

Supporting information

Facile and sustainable fabrication of transparent mesoporous IrO_x films formed by nanoparticles assembly for efficient electrocatalytic water oxidation

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Experimental Section

Materials.

Potassium hexachloroiridate(IV) (K_2IrCl_6) and sodium hydroxide (NaOH) were obtained from Wako Chemical Co. Pluronic F127 was purchased from Sigma-Aldrich. The F-doped tin oxide (FTO) glass substrate was obtained from Asahi Glass Co. All the chemicals of analytical grade were used as received. All the solutions were prepared with Millipore water.

Preparation of mesoporous IrO_x electrodes

In a typical synthesis, 0.04 g of Pluronic F127 was dissolved in 0.4 mL of a 0.1 M aqueous NaOH solution, and then to the solution 0.01 g (20.7 μmol) of K_2IrCl_6 was slowly added under vigorous stirring at 40 °C. After stirring for 15 min, the initial dark brown solution gradually changed to light amber in color due to hydrolysis of the Ir-precursor. The resultant homogeneous solution (pH \approx 7.0) was diluted 100 times by water. 10 μL of this solution (corresponding to 5.2 nmol of Ir) was spread on a FTO substrate (placed on a hot plate at 40 °C) by drop-cast and allowed to dry. Before drop-cast, the FTO substrate was cleaned up by a UV-ozone treatment (SEN LIGHTS Co. Photo Surface Processor PL16-110) for 15 min and the coated area was fixed to be 0.8 \times 1.25 cm. After keeping the as-coated film at 70 °C for 15 min, the electrode was heated at 400-550 °C (1 °C min^{-1}) in flowing N_2 and maintained at these temperatures for 1 h, followed by calcination at these temperatures for 3 h in flowing O_2 . (Heating the electrode directly under the air provided inferior performance to the present IrO_x film.) After cool down to room temperature the IrO_x -coated substrate was washed by copious amount of water and dried in air. The resultant sample was denoted as IrO_x -F127. The control sample was prepared under the identical synthesis procedures except the addition of Pluronic F127, denoted as IrO_x -untemplate.

Structural characterization

The surface morphology was observed by scanning electron microscopy (SEM; JEOL, JSM-6500F). The nanostructures and the crystalline phase were characterized by transmission electron microscopy (TEM; JEOL, JEM 2100F, operated at 200 kV) and powder X-ray

diffraction (XRD; Rigaku MiniFlexII diffractometer) using monochromated Cu K α ($\lambda = 1.54$ Å) radiation, respectively. Nitrogen adsorption-desorption isotherms were measured using BELSORP-miniII (BEL Japan Inc.) at 77 K. Prior to gas adsorption, samples were degassed in vacuum for 4 h at 150°C. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the surface areas. The pore size distributions were analyzed from the adsorption branches of the isotherms by the Barrett-Joyner-Halenda (BJH) method. The TEM images, XRD and N₂ sorption data were taken of powders scratched off from the annealed films on the glass substrate. Raman spectra were recorded using a Raman spectrophotometer (a Horiba-Jobin-Yvon LabRAM HR) using 532 nm excitation and silicon standard wavenumber (520.7 cm⁻¹). Fourier transformed infrared (FTIR) spectra were recorded on a Jasco FT/IR-4200 spectrophotometer. Dynamic light scattering (DLS) measurements were carried out using a ζ -potential and particle size analyzer (Photal Otsuka Electronics, ELSZ-2N). For analysis of the iridium amount, as-coated films on the FTO electrode was dissolved in a concentrated nitric acid solution (60%) and the iridium amount in the dissolved solution was measured using an inductively coupled atomic emission (ICP-AES) spectrometer (Seiko Instruments Inc., SPS1500).

Electrochemical measurements

Electrochemical measurements were carried out using an electrochemical analyzer (Hokutodenkou HZ-7000). A two-compartment electrochemical cell separated by a Nafion membrane was used. A three-electrode-type system has been employed by using an IrO_x-coated FTO electrode (1.0 cm² geometrical area) as working electrode and an Ag/AgCl reference electrode in one compartment and a Pt wire counter electrode in the other compartment. The potentials were expressed as the values versus Ag/AgCl unless otherwise noted. An aqueous 0.1 M phosphate solution (pH \approx 7.0) was used as an electrolyte in both compartments of the electrochemical cell, which was sealed and saturated with Ar gas prior to the electrochemical measurement. CVs were recorded at a scan rate of 50 mV s⁻¹ between the ranges of 0 V and 1.5 V at 25 °C. 3 cycles of CV have been measured, and the CV of the 2nd cycle is shown in Fig. 4. Tafel plots were derived using a linear sweep voltammogram (LSV)

measured at a scan rate of 0.5 mV s^{-1} between the ranges of 0.8 V and 1.1 V. The resistance of the electrolyte was measured to be $24 \text{ } \Omega$. The IR drop was at most 140 mV for CV measurement and was neglected in the present study. Electrochemical impedance spectra were measured at an applied potential of 1.0 V vs Ag/AgCl in a 0.1 M phosphate solution ($\text{pH} \approx 7.0$) in a frequency range of 1 mHz to 20 kHz (amplitude of 10 mV) using the electrochemical analyzer. To detect H_2 and O_2 gasses evolved during electrocatalysis, the reaction cell was purged by Ar gas for 1 h prior to electrocatalysis to remove residual air. The electrolyte in the working compartment was 4 mL and the headspace volume was 87.3 mL. Electrocatalytic water oxidation was conducted at 1.2 V vs Ag/AgCl of applied potential for 1 h, and the current was recorded during the course of electrolysis by the electrochemical analyzer. The amounts of H_2 and O_2 evolved during electrocatalysis were analyzed in the gas phases (headspace regions) of the counter and working electrode compartments, respectively on a gas chromatograph (Shimadzu, GC-8A with TCD detector and molecular sieve 5A column and Ar carrier gas).

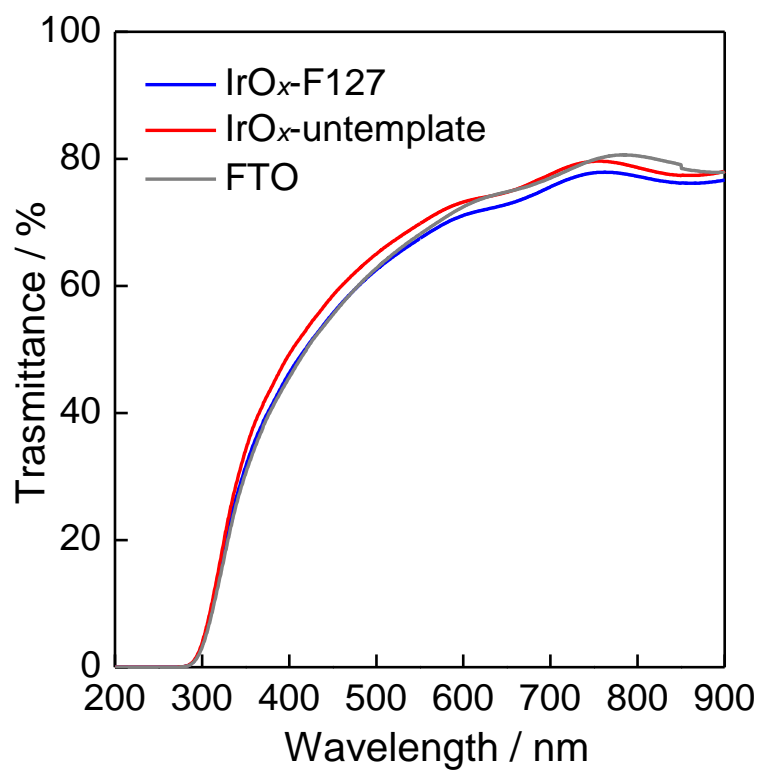


Fig. S1. Transmission spectra of IrO_x-F127, IrO_x-untemplate and bare FTO electrodes calcined at 400 °C.

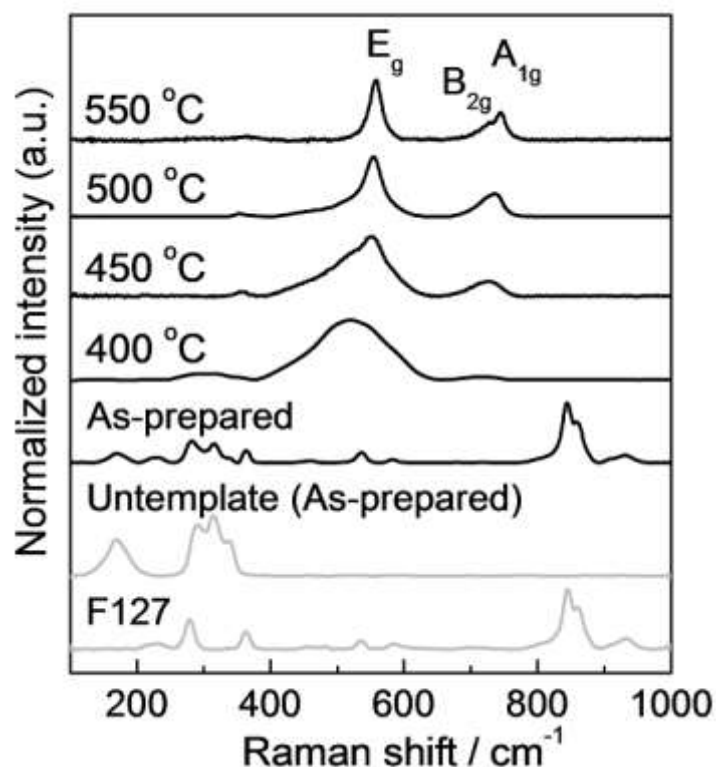


Fig. S2. Raman spectra of the IrO_x-F127 films as-prepared and calcined at 400-550 °C. Gray lines show the Raman spectra of as-prepared IrO_x-untemplate film and Pluronic F127.

Note S1.

The Raman spectra (Fig. S1) of as-prepared film showed Raman signals at 168, 285, 315 and 335 cm⁻¹ in addition to 228, 362, 537, 845 and 930 cm⁻¹ due to F127. These are assigned to Ir-OH moieties of the [Ir(OH)_x(OH₂)_yCl_z]ⁿ⁻ complex species, which is corroborated by the Raman spectrum of a monomeric hydroxyiridate complex produced by complete alkaline hydrolysis of K₂IrCl₆ at pH 13.^{S1} The Raman signals for Ir-OH moieties are more prominently observed for the as-prepared IrO_x-untemplate film.

References

S1. D. Chandra, D. Takama, T. Masaki, T. Sato, N. Abe, T. Togashi, M. Kurihara, K. Saito, T. Yui, M. Yagi, *ACS Catal.*, 2016, **6**, 3946-3954.

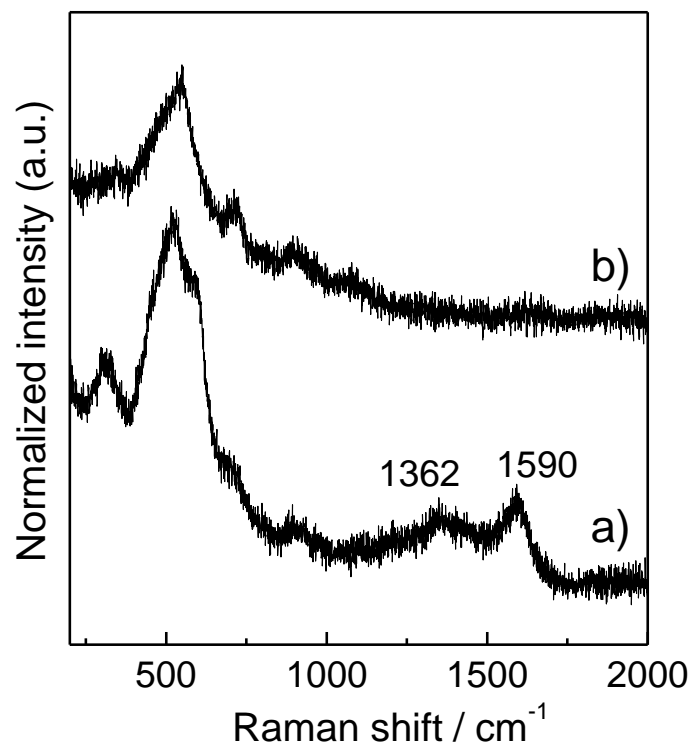


Fig. S3. Raman spectra of the IrO_x-F127 films annealed at 400 °C a) under N₂ for 1 h and b) under N₂ for 1 h followed by calcination under O₂ for 3 h.

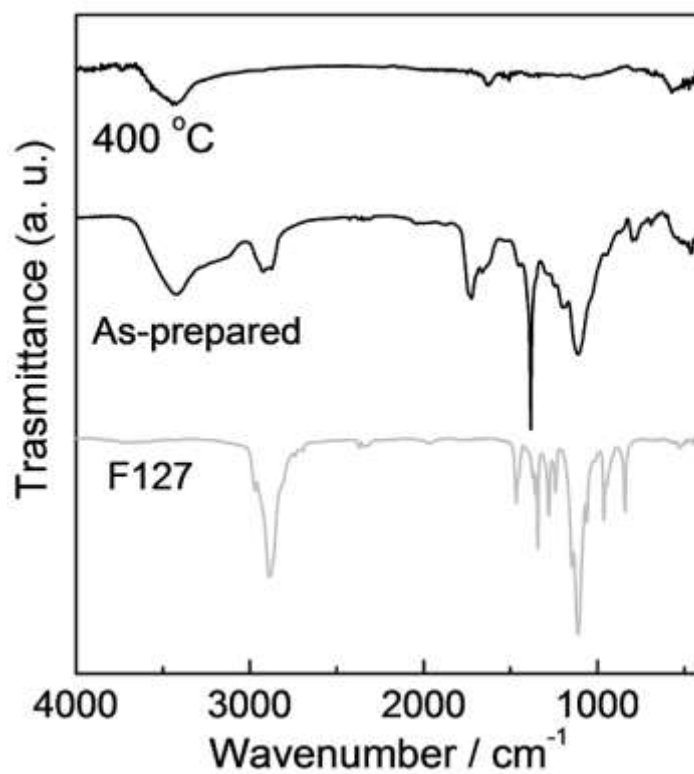


Fig. S4. FTIR spectra of the IrO_x-F127 films as-prepared and calcined at 400 °C. Gray line shows the FTIR spectra of Pluronic F127.

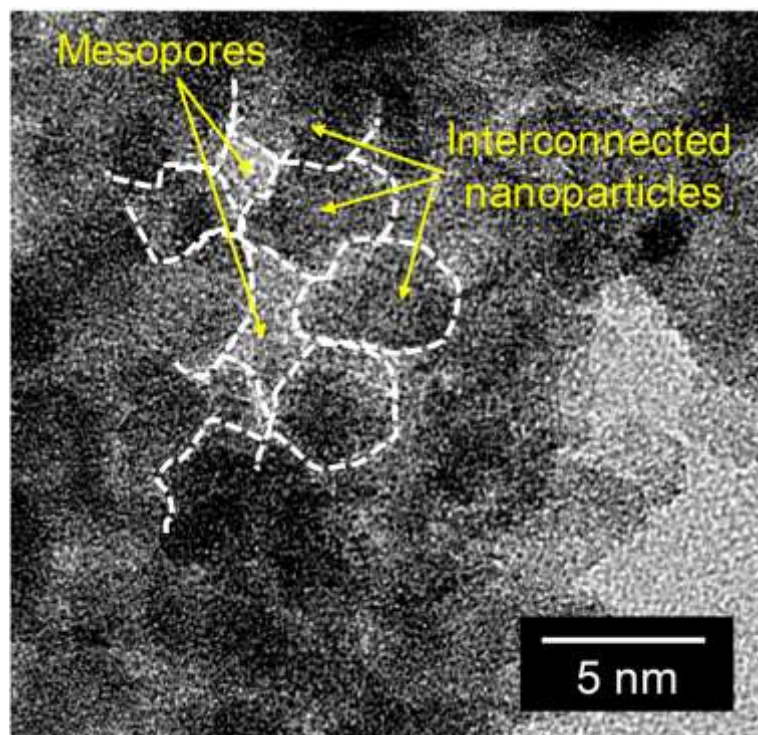


Fig. S5. HRTEM image of IrO_x-F127 film calcined at 400 °C. Boundaries of few nanoparticles are highlighted by white circles.

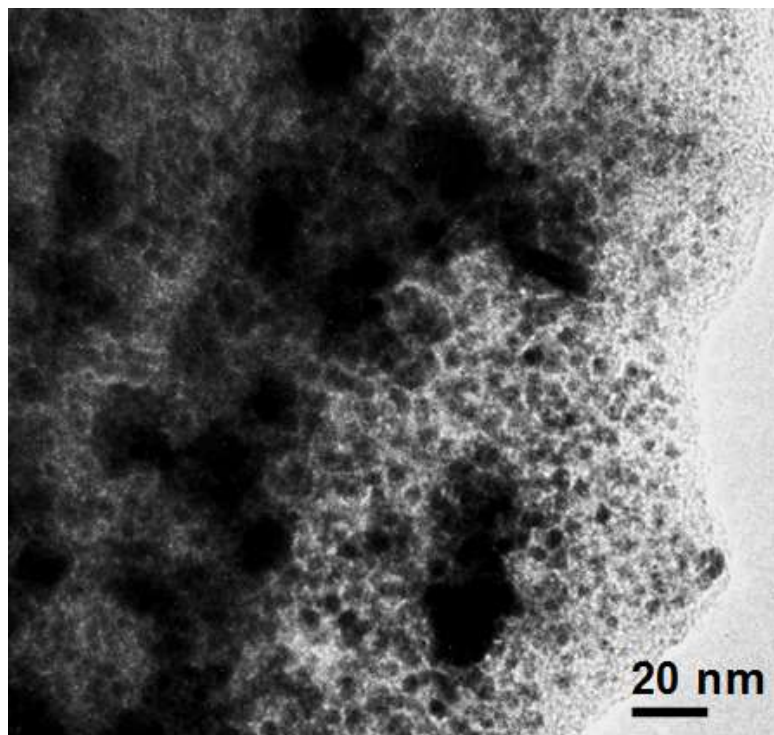


Fig. S6. TEM image of IrO_x-unttemplate film calcined at 400 °C.

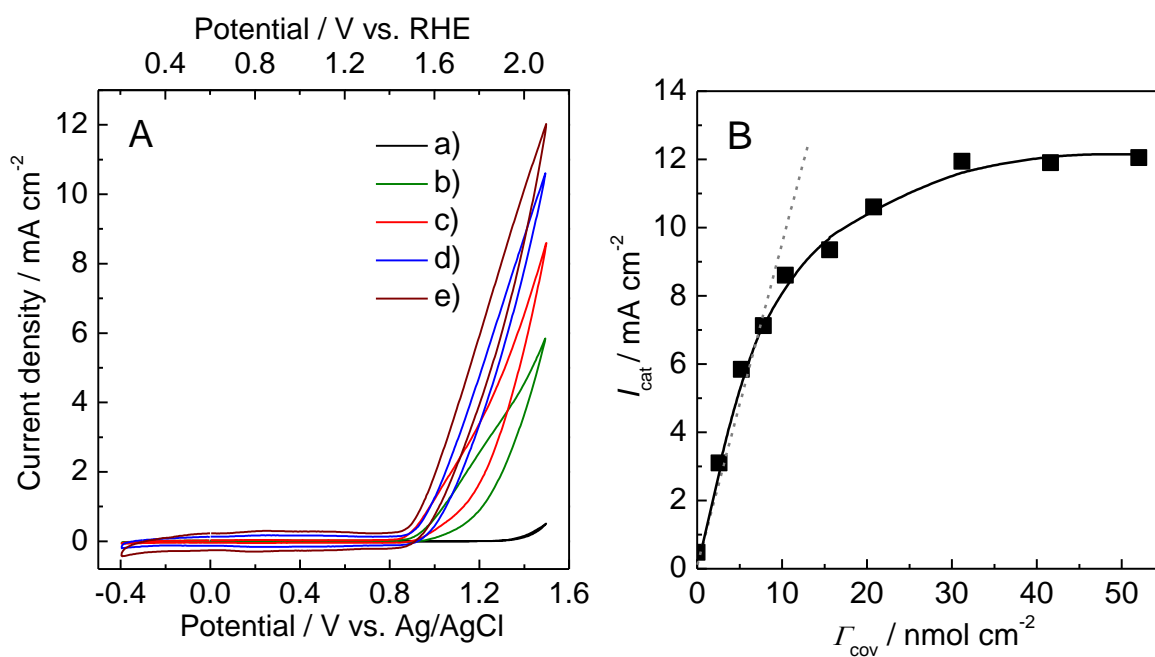


Fig. S7. (A) Cyclic voltammograms (CVs) of IrO_x-F127 electrodes calcined at 400 °C prepared with different Γ_{cov} of a) 0.0, b) 5.2, c) 10.4, d) 20.8 and e) 52 nmol cm⁻², as measured in a 0.1 M phosphate solution (pH \approx 7.0). (B) Plots of I_{cat} (at 1.5 V vs. ag/AgCl for CVs) versus Γ_{cov} .

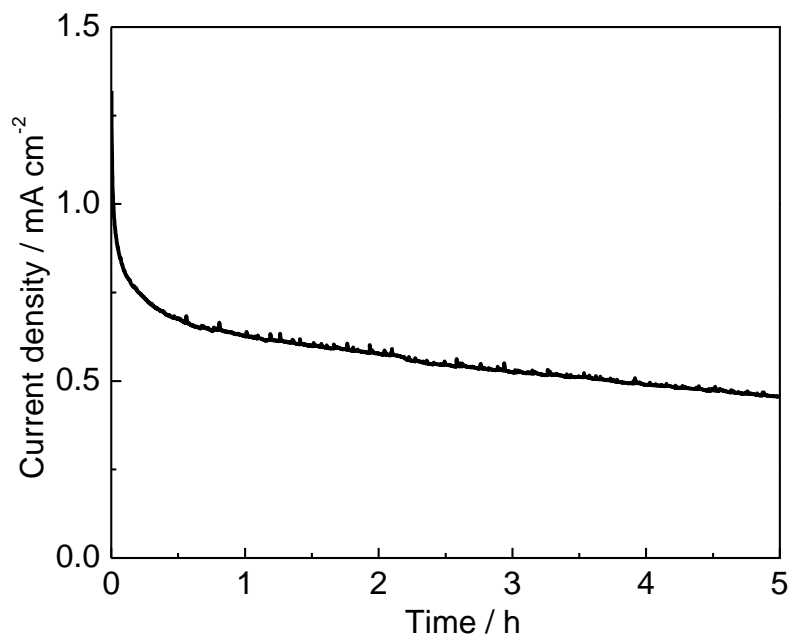


Fig. S8. Current-time profile during 5 h electrocatalysis in a 0.1 M phosphate solution (pH \approx 7.0) at 1.2 V vs Ag/AgCl using IrO_x-F127 electrode calcined at 400 °C.

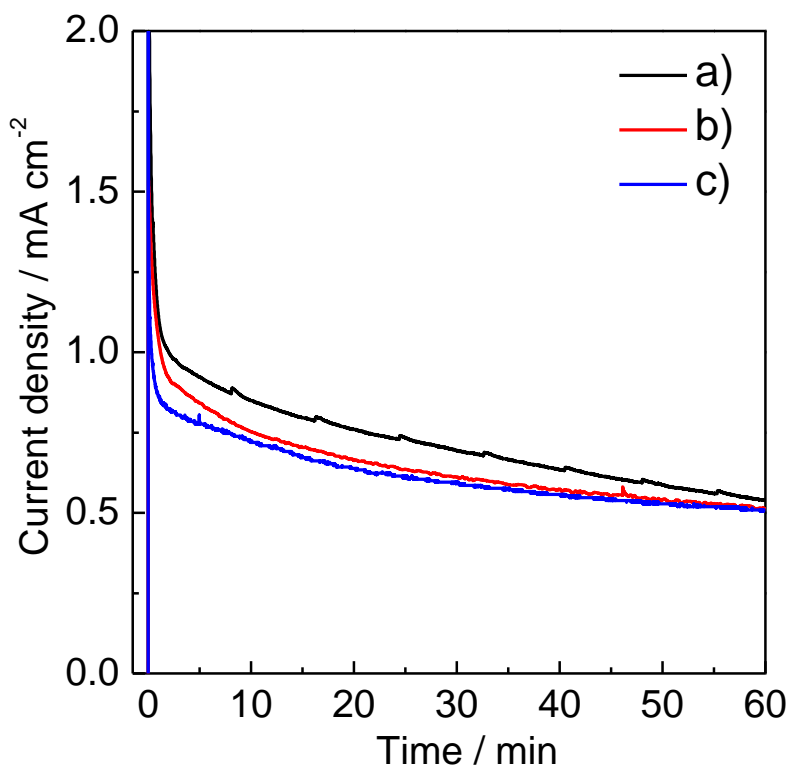


Fig. S9. Current-time profiles during electrocatalysis using a (a) fresh IrO_x-F127 electrode calcined at 400 °C (traced from Fig. 8a) and (b) 2nd and (c) 3rd trail run by the reused electrode as measured in a 0.1 M phosphate solution (pH ≈ 7.0) at 1.2 V vs Ag/AgCl.