode, the production of peroxo-species during charging remarkably changes the Ru⁵⁺-related environment. This has also been illustrated by DFT calculations on the Ru-induced anionic redox process in related Li-ion battery system, in which a strong distortion of the oxygen network on lithium removal during anionic redox-related charging process.¹¹ This variation in the Ru⁵⁺ environment in conjunction with some (Ru⁵⁺ \rightarrow O₂²⁻) electronic redistribution would be rationally explain the Ru-related reverse shift in XPS spectra. Besides, as shown in Figure S7, the Raman assignment on Ru-O stretching modes also prove the obvious variation of Ru-O bond environment (bond length/distance), which would lead to the above-mentioned changes in coordination around the ionized atoms. **Figure S9.** Schematic of the density of states (DOS) of Na₃RuO₄. The Fermi level (E_F) is represented by a horizontal dashed line. The atomic Ru⁵⁺ 4d, and O²⁻ 2p energy levels are shown in different colors with an obvious strong Ru 4d-O 2p hybridization region (overlapped area). The Na₃RuO₄ band structures show the electronic levels of the pure/single Ru⁵⁺(t_{2g})-O²⁻/O⁻(2p) redox process. The virtual oxidation of Ru⁵⁺ into Ru⁶⁺ is shown inset as a virtual process.



 Na_3RuO_4 Ru^{5+} (4d) $(t_{2g})^3$ \uparrow \uparrow \uparrow (half filled)

Based on typically physical explanation, the redox of LiCoO₂ (and Li₂MnO₃) can be assigned to the formation of holes on oxygen. For instance, high oxidation state of "Mn⁵⁺", which owing to hybridization issues, could be regarded as Mn⁴⁺ + hole on the oxygen. This would be the reason why we do not observe any increasing of Mn valence state by XPS etc. Herein, the atomic Ru 4d orbitals are spatially expanded, resulting the formation of a strong hybridization for Ru 4d-O 2p (the overlapped region).¹⁴ Na₃RuO₄ shows a Ru⁵⁺(t_{2g})-band in which the electrons are localized on the transition metal. This Ru-related band being half-filled, it splits through the coulombic repulsion, resulting the formation of one low-lying band filled with three spin-up and one high-lying band of spin-down fully empty, respectively. Once the Fermi level (E_F) goes lying in the Ru⁵⁺(t_{2g})-band upon charging, the t_{2g}-band of Ru⁵⁺ merges the top portion of the O(2p)-band, presenting that further oxidation of Ru⁵⁺ from the Na₃RuO₄ structure, which leads to the virtual creation of "Ru⁶⁺". This phenomenon can also be described as Ru⁵⁺ + hole on the O²⁻ band. In this case, the charging process (electron transfer process) is favored by the initial splitting of the half-filled t_{2g}-band of the Ru⁵⁺. Subsequently, the formation of oxygen vacancies on O 2p-band (O⁻) is further triggered by the formation of a virtual "Ru⁶⁺". Actually, the Ru⁶⁺ cannot stably exist in an octahedral coordinate structure (C2/m). Moreover, very high energy is required to oxidize Mn⁴⁺ to form Mn⁵⁺ with an octahedral coordination mode, which indicates an extremely high charging potential. However, based on Tarascon et al.,¹⁵ the Ru still stayed in +5 state, while the potential had already rised up to 4.6 V vs. Li/Li⁺ (equals to 4.27 V vs. Na/Na⁺) in a octahedral coordination structure. The inactive redox behavior of Ru⁵⁺ in Na₃RuO₄ presents well coincide with the behavior of Mn⁴⁺ (cannot reach +5 state) observed in typical Li₂MnO₃ prototype cathode in Li-ion battery system.

Figure S10. Ex-situ Ru K-edge X-ray absorption near-edge structure (XANES) spectra collected from Na₃RuO₄-based cathode at pristine (black trace), initial charged (red trace) and discharged (blue trace) states, respectively.



Note that, during charging and discharging process, the adsorption edge of the Ru K-edge do not present obvious shift.^{16, 17} While the very slight change upon changing would be ascribed to the evolution of Ru-O local environment after oxygen activity.¹⁸ This result is well consistent with the inert redox character of Ru⁵⁺ ion obtained by related XPS results shown in Figure 3 and Figure S8.

Figure S11. Galvanostatic charge/discharge curves (current density: 50 mA/g, cut-off potential 1.5-4.0 V vs. Na/Na⁺) of Na₃RuO₄-based Na-ion cells fabricated with different electrolyte system: (a) NaClO₄-PC; (b) NaPF₆-PC and (c) NaPF₆-EC/DMC.





Figure S12. Cycling performance of Na₃RuO₄ cathode: discharge/charge voltage hysteresis against cycle number.

Figure S13. Schematic of the density of states (DOS) of Na₂RuO₃, Na₃RuO₄ and proposed Narich Na_{2+x}M_yRu_{1-y}O₃ (M=Mn and Fe, etc.) layer cathode.



The Fermi level (E_F) is represented by a horizontal dashed line. The atomic Ru⁴⁺/Ru⁵⁺ 4d, and O²⁻ 2p energy levels are shown in different colors with an obvious strong Ru 4d-O 2p hybridization region (overlapped area). For Na₂RuO₃ band structure, the disordered structure shows the electronic levels of the pure/single Ru⁴⁺(t_{2g})- Ru⁵⁺(t_{2g}) cathodic redox process,¹⁹ while the specific-designed ordered structure reveals the electronic levels of both the Ru⁴⁺(t_{2g})-Ru⁵⁺(t_{2g}) cathodic redox process.²⁰ The

 Na_3RuO_4 band structure shows the electronic levels of the pure/single $Ru^{5+}(t_{2g})-O^{2-}/O^{-}(2p)$ anionic redox process.

Different from the ordered Na₂RuO₃ cathode, for the proposed Na-rich layer cathode, Na_{2+x}M_yRu_{1-y}O₃, we want to change the cathodic redox core element from expensive Ru to relatively cheaper Mn and/or Fe. In this case, the price advantage of low-cost Na-ion battery would be further extended/developed. At the same time, we want to retain the Ru-induced oxygen-related anionic redox achievement to enlarge the capacity (remedy the capacity "short slab" of Na-ion battery). In summary, finding this pure anionic redox-related layered prototype/matrix cathode, Na₃RuO₄, is not the final target (finding the Li₂MnO₃ prototype is also not the final target for the Li-ion battery system). From our point of view, how to effective employ this prototype and further develop related Na-rich layer cathode with both Mn/Fe-based cathodic redox and Ru-induced anionic redox activities is the future design target. For Li-ion battery, benefit from the Li₂MnO₃ prototype, huge amount of Li-rich cathode can be developed with extended capacity. While, it is precisely because, to the best of our knowledge, the absence of the Na-rich prototype in Na-ion battery system (no corresponding layered structure Na₂MnO₃ has been reported for Na-ion cathode till now), the introduction of this Na₃RuO₄ prototype with pure anionic redox activity become important/valuable.

Reference

- 1. J. T. Haraldsen, M. B. Stone, M. D. Lumsden, T. Barnes, R. Jin, J. Taylor and F. Fernandez-Alonso, *J. Physics: Condensed Matter*, 2009, 21, 506003.
- F. J. Li, S. C. Wu, D. Li, T. Zhang, P. He, A. Yamada and H. S. Zhou, *Nat. Common.*, 2015, 6, 8843.
- 3. J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L. Wang and Z. Q. Tian, *Nature*, 2010, 464, 392-395.
- 4. Y. Qiao, S. Wu, J. Yi, Y. Sun, S. Guo, S. Yang, P. He and H. Zhou, *Angew. Chem. Int. Ed.*, 2017, 56, 4960-4964.
- 5. S. Hy, F. Felix, J. Rick, W.-N. Su and B. J. Hwang, J. Am. Chem. Soc., 2014, 136, 999-1007.
- 6. Y. Qiao and S. Ye, J. Phys. Chem. C, 2015, 119, 12236-12250.
- 7. Z. Q. Peng, S. A. Freunberger, L. J. Hardwick, Y. H. Chen, V. Giordani, F. Barde, P. Novak, D. Graham, J. M. Tarascon and P. G. Bruce, *Angew. Chem. Int. Ed.*, 2011, 50, 6351-6355.
- 8. L. Johnson, C. M. Li, Z. Liu, Y. H. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J. M. Tarascon and P. G. Bruce, *Nat. Chem.*, 2015, 7, 1091-1099.
- 9. Y. Qiao and S. Ye, J. Phys. Chem. C, 2016, 120, 8033-8047.
- S. A. Freunberger, Y. H. Chen, Z. Q. Peng, J. M. Griffin, L. J. Hardwick, F. Barde, P. Novak and P. G. Bruce, J. Am. Chem. Soc., 2011, 133, 8040-8047.
- M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M. L. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. Dupont and J. M. Tarascon, *Nat. Mater.*, 2013, 12, 827-835.
- 12. D. Foix, M. Sathiya, E. McCalla, J.-M. Tarascon and D. Gonbeau, *J. Phys. Chem. C*, 2016, 120, 862-874.
- 13. P. S. Bagus, F. Illas, G. Pacchioni and F. Parmigiani, J. Electron Spectrosc. Relat. Phenom., 1999, 100, 215-236.
- 14. A. James and J. Goodenough, J Solid State Chem, 1988, 74, 287-294.
- 15. M. Sathiya, K. Ramesha, G. Rousse, D. Foix, D. Gonbeau, A. Prakash, M. Doublet, K. Hemalatha and J.-M. Tarascon, *Chem Mater*, 2013, 25, 1121-1131.
- 16. G. Assat, A. Iadecola, C. Delacourt, R. Dedryvère and J.-M. Tarascon, *Chem. Mater.*, 2017, 29, 9714-9724.
- 17. B. Li, H. Yan, Y. Zuo and D. Xia, Chem Mater, 2017, 29, 2811-2818.
- X. Rong, J. Liu, E. Hu, Y. Liu, Y. Wang, J. Wu, X. Yu, K. Page, Y.-S. Hu, W. Yang, H. Li, X.-Q. Yang, L. Chen and X. Huang, *Joule*, 2017, DOI: http://dx.doi.org/10.1016/j.joule.2017.1010.1008.
- 19. M. Tamaru, X. Wang, M. Okubo and A. Yamada, *Electrochem. Commun.*, 2013, 33, 23-26.
- B. M. De Boisse, G. Liu, J. Ma, S.-i. Nishimura, S.-C. Chung, H. Kiuchi, Y. Harada, J. Kikkawa, Y. Kobayashi, M. Okubo and A. Yamada, *Nat. Commun.*, 2016, 7, 11397.