

Experimental Section

Materials. Triblock copolymer poly(ethylene glycol)-*block*-poly-(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic F127, $M_{av} = 12600$, $EO_{106}PO_{70}EO_{106}$) and tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) were purchased from Sigma-Aldrich. Orthophosphoric acid (H_3PO_4), hydrochloric acid (HCl), hydrofluoric acid (HF), Graphene oxide (GO), ammonium hydroxide (NH_4OH) and ethanol (EtOH) were purchased from Wako. The chemicals were used without further purification.

Synthesis of as-prepared SnPi. In a typical synthesis of SnPi, a mixed solvent (25 mL) consisting of 23 mL of EtOH and 2 mL of H_2O was acidified with 1.0 g (35 wt %) hydrochloric acid. Then, 1 g of triblock copolymer (Pluronic F127) was added to the acidified mixed solvent and magnetically stirred for 3 h at room temperature (298 K). Then 10 mmol of H_3PO_4 (85 wt %) was added to the pluronic F127 solution under stirring. In another beaker, 5 mmol of $SnCl_4$ was dissolved in 10 mL of absolute ethanol containing 20 μ L of HF (46 wt%). Then, the $SnCl_4$ solution was added to the H_3PO_4 -containing F127 solution over 1 h, and the stirring was continued for another 12 h at room temperature. After that, the solution was kept inside an oven at 333 K, dried for 72 h, and then transferred to a vacuum oven for 10 h. Then, the as-prepared material was transferred to a high temperature oven and calcined at 723 K for 3 h in nitrogen atmosphere to obtain carbonized SnPi material, and finally, this carbonized material was calcined at 773 K in air for 2 h to obtain the template-free hexagonally ordered mesoporous tin phosphate material (*meso*SnPi) with a crystalline framework.

Synthesis of SnPi@GO nanocomposite. The commercially available graphene oxide (0.1 mg mL^{-1}) was placed in a beaker and ultrasonicated for 30 min and the pH of the corresponding solution was maintained at around ~ 10 by using NH_4OH . The mixture was transferred to an autoclave and kept at 180 °C for 6 h. After that, the mixture was centrifuged and washed repeatedly with water and ethanol to remove the impurities. The obtained material (0.2 mg mL^{-1}) was suspended in a mixed solvent (H_2O : EtOH = 8:2) to obtain thin layers of graphene oxide. Then, the *meso*SnPi dispersion (0.2 mg mL^{-1}) was added to the GO suspension and sonicated for 5 min. Finally, the nanocomposite material (SnPi@GO) was collected by vacuum filtration and dried overnight in a vacuum oven.

Characterizations. Scanning electron microscope (SEM) images were collected with a Hitachi SU-8000 SEM at an accelerating voltage of 15 kV. Small and wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT 2500X diffractometer using monochromated Cu-K α radiation (40 kV, 40 mA) at a scanning rate of $0.1^\circ \cdot min^{-1}$. Nitrogen adsorption-desorption measurements were performed using a Belsorp-mini II Sorption System at 77 K. The specific surface areas were calculated by the Multipoint Brunauer-Emmett-Teller (BET) method at a relative pressure, P/P_0 , range from 0.05 to 0.30, while the total pore volumes were calculated by the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared (FT-IR) spectra were collected on a ThermoScientific Nicolet 4700 spectrometer using the KBr pellet technique. X-ray photoelectron spectroscopy

(XPS) was implemented on a JEOL JPS-9010 instrument. All binding energies were calibrated in relation to the C 1s line from adventitious carbon (285 eV). The Raman spectra were acquired with a Horiba-Jovin Yvon T64000 instrument at an excitation wavelength of 514.5 nm (ArKr laser).

Electrochemical measurements. Electrochemical measurements, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (*i-t*) were performed using a CHI 842B electrochemical analyzer with a conventional three-electrode configuration. A Pt wire and Ag/AgCl electrode were used as a counter and reference electrode, respectively. The working electrode was prepared as follows: the catalysts were ultrasonicated in a mixture of water, alcohol and 5% Nafion solution. The catalyst slurry was then uniformly coated on the polished glassy carbon electrode (4 mm in diameter) of rotating ring disk electrode (RRDE) and dried at room temperature. The loading amounts of the catalysts were 5.0 μL . The electrolyte solution was saturated with ultra-pure N_2 and O_2 for at least 1 hour before the measurements. The potentials were referenced to the reversible hydrogen potential electrode (RHE).

Oxygen reduction reaction (ORR) kinetics. The overall electron transfer process involved in a typical ORR can be calculated from the slope of the Koutecky-Levich plots using the following equation.^{R1}

$$1/j = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

where ω is the angular velocity of the disk and B is the reciprocal of the slope:

$$B = 0.620nFC_{\text{O}_2}D^{2/3}\nu^{-1/6} \quad (2)$$

in which n is the number of electron transfer per oxygen molecule, F is the Faraday constant ($F = 96\,485 \text{ C mol}^{-1}$), C_{O_2} is the concentration of O_2 , D is the diffusion coefficient of O_2 and ν is the kinematic viscosity of the electrolyte. For an O_2 -saturated 0.1 M KOH solution, C_{O_2} , D and ν are estimated to be $1.2 \times 10^{-3} \text{ M}$, $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $0.01 \text{ cm}^2 \text{ s}^{-1}$, respectively.^{R1}

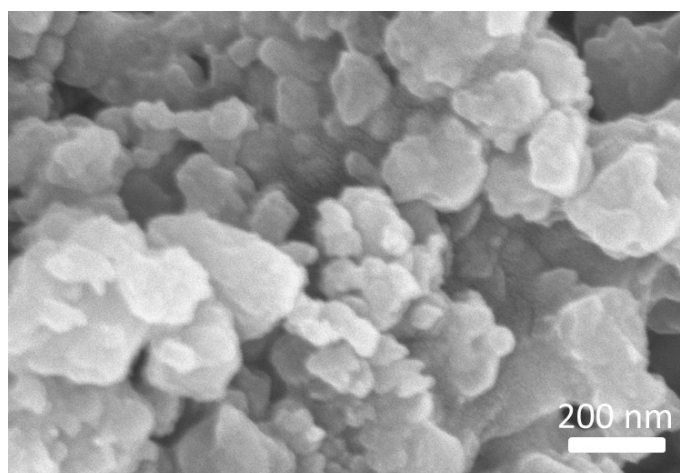


Fig. S1. SEM image of *bulkSnPi* prepared in the absence of Pluronic F127.

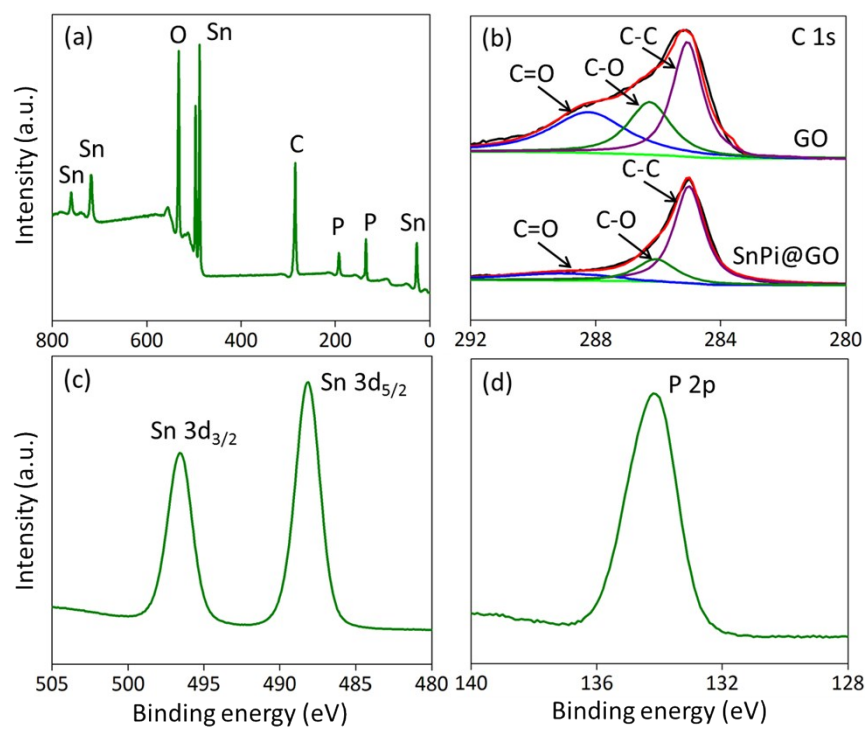


Fig. S2. (a) XPS survey spectrum of SnPi@GO. High resolution XPS spectra of (b) C1s of GO and SnPi@GO, (c) Sn3d and (d) P2p, respectively.

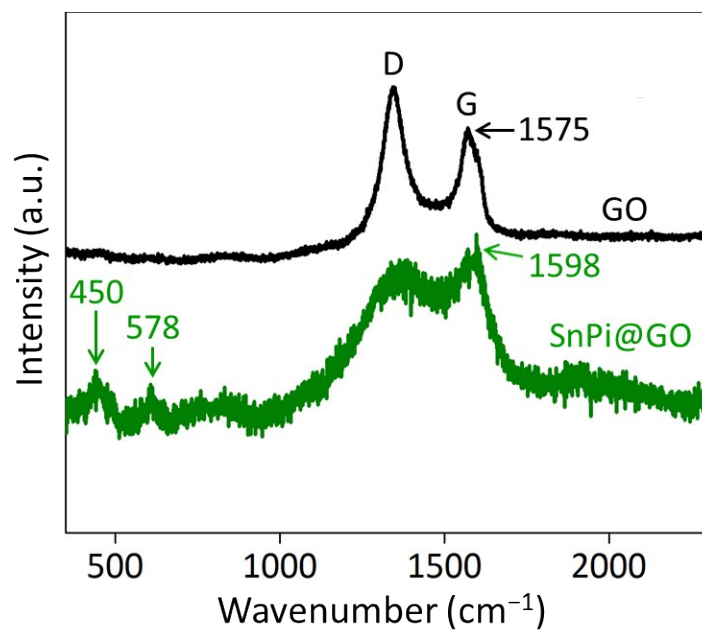


Fig. S3. Raman spectra of (a) GO and (b) SnPi@GO.

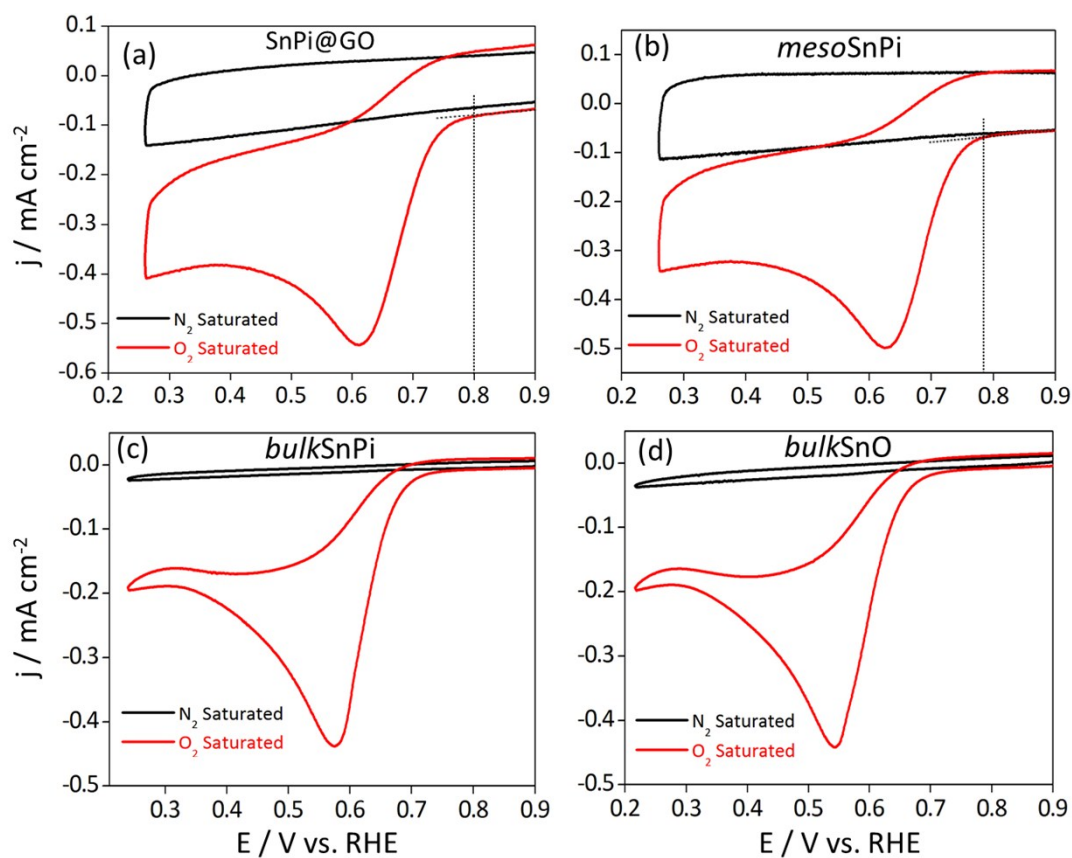


Fig. S4. CV curves of SnPi@GO, *meso*SnPi, *bulk*SnPi and *bulk*SnO measured in O₂- or N₂-saturated 0.1 M KOH solutions, at a scan rate of 20 mV s⁻¹.

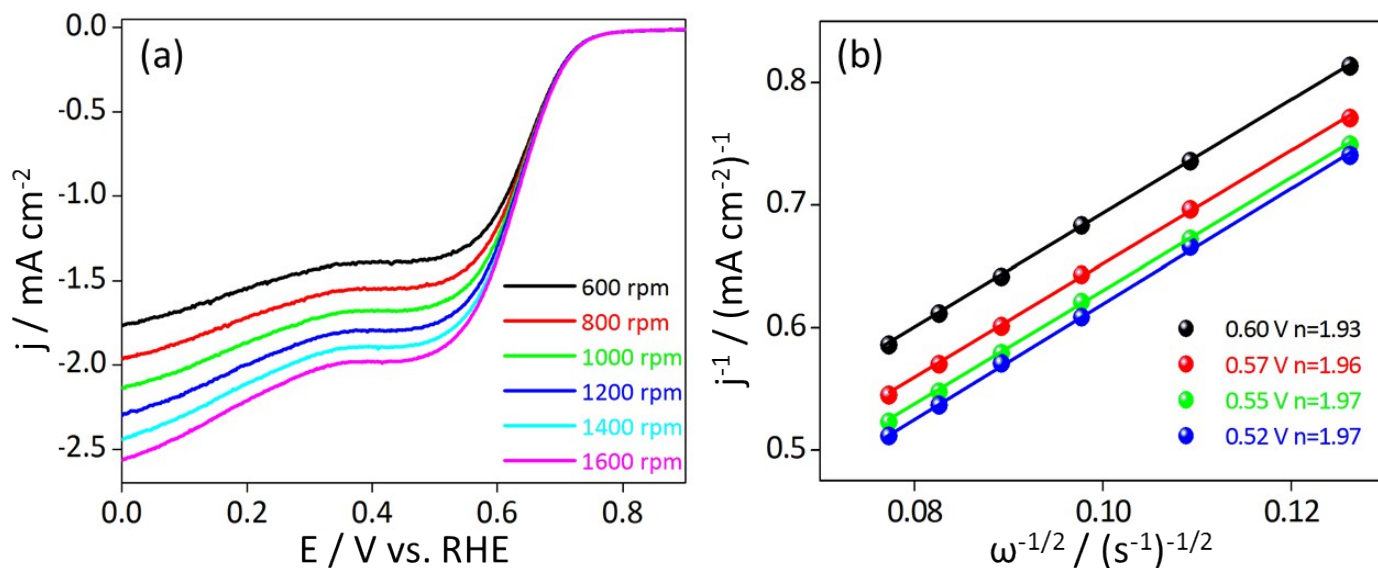


Fig. S5. (a) Polarization curves of *meso*SnPi at different rotation speeds and (b) the corresponding Koutecky–Levich (K-L) plots for *meso*SnPi.

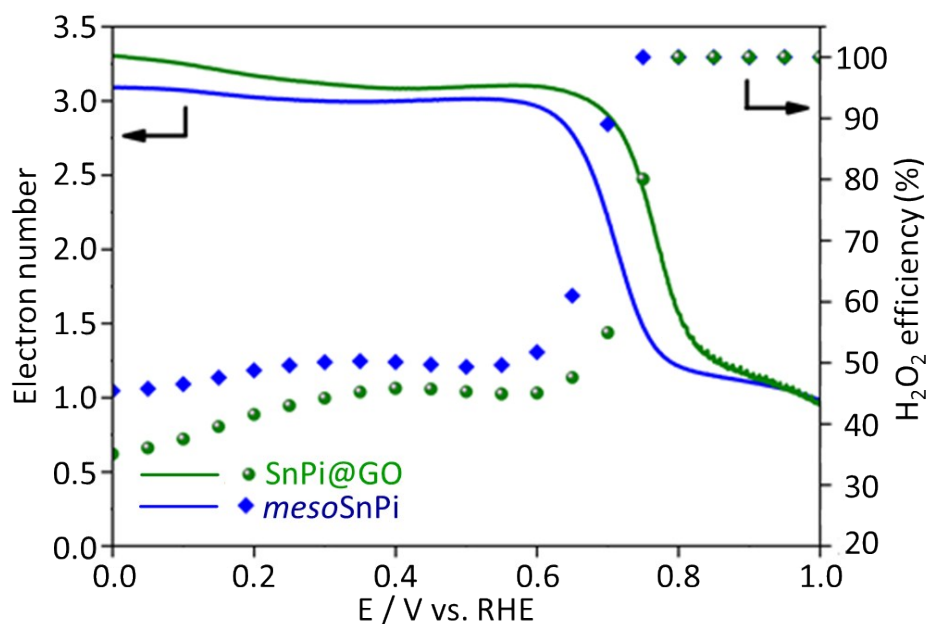


Fig. S6. Electron transfer numbers (n) and percentage of hydrogen peroxide (H_2O_2) formation for SnPi@GO and *meso*SnPi at various potentials based on the RRDE measurements.

Notes on Fig. S6. we have checked the RRDE data for both samples (*meso*SnPi and SnPi@GO). Based on the RRDE data, the electron number (n) and the H_2O_2 ratio ($p_{H_2O_2}$) were calculated by using Equations (1) and (2), respectively and the results are shown in Fig. S6:^{R2}

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}} \quad (3)$$

$$p_{H_2O_2} = \frac{\frac{200I_r}{N}}{I_d + \frac{I_r}{N}} \quad (4)$$

where, N is the collection efficiency of the RRDE. I_d and I_r are the faradic-disk and ring currents.

Table S1. Comparison of the ORR activity of the synthesized SnPi@GO composite with some state-of-the-art manganese oxides and other phosphate based nanomaterials.

Catalyst	Electrolyte medium	Catalyst loading (μg)	Scan rate (mV s^{-1})	Onset potential (V vs RHE)	References
SnPi@GO	0.1 M KOH	25	20	0.80	This work
Mn_3O_4	0.1 M KOH	20	5	0.59	R3
MnO	0.1 M KOH	100	5	0.61	R4
MnO_2 nanosheets	0.1 M KOH	80	10	0.62	R5
Mesoporous Mn_2O_3	0.1 M KOH	25	10	0.71	R6
MnPO (Manganese Phosphate)	0.1 M KOH	20	5	0.80	R7
FePO (Iron Phosphate)	0.1 M KOH	20	5	0.71	R7
CoPO (Cobalt Phosphate)	0.1 M KOH	20	5	0.73	R7
NiPO (Nickel Phosphate)	0.1 M KOH	20	5	0.72	R7
Pt/C	0.1 M KOH	100	10	0.96	R8

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