Hierarchical nanoporosity enhanced reversible capacity of bicontinuous nanoporous metal based Li-O$_2$ battery

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High-energy-density rechargeable Li-O$_2$ batteries are one of few candidates that can meet the demands of electric drive vehicles and other high-energy applications because of the ultra-high theoretical specific energy. However, the practical realization of the high rechargeable capacity is usually limited by the conflicted requirements for porous cathodes in high porosity to store the solid reaction products Li$_2$O$_2$ and large accessible surface area for easy formation and decomposition of Li$_2$O$_2$. Here we designed a hierarchical and bicontinuous nanoporous structure by introducing secondary nanopores into the ligaments of coarsened nanoporous gold by two-step dealloying. The hierarchical and bicontinuous nanoporous gold cathode provides high porosity, large accessible surface area and sufficient mass transport path for high capacity and long cycling lifetime of Li-O$_2$ batteries.

The working principle of the non-aqueous Li-O$_2$ battery is based on an electrochemical reaction: 2Li$^+ + 2e^- +$ O$_2$ $\leftrightarrow$ Li$_2$O$_2$ ($E_o = 2.96$ V vs Li$^+/Li$) with the solid Li$_2$O$_2$ formation and decomposition at cathodes$^{1-11}$. Based on the reaction, the theoretical specific energy of Li-O$_2$ battery is estimated to be ~3600 Wh/kg. However, the realization of a large rechargeable capacity of Li-O$_2$ battery is facing many challenges. Since three phases (gas, liquid and solid) are involved into the electrode reactions during discharging and charging, the cathodes are required to be porous for fast transport of oxygen and electrolytes and for accommodation of the solid reaction products. Various conductive porous materials, such as carbon$^{12-33}$, carbides$^{34-36}$ and metals/composites$^{37-48}$ have been widely explored as cathodes for Li-O$_2$ batteries. Particularly, nanoporous gold (NPG), fabricated by dealloying, shows high kinetic efficiency for the Li$_2$O$_2$ formation and decomposition at low overpotentials. However, the attainable capacity from the NPG cathodes is very low (~300 mAh/g) because of the high mass density of gold electrode and the limited porosity (~50%) of NPG to host the discharge products$^{47}$. In general, higher porosity with the low mass density of the porous cathodes can host more Li$_2$O$_2$ for higher capacity and, meanwhile, a larger accessible surface area promotes the reaction kinetics of Li$_2$O$_2$ formation and decomposition during discharging and charging. However, it is usually intolerable to realize both high porosity and large surface area simultaneously in porous materials because larger surface areas need a smaller pore size while higher porosity requires larger pores. Although the NPG cathode may not be an ideal choice for practical application of Li-O$_2$ battery because of the usage of gold, it is an ideal system to study the solution of the conflict requirements because of the tunable nanopores in a controllable manner. Therefore, we developed a hierarchical nanoporous gold ($h$-NPG) cathode with a high effective surface area for Li$_2$O$_2$ formation/decomposition and large porosity for the storage of the solid products. The $h$-NPG based Li-O$_2$ battery shows a highly enhanced reversible capacity of ~1500 mAh/g with over 140 cycles at low discharge/charge overpotentials.

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Results

The \( h \)-NPG electrodes were prepared by a dealloying method (Fig. 1a)\(^ {49-52} \). The constitute Ag in a \( \text{Au}_{15}\text{Ag}_{85} \) (at%) alloy was partially leached away in an acid solution to form a nanoporous \( \text{AuAg} \) alloy (np-AuAg) with an average pore size of \( \sim 20 \) nm and residual Ag of \( \sim 70 \) at% (Figs 1b and S1). Subsequently, the np-AuAg was annealed in air and a coarsened nanoporous structure with pore and ligament sizes of \( \sim 80-100 \) nm was achieved (Fig. 1c). The residual Ag in the coarsened porous alloy was further selectively removed by second-step dealloying, leading to the formation of \( h \)-NPG with \( \sim 5-20 \) nm pores on \( \sim 80-100 \) nm ligaments (Fig. 1d). The distributions of pore sizes in the NPG samples with different morphology were carefully measured and plotted in Fig. S2. The \( h \)-NPG has a large porosity of \( \sim 80-82 \) vol.% and a large effective surface area of \( \sim 82.9 \) m\(^2\)/g (Fig. S3). In contrast, the as-prepared and coarsened np-AuAg samples with \( \sim 50 \) vol.% porosity have the effective surface areas of \( \sim 59.8 \) and \( 27.4 \) m\(^2\)/g, respectively (Table S1). Apparently, the hierarchical nanoporous configuration gives rise to both large effective surface area and high porosity, which cannot be achieved from conventional monolithic porous structure.

The free-standing and bicontinuous NPG samples were directly used as the cathodes of Li-O\(_2\) batteries. Figure 2a shows the schematic configuration of the testing battery, in which \( h \)-NPG was utilized as the cathode and the propylene carbonate pretreated Li metal as the anode in a 1M LiClO\(_4\) dimethyl sulfoxide (DMSO) solution\(^ {47-48} \). For comparison, the as-prepared and coarsened np-AuAg cathodes were also tested using the same setup. The three electrodes show the large difference in the maximum discharge capacity. The \( h \)-NPG has the highest discharge capacity of \( \sim 2400 \) mAh/g while the as-prepared and coarsened np-AuAg cathodes are only about 1400 and 1100 mAh/g, respectively (Figs 2b and S4a). All the capacities and current densities in this study are calculated by the weight of the cathodes. Because of the free-standing nature, the NPG cathodes do not have a current collector. Although the as-prepared and coarsened np-AuAg samples have a nearly identical porosity of \( \sim 50 \) vol%, the as-prepared sample with a larger specific surface area and a smaller pore size has higher capacity. This suggests that large effective surface areas provide more active sites for the formation of solid Li\(_2\)O\(_2\), which is consistent with the conventional wisdom that the capacity is closely related to the effective surface of cathodes\(^ {9} \). Interestingly, after normalizing the maximum discharge capacities using the electrochemically effective surface areas (EESA), the capacities noticeably depend on the porous morphology of the cathodes (Fig. 2c) while the dependence on the geometric surface area of NPG is weak (Fig. S4b). The coarsened np-AuAg has the largest normalized capacity, followed by the \( h \)-NPG and as-prepared np-AuAg (Fig. 2c). Apparently, the discharge capacity is not solely determined by the electrode surface areas, the geometric morphology of porous structure also plays a critical role in the maximum capacity. Although small pores with a high surface area are important to maximize active sites for oxygen reduction reaction (ORR) and hence a large discharge capacity, the ORR during discharging involves heavy mass transport and the solid reaction products of Li\(_2\)O\(_2\) may block pore channels to prevent the effective utilization of the surface area in nanoporous structure. For coarsened porous structure, the large pore channels cannot be easily clogged by the solid reaction products and thus the effective surface area can be well exploited for ORR. However, the coarsened porous structure does not have a large surface area for a high capacity. Therefore, the battery performance of NPG cathodes is closely related to both morphology and accessible surface area of porous electrodes, which underlines the importance of the hierarchical nanoporous structure for the cathode design that can utilize concurrently large pore channels for operative mass transport, and small pores for a large effective surface area.
The maximum discharge capacity apparently correlates with the reversible capacity of NPG cathodes. The fully reversible capacity of the \( h \)-NPG cathode can reach ~1000 mAh/g at the cut-off charging potential of 4.0 V while the coarsened and as-prepared np-AuAg cathodes can only be ~500 and ~800 mAh/g, respectively (Fig. 2d). Interestingly, both charge and discharge overpotentials of the NPG cathodes show the noticeable dependence on the morphology of the nanoporous cathodes. The charge potential (Table S2) of the \( h \)-NPG is ~0.14 V and 0.07 V lower than that of the coarsened and as-prepared np-AuAg, respectively. This tendency could be explained by the fact that a smaller ligament/pore size yields a larger effective surface area and high density of geometrically required surface defects for enhanced oxidation reaction of Li\(_2\)O\(_2\)\(^{53-54}\). The discharge overpotential of the \( h \)-NPG is also lower than those of the coarsened and as-prepared np-AuAg as shown in Fig. 2d and Table S2. It has been verified that NPG is active for ORR\(^{54}\), and, particularly, the small nanopore channels of nanoporous metals can effectively enhance ORR kinetics by trapping oxygen at a low overpotential for multiple molecule/catalyst contacts\(^{55}\). Since the \( h \)-NPG contains much lower residual silver (~10 at%) in comparison with the as-prepared and coarsened np-AuAg (~70 at%), the chemical composition difference may play a role in the electrode reactions kinetics during discharging and charging. In order to investigate the possible chemical effect, we developed as-prepared and coarsened NPG with the same composition as the \( h \)-NPG with similar pore sizes as the as-prepared and coarsened np-AuAg (Fig. S5a–d). As shown in Fig. S5e, the battery performances of the NPG cathodes with the nearly identical chemical composition but different porous structures are analogous to Fig. 2d, suggesting that the cathodic performances of the nanoporous samples are primarily controlled by porous morphology. The insignificant effect of the residual silver in the discharge/charge reactions may be related to the fact that the internal surfaces of the nanoporous cathodes are passivated by pure gold by dealloying while the residual Ag only resides in the interior of gold ligaments and does not participate into the cathodic reactions\(^{56}\).

Although the \( h \)-NPG cathode with an optimal hierarchical nanoporosity shows a high reversible capacity at low charge/discharge overpotentials, it does not have a good cycling retention and often fails with tens of cycles. This is probably limited by the slow kinetics of dissolving Li\(_2\)O\(_2\) from deep nanopore channels. Following the work that the redox mediator, tetrathiafulvalene (TTF), can significantly enhance the charging kinetics of NPG cathodes\(^{48}\), we modified the 1M LiClO\(_4\)/DMSO electrolyte by adding TTF and kept the Li metal plate as the anode. With this modified electrolyte, the galvanostatic charge curves of the three nanoporous cathodes become obviously flat with lower charge overpotentials (Fig. S6a), compared to those tested in the electrolyte without TTF (Fig. 2d). In contrast, the discharge potentials of the three electrodes do not show noticeably changes (Table S2).
indicating that TTF mainly benefits the oxidation kinetics of Li2O2 during charging. It is worth noting that the discharge/charge overpotentials of the nanoporous cathodes still show the obvious porous morphology dependence after the electrolyte is modified by the redox mediator (Fig. S6a and Table S2). The h-NPG electrode keeps the lowest charge/discharge overpotentials, followed by the as-prepared and coarsened np-AuAg. Furthermore, the effect of TTF has been investigated by cyclic voltammetry (CV) of the electrode reactions with fixed scan potential window (Figs S6–S7) and ex-situ SEM after the battery was fully discharged and recharged for the first cycle (Fig. S8). Both of these characterizations have confirmed that the TTF enhanced Li2O2 oxidation takes place at the potentials above ~3.4–3.55 V, which contributes to the majority of the charge capacity achieved by the h-NPG based Li-O2 battery as shown in Fig. 3a.

With the redox mediator, the reversible capacity and cyclic retention of the h-NPG cathodes are dramatically improved. Although the fully reversible capacity cannot be obtained for long cycles, the h-NPG shows an excellent cycling retention at a high capacity of 1500 mAh/g for over 140 cycles at a high current density of 2.0 A/g (Fig. 3a). The discharge potential of the Li-O2 battery keeps the near constant of ~2.70 V for the initial 50 cycles and then gradually decreases to ~2.50 V after 100 cycles (Fig. 3b). The charge potential of the Li-O2 battery also shows a lower value of ~3.5 V for first 50 cycles and preserves below ~3.6 V even at 100th cycle, which is much lower than those of other cathodes reported in the literature. Furthermore, the h-NPG based batteries show the good cycling stability at the same reversible capacity of 1500 mAh/g for over 120 cycles with the low concentration of TTF (5 mM) (Fig. S9a), and for over 84 cycles at a low current density of 0.5 A/g (Fig. S9b), respectively, indicating the insignificant influences of the TTF concentration and the current density on the battery performances. Therefore, the highly enhanced reversible capacity and long cycling stability of the h-NPG based Li-O2 battery could be attributed to the unique and hierarchical nanoporosity structure of the NPG cathode. The large pores provide a fast path for oxygen and Li ion diffusion and a large open space for solid Li2O2 storage while the high effective surface area that mainly contributed by the smaller pores can promote the formation of thinner Li2O2 films for easy decomposition at low charge/discharge overpotentials. Moreover, the TTF kinetically profits the decomposition of Li2O2 within nanopores for a high capacity at lower charge overpotentials.

We investigated the rate dependence of the h-NPG based Li-O2 battery at varied current densities from 0.2 to 10.0 A/g with a cut-off capacity of 500 mAh/g (Fig. 3c). The discharge potential gradually decreases from ~2.80 to 2.50 V while the charge potentials increase from ~3.40 to 3.65 V as the current density increases from 0.2 to 10.0 A/g (Fig. 3d), showing a typical rate dependence of polarization resistance. It is worth noting that the charge potential is only ~3.65 V even at the high current density of 10.0 A/g, which is significantly lower than that of the carbon based electrodes which is usually above ~4.5 V at the similar current density. Additionally, the discharge
potential keeps higher than those of the carbon electrodes, giving rise to a high energy efficiency of the h-NPG based Li-O2 battery. When the current density is set back to 1.0 A/g after the rate change tests, the discharge/charge potentials are identical to the initial ones at 1.0 A/g. This performance further confirms the excellent stability and feasibility of the h-NPG based Li-O2 battery. The low rate dependence of the discharge/charge potentials has also been verified with a large cut-off capacity of 1500 mAh/g at the current densities of 0.5 and 3.0 A/g (Fig. S9c).

The energy efficiency of the Li-O2 battery at different current densities is plotted in Fig. 3d. With the current density increasing from 0.2 to 1.0 A/g, the energy efficiency of the h-NPG based Li-O2 battery gradually decreases from ~82% to 76%, which are much higher than those (~55–65%) of carbon-based Li-O2 batteries3,5.

The h-NPG cathodes have been further inspected by the SEM and transmission electron microscopy (TEM) after the battery was cycled with the cut-off capacity of 1500 mAh/g. From the SEM of the discharged electrode (Fig. 4a), it can be observed that the solid reaction products uniformly grow in the porous electrode and the fuzzy contrast is probably caused by the insulator nature of the reaction products and extremely small Li2O2 grain sizes. After recharging (Fig. 4b), the fuzzy reaction products are almost removed and the SEM image of the electrode is the nearly same as the as-prepared h-NPG. The discharged and charged NPG electrodes were also inspected by TEM. As shown in Fig. 4c, the reaction products homogeneously distribute in the nanopores with a relatively bright contrast. The selected area electron diffraction shows the ring patterns of the reaction products, which can be index as the lithium peroxide (Li2O2) nanocrystals with a hexagonal (P6/mmc) crystal structure (Inset in Fig. 4c). The smooth electron diffraction rings indicate that the Li2O2 crystals have a very small grain size and random orientations. Separated high-resolution TEM confirms that the Li2O2 products have a crystalline grain size smaller than 10 nm formed at a discharge current density of 0.5 A/g. After recharging, the reaction products are removed from the cathode, which cannot be recognized from the bright-field TEM image and electron diffraction pattern of the charged sample (Fig. 4d). The direct microscopic observations demonstrate that the nanoporous structure of gold is advantageous for the preferential formation and decomposition of Li2O2 at low overpotentials by forming nano-sized reaction products as thin films on the electrode surface. The full reversibility of the h-NPG based Li-O2 battery is tested by the electrochemical impedance spectroscopy (EIS) at discharge/charge states. As shown in Fig. S10a, the impedance of the battery increases significantly after the discharge because of the formation of insulated Li2O2 on the h-NPG cathode. After recharging, the impedance is fully recovered to the initial state, demonstrating that the Li2O2 is fully decomposed after recharging. Furthermore, XPS measurements confirm that the discharge product is pure Li2O2 and no other side reaction products (Fig. S10b). After recharging, Li2O2 can be completely decomposed, indicating the excellent reversibility of the h-NPG cathode.

The stability of TTF and the DMSO-based electrolyte have been explored by 1H NMR and GC-MS. The 1H NMR spectra of the TTF for the 1st, 50th and 100th cycles are obtained (Fig. S11) and show that there is no obvious change of the TTF peak after long cycles, indicating that the large reversible capacity with excellent cycling stability of the h-NPG based Li-O2 battery was not caused by the TTF oxidation/decomposition. Similarly, the
stability of DMSO-based electrolyte has also been confirmed by the $^1$H NMR spectra (Fig. S12a). However, by the GC-MS with much higher sensitivity, a very low amount of byproducts (Dimethyl Sulfone) indicated by the weak peak can be observed after 100 cycles, demonstrating that the decomposition of DMSO in each cycle is very limited and accumulated to only ~2% after 100 cycles (Fig. S12b). Both of the H NMR and GC-MS have revealed that the large reversible capacity with good cycling stability of the h-NPG based Li$_2$O$_2$ battery was contributed by the reversible Li$_2$O$_2$ formation/decomposition in the hierarchical nanoporosity of the cathode.

**Discussion**

For conventional carbon based electrodes, they usually require binders, which makes the porosity tuning become very difficult in a controllable manner. In our study, it is the first report on the morphology tuning of NPG for the application in Li-air batteries. The free-standing NPG cathode with a uniform porous structure allows us to precisely control the pore size, morphology and porosity to uncover the intrinsic correlation of these porous parameters with batteries performances. More importantly, the hierarchical nanoporous structure developed in this study effectively overcomes the dilemma issue in specific surface area and porosity of conventional porous materials. Apparently, a large effective surface area benefits the reaction kinetics of Li$_2$O$_2$ formation and decomposition during discharging and charging while high porosity with the low mass density can host more Li$_2$O$_2$ for a high specific capacity. However, it is usually intolerable to realize both high porosity and large surface area simultaneously in a porous material because larger surface areas need a smaller pore size while higher porosity requires larger pores. The hierarchical porosity offers both high surface area and large porosity simultaneously which give rise to the excellent battery performances of the h-NPG cathode, in comparison with all previously reported nanoporous gold based Li-air batteries. Moreover, since the porous parameters of NPG can be well controlled by the dealloying method in comparison with porous carbon materials, dealloyed NPG is an excellent model system to explore the intrinsic correlation between porous structure and battery performance. In this sense, the current results from a simple and clean system is extremely valuable and could be as a universal law to guide the future cathode design regardless of materials.

From practical application viewpoint, gold appears expensive and it seems not practical to use NPG in large-scale commercial Li$_2$O$_2$ batteries. However, this may not be true for h-NPG. After introducing up to 80% porosity by the hierarchical configuration, the loading amount of gold in a cathode becomes very low. In term of the efficiency of the cathode materials, the material cost of h-NPG is actually obviously lower than those of the carbon-RuO$_2$ cathode, the most promising one for practical applications in Li$_2$O$_2$ batteries (Table S3). Therefore, the hierarchical configuration not only provides excellent battery performances, but also benefits the material costs of cathodes by increasing porosity and decreasing loading amount of cathode materials.

In summary, we have developed a hierarchical NPG with a large surface area and high porosity for Li$_2$O$_2$ battery. A highly enhanced reversible capacity and long cycling lifetime can be simultaneously achieved at low charge/discharge overpotentials and a high current density with the assistance of the redox mediator TTF. The h-NPG based Li$_2$O$_2$ battery also shows much high energy efficiency and extraordinarily low rate dependence. Since the h-NPG electrode used in the battery is free-standing, it can work as the current collectors simultaneously in addition to the high-performance cathodes. The excellent battery performance of this model system demonstrates that the capacity and stability of Li$_2$O$_2$ batteries can be dramatically improved by enlarging both porosity and specific surface area with the hierarchical porous structure. The large porosity introduced and stabilized by the hierarchical configuration also significantly increases the efficiency of cathode materials and thus reduces the material costs by decreasing the loading amount of cathode materials. Therefore, this study may pave a new way to develop high capacity and highly stable nanoporous metals with low materials costs as cathodes for full-performance metal-O$_2$ (Li$_2$O$_2$ and Na$_2$O$_2$) batteries. Moreover, the realization of enhanced battery properties by optimizing the nanoporous morphology has an important implication in developing high performance cathodes by designing hierarchical porous structure.

**Methods**

**Materials.** Commercial Au$_{15}$Ag$_{85}$ (at%) alloy leaves with a thickness <1 μm were used as precursors to fabricate hierarchical NPG by a two-step dealloying process. The Au$_{15}$Ag$_{85}$ alloy was first electrochemically dealloyed in a 1M HNO$_3$ solution at 0.82 V for 900s using an electrochemical workstation (IVIUM Technology) in a standard three-electrode cell with a Ag-AgCl reference electrode and a Pt counter electrode. The dealloyed samples (as-prepared np-AuAg) were rinsed by deionized water (18.2 MΩ·cm) for more than three times to remove the residual chemical substances in the pore channels. Subsequently, the as-prepared np-AuAg films were annealed at the temperature of 250 °C for 1 h. The annealed np-AuAg films with coarsened nanopores and ligaments were further electrochemically dealloyed at a higher potential of 0.98 V for 1200s. By the two-step delloying, a hierarchical nanoporous structure with large primary pores of ~80-100 nm and small secondary pores of ~5-20 nm can be fabricated. The surface areas of the as-prepared np-AuAg, coarsened np-AuAg and hierarchical NPG were measured to be ~59.8, 27.4 and 82.9 m$^2$/g in 0.5M H$_2$SO$_4$ in the potential range of 0.0-1.5 VAg/AgCl at the scan rate of 100 mV/s, respectively (Fig. S2b). The mass of the electrodes (~0.2-1.0 mg) was measured with an ultra-micro balance. The geometric surface areas were ~1.0 cm$^2$. After dealloying the thickness of the samples has almost not changed. NPG films with the nearly same Ag concentration as the hierarchical NPG were prepared by one-step electrochemical dealloying of Au$_{15}$Ag$_{85}$ alloy at 0.82 V vs. Ag/AgCl for 1.5h at room temperature. The as-prepared NPG was then annealed at 200 °C to obtain the coarsened nanoporous structure.

**Microstructural characterization.** The microstructures of the NPG cathodes and reaction products were investigated by a field-emission scanning electron microscope (JEOL JIB-4600F SEM, 15 keV) equipped with an energy dispersive X-ray spectrometer and a transmission electron microscope (JEOL JEM-2100F) with double
Electrochemical characterization. The R2032-type coin batteries (MTI Corporation) were assembled using the as-prepared np-AuAg, coarsened np-AuAg and hierarchical NPG films as the working electrodes and pretreated Li metal plates as the anodes.

Distilled DMSO was used as the solvent to make 1 M LiClO4 electrolyte using the as-prepared np-AuAg, coarsened np-AuAg and hierarchical NPG films as the working electrodes and discharged/charge tests were conducted by using a Hokuto discharging/charging system. The current density and specific capacity were both calculated based on the loading mass of NPG or np-AuAg. Discharged and recharged NPG cathodes were inspected by SEM and TEM after the electrolyte was washed away in a glove box.

Cyclic voltammetry (CV) measurements were carried out in a non-aqueous 1.0 M LiClO4/DMSO electrolyte using a three-electrode electrochemical system (Fig. 5). Hierarchical NPG films were mounted on a glassy carbon disk electrode (5 mm in diameter) by lithiated Nafion® (LITHion dispersion, Ion-Power, USA). A freshly Li metal in 1M LiClO4/DMSO (0 V Li = −3.38 ± 0.01 V vs. Ag/Ag+). The electrolyte was bubbled with pure O2 for 30 min before CV measurements. To test the TTF effect, 50 mM TTF was added into the 1.0 M LiClO4/DMSO electrolyte.

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This work is sponsored by JST-CREST “Phase Interface Science for Highly Efficient Energy Utilization”, JST, Japan; and World Premier International (WPI) Research Center Initiative for Atoms, Molecules and Materials, MEXT, Japan.

Author Contributions
M.C. conceived and supervised this research. X.G., J.H. and Y.I. constructed the Li-O2 cells and performed the battery measurements; X. G. and L.C. prepared the nanoporous gold samples; P.L., J.H., A.H., T.J., N.A. and T.F. conducted the microstructure characterization; Z.J., F.L. and H.Z. helped in the battery testing; X.G. and M.C. wrote the manuscript. All author contributed to data analysis and discussion.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

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

How to cite this article: Guo, X. W. et al. Hierarchical nanoporosity enhanced reversible capacity of bicontinuous nanoporous metal based Li-O2 battery. Sci. Rep. 6, 33466; doi: 10.1038/srep33466 (2016).

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