Supporting Information

Efficient Electrochemical Water Oxidation in Neutral and Near-Neutral Systems by Nanoscale Silver-Oxide Catalyst

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Experimental Details

Materials and Methods:

AgNO₃ (99.999%) and sodium bicarbonate (NaHCO₃, 99.5-100.5%) were purchased from Sigma Aldrich. CO₂ gas (99.999%) was obtained from Linde, B.V. Netherlands. Indium-tin-oxide (ITO) coated glass slides (8-12 Ω /sq surface resistivity) were purchased from Aldrich. A glassy carbon disk (diameter d=0.5 mm) was obtained from Pine research instrumentation. All solutions were prepared in ultra-pure water (Millipore MilliQ[®] A10 gradient, 18.2 M Ω cm, 2–4 ppb total organic content) and all electrochemical measurements were performed in deoxygenated aqueous solutions at room temperature. The glassware and the electrochemical cell and electrodes were cleaned and prepared as described previously.^[1]

A three electrode configuration pyrex glass cell was employed for cyclic voltammetry (CV). ITO coated glass slides (1 cm x 2.5 cm, exposed surface area 1.0 cm²) were used as working electrodes (WE). The catalytic water electrolysis experiments were carried out in a three electrode double junction H-type glass electrolysis cell. A platinum wire (thickness: 1 mm), shaped into a spiral, was used as a counter electrode (CE). A silver-silver chloride electrode (SSCE: Ag/AgCl/KCl) was applied as the reference electrode. However, all potentials are referred to a normal hydrogen electrode (NHE). Cyclic voltammetry experiments were performed with an Autolab PG-stat10 potentiostat controlled by GPES-4 software.

For the electrochemical measurements, CO₂ gas was purged (1 atm) through the NaHCO₃ electrolyte solution throughout the course of the entire experiment, and at least 20 minutes before each test (pH=6.7–6.8). Oxygen evolution was characterized by online gas chromatography (GC) measurements using micro-GC, T-3000 SRI instruments. The gas mixture from the cell was delivered directly to the sampling loop of the gas chromatograph. Sampling points were collected every 10 minutes, and the gaseous products were analyzed using a packed MolSieve 5A coupled with a thermal conductivity detector (TCD). Ar (99.9999%) was used as the carrier gas during the GC analysis.

The SEM (scanning electron microscopy) images were taken with a FEI NanoSEM 200 microscope. After the electrodeposition of a catalytic film on the electrode, the catalyst samples were rinsed with deionized water and allowed to dry in air before loading into the instrument. The SEM images were taken with an acceleration voltage of 5-15 kV. The resolution at 15 kV is 1 nm and 1.8 nm at 1 kV. The XPS measurements are carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K α = 1486.6 eV) operating at 72W and a spot size of 400µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2 x 10⁻⁹ mbar and during measurement 3 x 10⁻⁷ mbar Argon because of the charge compensation dual beam source. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced A25diffractometer equipped with a Cu X-ray tube (Cu–K_{α}; λ = 0.154 nm) operated at 40 kV and 40 mA.

TEM experiments were performed in a Titan 80-300 ST electron microscope from FEI Company that was equipped with a spherical aberration corrector for its probe. The entire experiments were performed by setting the primary electron beam energy to 300 keV. Several bright-field TEM (BF-TEM) images were acquired by setting the microscope at nominal magnifications of tens of thousands to few hundred thousand. Selected-area electron diffraction (SAED) patterns from different areas of samples were acquired by inserting a 10 micron of SAED-aperture and then switching the microscope to diffraction mode. The typical camera-lengths were set to 230 to 330 mm prior to acquiring these SAEDs. Aberration corrected high-angle annular dark-field (HAADF) scanning TEM (STEM) analysis was also performed on the AgOx samples. It should be noted that the spherical aberration corrector was aligned so that the third-order coefficient (C3) was reduced to about one micron. This allowed performing the HAADF-STEM analysis by kepping the convergence angle at 17 mrad. Hence high quality micrographs in terms of both contrast and resolutions were acquired with this microscope. Moreover, the camera-lengths during these experiments were kept in the range of 90 to 145 mm to ensure the image contrast could be dominated by atomic-number (Z).

The **AgOx-NP** type electrocatalyst is generated *in situ* from a CO₂ saturated (1 atm) bicarbonate solution (0.1 M – 1.0 M) containing Ag⁺ (0.25 mM – 1 mM), on ITO or a glassy carbon disk during constant potential experiment while holding the potential of the working electrode above at 1.3 V (vs. NHE). The catalyst film is also generated during the CV's between 0.0 V – 1.35 V (vs. NHE).



Figure S1. Cyclic voltammetry (at scan rate of 50 mV sec⁻¹) data for the in situ surface-deposited **AgOx-NP** based electrocatalyst and for the IrO_2 and RuO_2 catalysts in borate buffer (pH=9.2).



Figure S2. SEM (scanning electron microscopy) images of the electrodeposited **AgOx-NP** type electrocatalyst at (top) 20,000 X and (bottom) 135,000 X magnifications.



Figure S3. XPS (x-ray photoelectron spectroscopy) spectra of the (a) electrodeposited **AgOx-NP** on an ITO anode; enlarged view of the XPS for Ag 3d and O 1s present in the electrodeposited catalytic layer.



Figure S4. Raman spectrum for the electro-generated **AgOx-NP** film. (The **AgOx-NP** electrocatalyst is developed by CPE at 1.40 V in HCO_3^-/CO_2 system with 0.5 mM Ag⁺).



Figure S5. EDX (Energy dispersive X-ray) spectroscopy of the electrodeposited **AgOx-NP** film. (For EDX analyses, the **AgOx-NP**@ITO based catalyst system is developed by CPE at 1.40 V in HCO_3^{-}/CO_2 system with 0.5 mM Ag⁺).



Figure S6. EDX (Energy dispersive X-ray) elemental mapping for electrodeposited **AgOx-NP** film. (The **AgOx-Np** @ITO based catalyst system is developed by CPE at 1.40 V in HCO_3^{-}/CO_2 system with 0.5 mM Ag⁺).



Figure S7. Controlled-potential water electrolysis with a blank ITO in deoxygenated 0.2 M bicarbonate solution with (ITO/**AgOx-NP**) and without (ITO) 0.5 mM Ag^+ at constant potential of 1.41 V (vs. NHE).



Figure S8. Online Gas chromatographic measurements during water electrolysis with bare ITO (blue) and for the AgOx@ITO system (green) in clean bicarbonate electrolytes. The oxygen chromatographic traces are normalized to residual O_2/N_2 from ambient air.

Catalyst Materials ^[a]	O₂ Onset Potential (vs RHE) ^[b]	Tafel Slope (mV/dec) ^[c]	Overpotential @10mA cm ⁻²	Current Density@2.0 V (vs RHE)	Ref.
RuO₂	~1.48 V	39	~510 mV	7.2 mA cm ^{-2}	2,3
IrO ₂	~1.58 V	45	~540 mV	5.0 mA cm ⁻²	3
AgOx-NP	~1.65 V	55	~590 mV	4.1 mA cm ⁻²	This work
CoOx	>1.71 V	90	~690 mV	3.3 mA cm^{-2}	2
NiOx	~1.75 V	59/120 ^[d]	~720 mV	2.8 mA cm ⁻²	4

Table S1. Electrochemical and catalytic water oxidation data for different electrodeposited metal-oxide materials tested in near-neutral phosphate or borate buffers.

^[a]The metal-oxides electrocatalysts in the list are prepared via electrodeposition, details are described in the respective references; ^[b]The oxygen onset is the calculated from the anodic current onset at $J > 0.1 \text{ mA cm}^{-2}$; ^[c]Tafel slope is taken from current – overpotential (log i vs η) plot in oxygen evolution regime from 0.1 to 1.0 mA cm⁻²; ^[d]Tafel slopes of 59 and 120 mV dec⁻¹ are taken with and without preconditioning respectively, for 12 h of pre-electrolysis at a current density of 1.0 mA cm⁻².

References

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