

Experimental details

Chemicals. Potassium tetracyanonickelate(II) hydrate was purchased from Sigma-Aldrich, USA. Nickel(II) chloride hexahydrate, trisodium citrate dihydrate, and sulfuric acid were purchased from Nacalai Tesque, Japan. Potassium hydroxide and sodium nitrate was purchased from Wako, Japan. Nanographite platelets (N008-100-N) of 100 nm thickness were used as raw material to prepare graphene oxide (GO), Angestron materials. KMnO_4 and H_2O_2 were purchased from Kanto chemicals Co., INC. Platinum, 5% on carbon was obtained from Alfa Aesar, A Johnson Matthey Company. All chemical reagents were used without further purification.

Synthesis of NiCNNi flakes. In a typical procedures, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (59.6 mg) and trisodium citrate dihydrate (300 mg) were dissolved in 20 mL water to form a clear solution. Meanwhile, $\text{K}_2[\text{Ni}(\text{CN})_4]$ (130 mg) was dissolved into 20 mL water to form another clear solution. The two solutions were then mixed together under constant magnetic stirring. The obtained solution was aged for 30 hours until the reaction was complete and the precipitate is formed. After washing with water and ethanol extensively, the green precipitates were dried at room-temperature. On the basis of elemental analysis, the resulting chemical compound was $\text{Ni}[\text{Ni}(\text{CN})_4]$, which is hereafter abbreviated as 'NiCNNi flakes'.

Synthesis of GO sheets. The preparation of GO solutions followed the modified Hummers' method. The procedures are briefly described as follows. Sodium nitrate (0.30 g) was dissolved in sulfuric acid (10 mL). N008-100-N carbon source was added to the solution, which was stirred for 30 min. KMnO_4 (0.30 g) was further added to the solution and stirred again for 1 h. Then, H_2O_2 (10 mL) was added to the solution under stirring. Finally, the solution was centrifuged and then redispersed in water 3 times at different time intervals such as 10, 30, and 45 min. Then, the material was extracted by adding water, mixing with methanol, and keeping for further processing. The GO (10 mg) sheets were dissolved in 25 mL water under stirring for 2 h followed by strong sonication for 30 min.

Synthesis of NiO-GO hybrids. The two previously prepared solutions were mixed under vigorous sonication for 30 min. The obtained solution was aged under stirring for 4 hours. The precipitate was obtained by centrifugation. After washing with water and ethanol extensively, the NiCNNi-GO hybrid was dried at room temperature. Then, the obtained NiCNNi-GO hybrid (100 mg) was heated inside an electronic furnace to the desired temperature (300 °C) with a heating rate of 5 °C·min⁻¹ and kept for annealing during 1 hour. After that, the powder was cooled inside the furnace naturally. Finally, the obtained powder (NiO-GO hybrid) was collected for characterization. The whole calcination process was carried out in the air.

Electrochemical measurements. A conventional three-electrode cell was used for oxygen reduction reaction (ORR) measurement, including an Ag/AgCl (saturated KCl) reference electrode, a platinum wire as a counter electrode, and a modified rotating disk electrode (RDE) as a working electrode. The working electrode was prepared as follows. 5 mg of catalyst was dispersed in a mixture of water/ethanol (v/v=3:1, 950 μl) and Nafion (5 wt%, 50 μl) under sonication for 30 min. Then, 5 μL of the above suspension was dropped on the surface of the RDE and dried at room temperature. The cyclic voltammograms were checked at a scan rate of 50 mV·s⁻¹ without any rotation. The linear sweep voltammograms were performed at a

potential range between -1.0 V and 0.2 V (vs. Ag/AgCl) with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ and rotating speed of 1,600 rpm. All the measurements were carried out in 0.1 M KOH with N_2 - or O_2 -saturated.

Characterization. SEM images were acquired with a Hitachi SU8000 scanning microscope at an accelerating voltage of 5 kV. The TEM observations were performed using a JEM-2100F operating at 200 kV and equipped for energy-dispersive spectrometer analysis. The wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT 2500X diffractometer using monochromated Cu $K\alpha$ radiation (40 kV, 40 mA). Raman spectra were measured by Horiba-Jovin Yvon T64000 with the excitation Laser 364 nm. Nitrogen adsorption-desorption isotherms data were obtained with a Quantachrome Autosorb Automated Gas Sorption System at 77 K. The electrochemical measurements were conducted in a three-electrode electrochemical cell with a Pt counter electrode and Ag/AgCl as reference electrode in a 6 M KOH solution. A glassy carbon electrode coated with the sample was used as the working electrode. Linear sweep voltammetry measurements were obtained using an electrochemical workstation (ALS/HCH instruments, electrochemical analyzer/model: 842BZ) in the scan range from 0.2 to -1.0 V.

Figure S1

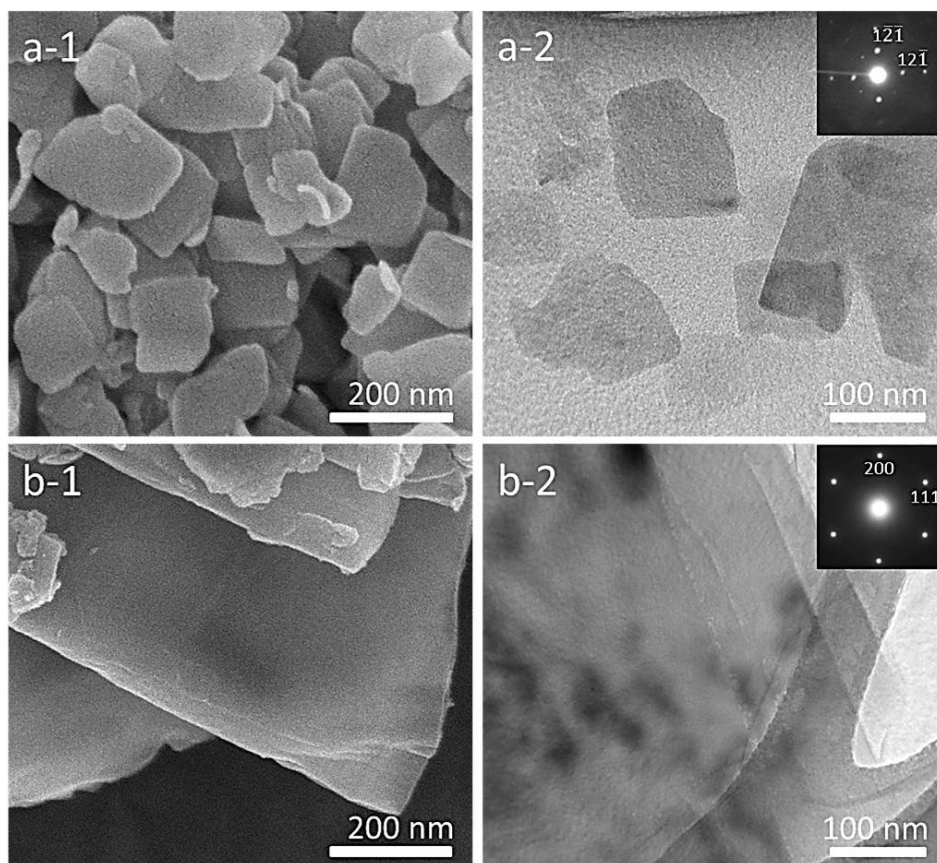


Figure S1 SEM and TEM images of (a) NiCNNi flakes and (b) GO sheets. The corresponding SAED patterns are shown as insets.

Figure S2

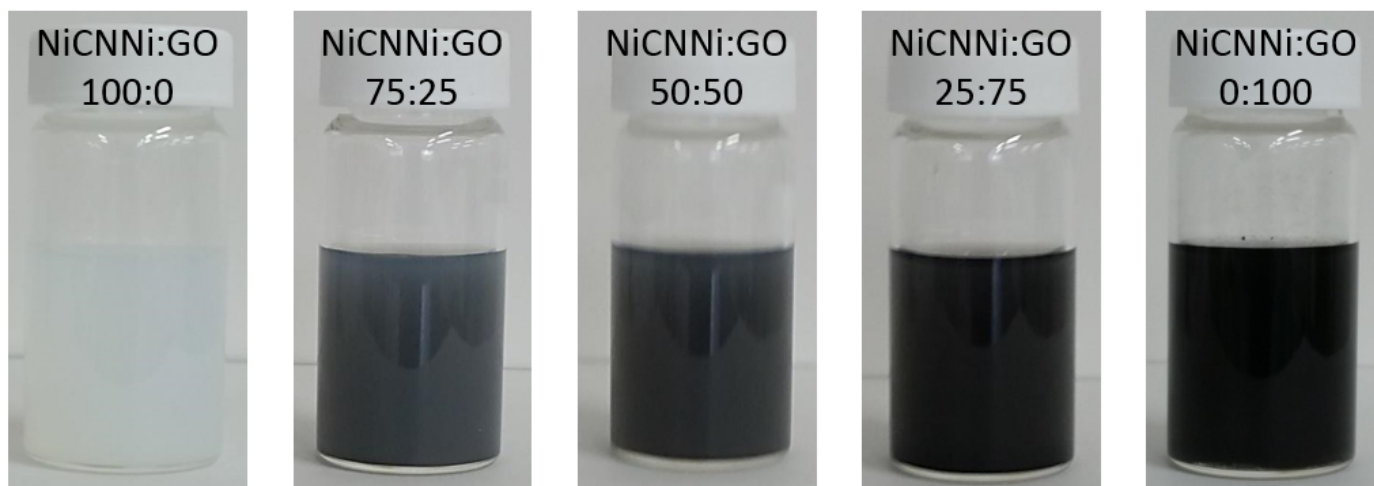


Figure S2 Photographs of the suspensions for the preparation of the NiCNNi-GO hybrids with different NiCNNi:GO ratios.

Figure S3

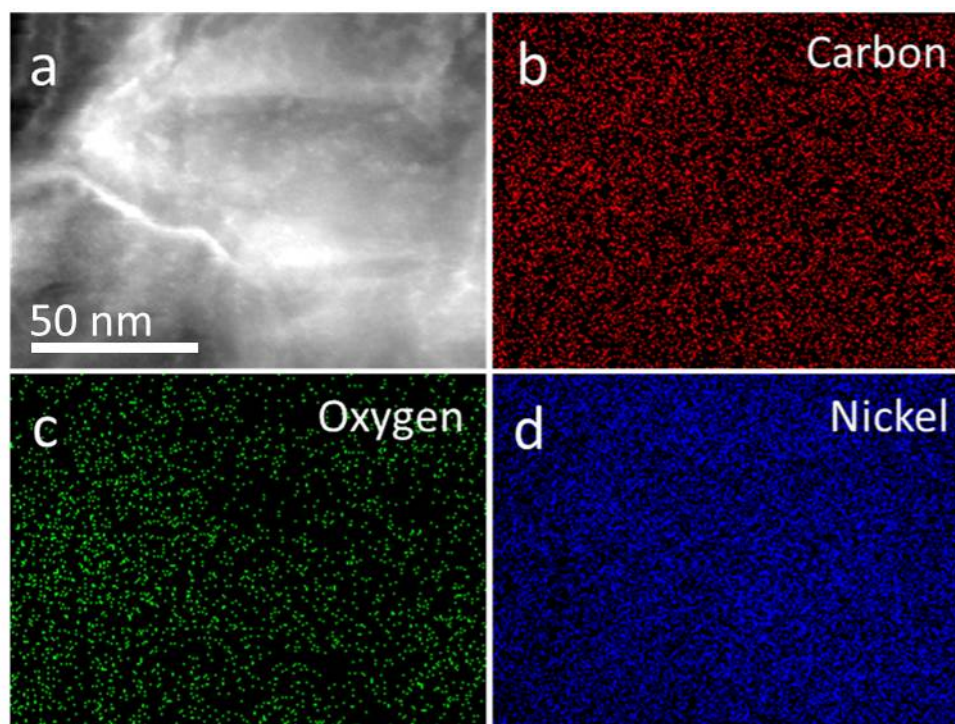


Figure S3 HAADF-STEM image and elemental mapping images (carbon, oxygen, and nickel atoms) of NiO-GO hybrid prepared from prepared from NiCNNi:GO = 75:25.

Figure S4

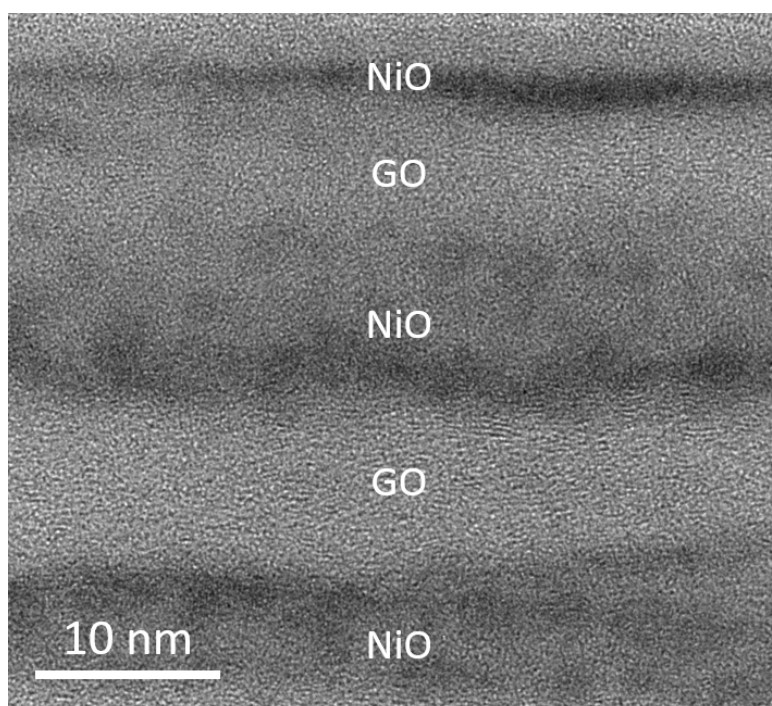


Figure S4 Cross-sectional TEM image of NiO-GO hybrid prepared from NiCNNi:GO = 75:25.

Figure S5

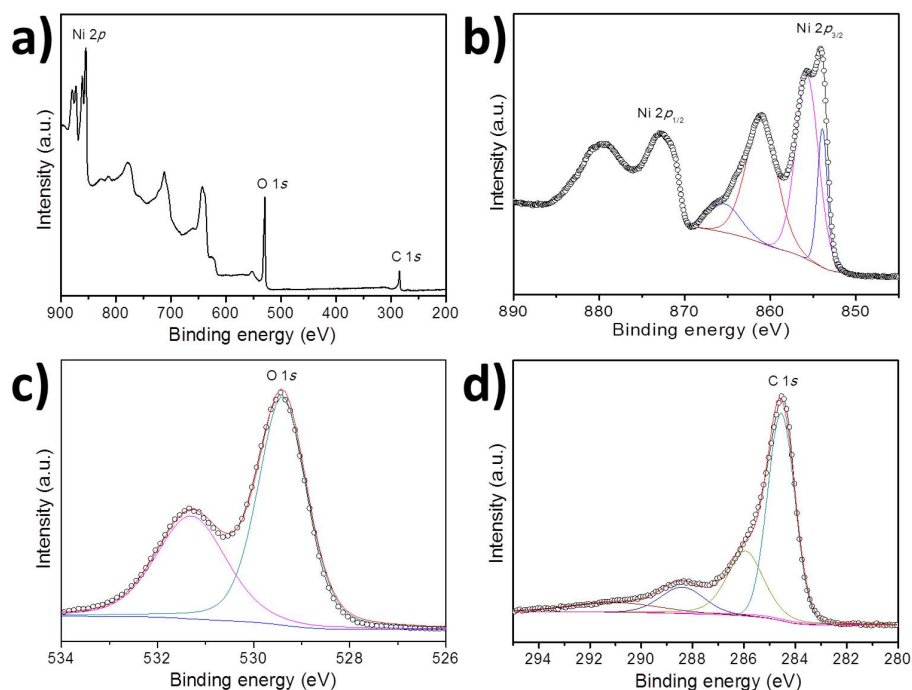


Figure S5 (a) XPS survey and (b, c, and d) high resolution XPS spectra of the NiO-GO hybrid prepared from prepared from NiCNNi:GO = 75:25 [(b) Ni 2*p*, (c) O 1*s*, and (d) C 1*s* spectra]. The Ni 2*p*_{3/2} peak contains the information necessary for the analysis, thus the Ni 2*p*_{1/2} contribution is not fitted.

Figure S6

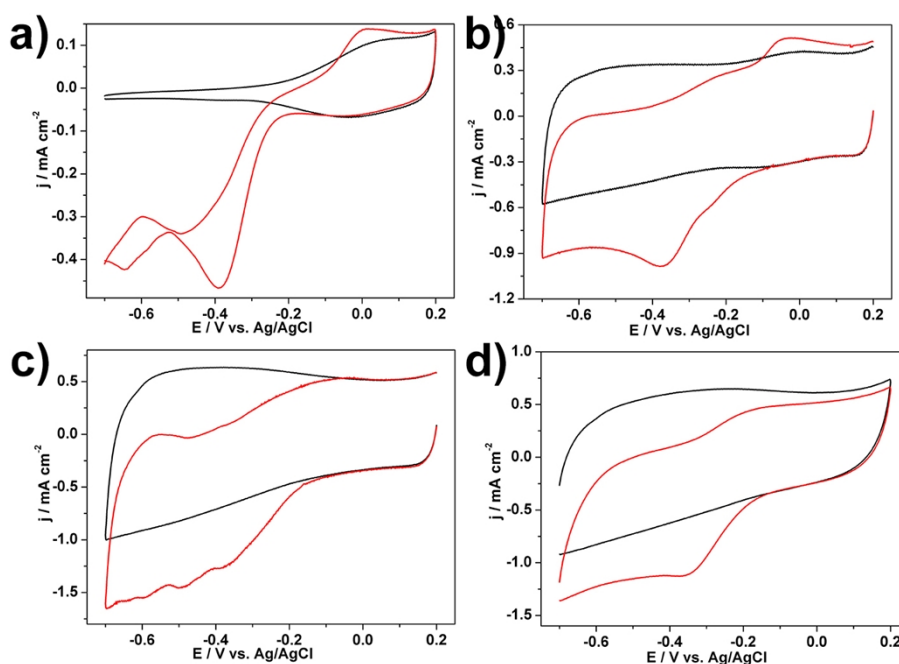


Figure S6 Cyclic voltammetric (CV) curves obtained under (black color) N₂-, and (red color) O₂-saturated 0.1 M KOH catalyzed by (a) the calcined NiO flakes, (b, c) the NiO-GO hybrids prepared from different NiCNNi:GO ratios [(b) NiCNNi:GO = 50:50, and (c) NiCNNi:GO = 25:75], and (d) the calcined GO sheets.