Electronic Supplementary Information

# Oxygen electroreduction promoted by quasi oxygen vacancies in metal oxide nanoparticles prepared by photoinduced chlorine doping

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## Experimental Section

### Synthesis of ITO Nanoparticles and Cl-ITO Nanoparticles

ITO nanoparticles were prepared according to literature procedures.[1] Briefly, 0.2672 g of indium acetylacetonate [In(acac)$_3$] and 0.02729 g of tin(IV) tert-butoxide [Sn(OtBu)$_4$] were mixed with 20 mL of benzyl alcohol and stirred overnight before being transferred to an autoclave. Subsequently, the autoclaves were heated up and maintained at 200 °C for 17 h. The products were isolated by filtration, washed with copious ethanol and acetone, and finally dried in air. After that, the dried products were treated by UV photoirradiation in a UV ozone cleaner for about 20 min to remove trace amounts of organic impurities adsorbed on the ITO surface, affording purified ITO NPs.

To prepare Cl-ITO nanoparticles, a calculated amount of the ITO nanoparticles prepared above were dispersed in *o*-dichlorobenzene (ODCB) in a quartz beaker, and the mixture was exposed to UV photoirradiation for a various period of time (Scheme 1).[2] The resulting nanoparticles were isolated by filtration, washed with copious ethanol and acetone, and finally dried in air. After that, the dried products were further treated by UV irradiation in a UV ozone cleaner for about 20 min to remove trace amounts of organic impurities adsorbed on the surface. The sample was denoted as Cl-ITO NPs.

### Characterizations

Transmission electron microscopic (TEM) measurements were conducted on a Tecnai G2-F20 equipped with an EDX detector at an acceleration voltage of 100 kV. The TEM samples were prepared by drop-casting a dispersion containing the catalysts directly onto a copper grid coated with a holy carbon film. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Phi X-tool instrument. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-Advance diffractometer using Cu Kα radiation.

## Electrochemistry

Electrochemical measurements were performed on a CH 750E electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) in a conventional three-electrode cell, with a platinum wire as the counter electrode, a Ag/AgCl as the reference electrode, and a catalysts-modified glassy carbon electrode as the working electrode. The catalyst inks were prepared by adding 1 mg of catalysts into a solution containing water, isopropanol and Nafion (5%) at a volume ratio of 4:1:0.025 to form a homogeneous suspension at a catalyst concentration of 1.0 mg/mL. A calculated amount (20 μL) of the suspension was then evenly cast on the clean glassy carbon electrode (GCE) surface with a syringe and dried in air, corresponding to a catalyst loading of 102.0 μg/cm$^2$. Linear sweep voltammograms (LSV) were acquired in an $O_2$-saturated 0.1 M KOH aqueous solution at various rotation rates (225 to 1600 rpm).

The Koutecky–Levich plots were analyzed by the K-L equations

$$\frac{1}{j}=\frac{1}{j_L}+\frac{1}{j_k}=\frac{1}{Bw^{1/2}}+\frac{1}{j_k}$$

$$B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

$$j_k=nFkC_0$$

where j is the measured current density, $j_k$ is the kinetic current density, $j_L$ is diffusion current density, w is the electrode rotation rate, F is the Faraday constant (96485 C/mol), $C_0$ is the bulk concentration of $O_2$ ($1.2 \times 10^{-6}$ mol/cm$^3$ ) at room temperature, $D_0$ is the diffusion coefficient of $O_2$ ($1.9 \times 10^{-5}$ cm$^2$/s), k is the electron-transfer rate constant and *v* is the kinematic viscosity of the electrolyte (0.01 cm$^2$/s).

The Tafel plot was calculated from the mass-transport correction of RDE by

$$j_k=\frac{j\times j_L}{(j_L-j)}$$

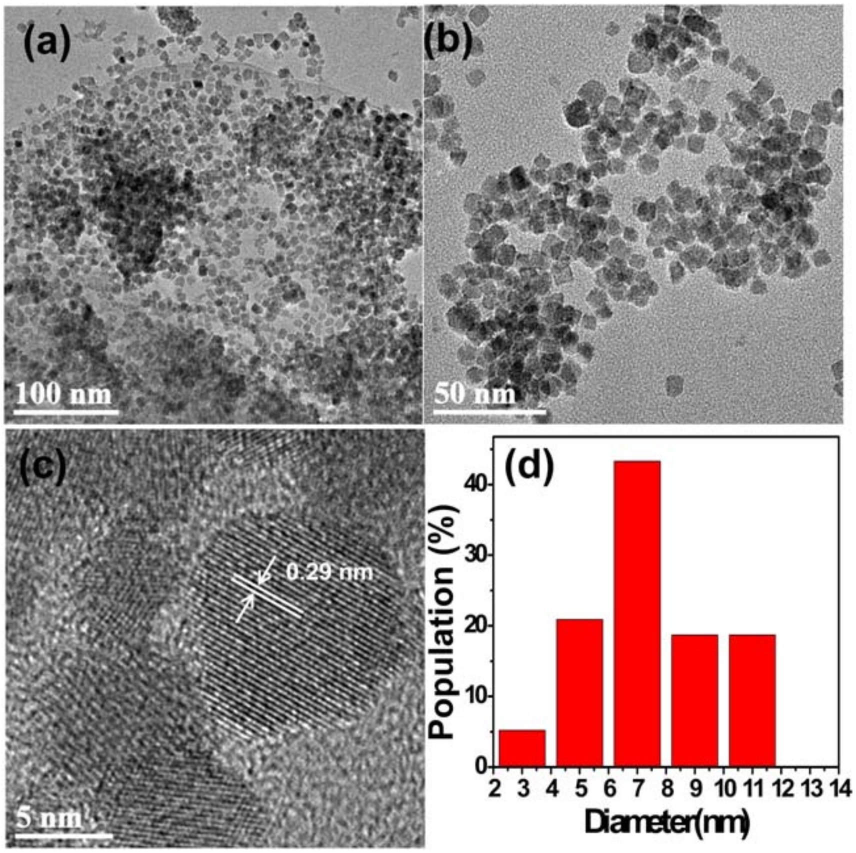

**Figure S1.** TEM images and corresponding size distribution plot of ITO nanoparticles.

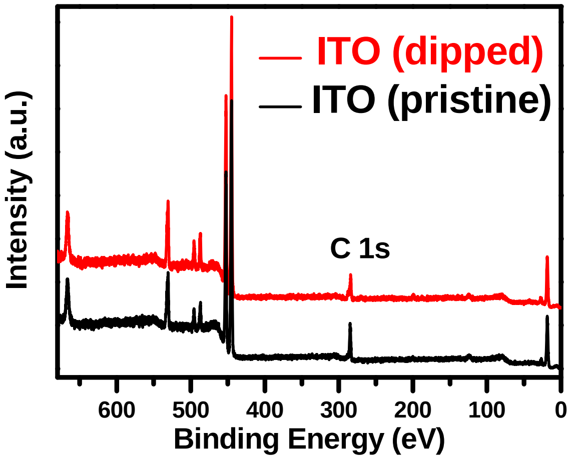

**Figure S2.** XPS survey spectra of ITO (indicated as ITO (pristine)) and ITO which was not exposed to UV irradiation while dipped in ODCB (indicated as ITO (dipped)). No signal of Cl was observed in either sample.

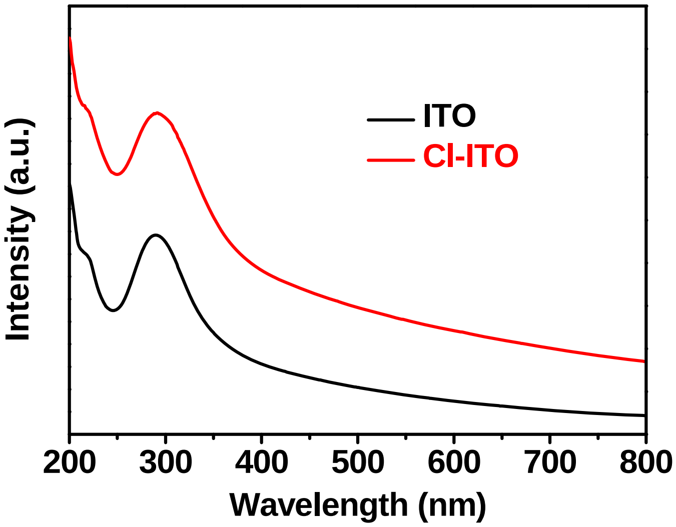

**Figure S3.** UV-vis absorption spectra of ITO and Cl-ITO NPs.

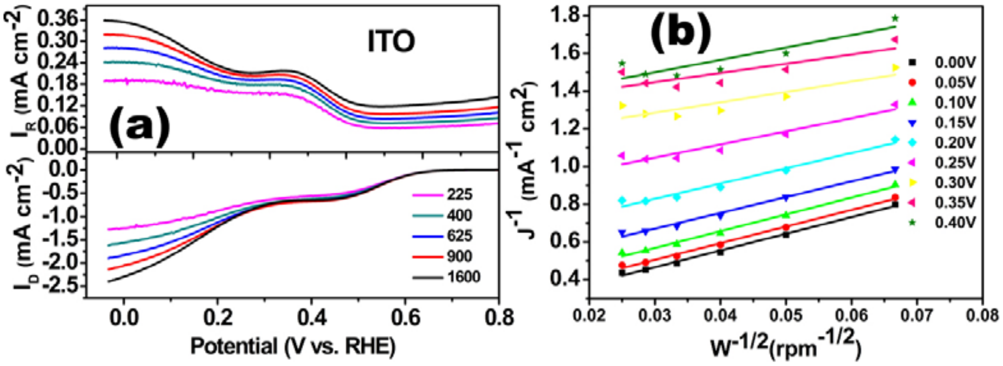

**Figure S4.** (a) LSV of ITO at different rotation rates and (b) the corresponding K-L plots at an electrode rotation rate of 900 rpm. The measurements were conducted on a glassy carbon electrode at a catalyst loading of 102.0 μg/cm$^2$ in $O_2$-saturated 0.1 M KOH at a potential sweep rate of 10 mV/s.

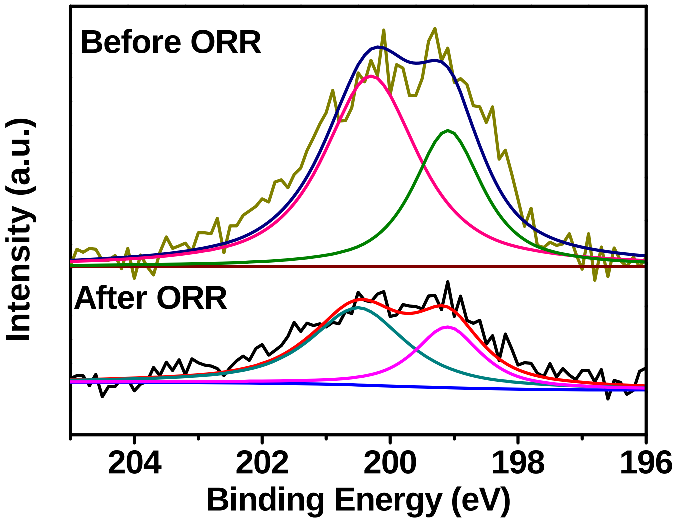

**Figure S5.** High-resolution XPS scans of Cl 2p electrons of Cl-ITO nanoparticles before and after ORR tests (100 cycles at a potential scan rate of 10 mV/s between -0.03 and +1.12 V in an $O_2$-saturated 0.1 M KOH solution). Based on the integrated peak areas, the loading of Cl dopants was estimated to be 3.9 at.% and 2.0 at.% for Cl-ITO before and after ORR tests, respectively.

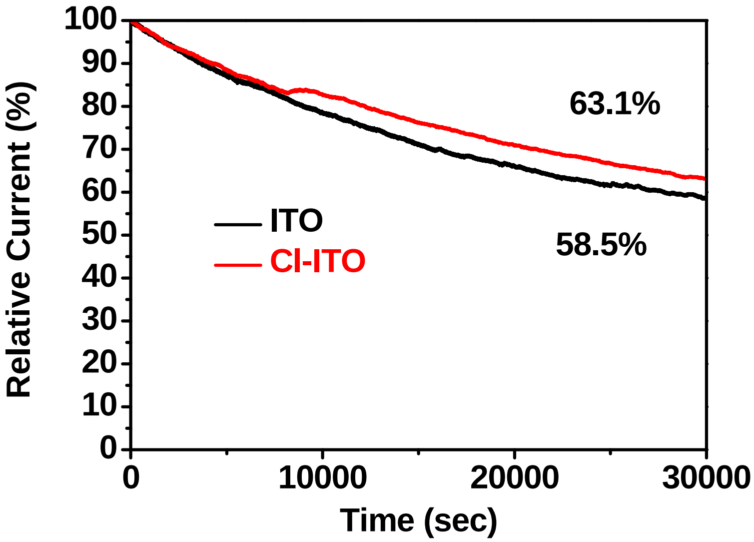

**Figure S6.** Chronoamperometric curves of a GCE modified with indicated samples at +0.45 V vs RHE in an $O_2$-saturated 0.1 M KOH solution. The electrode rotation rate was 900 rpm.

## References

[1] R. Kou, Y. Shao, D. Mei, Z. Nie, D. Wang, C. Wang, V. V. Viswanathan, S. Park, I. A. Aksay, Y. Lin, Y. Wang, and J. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 2541–2547.

[2] M. G. Helander, Z. B. Wang, J. Qiu, M. T. Greiner, D. P. Puzzo, Z. W. Liu, and Z. H. Lu, *Science*, 2011, **332**, 944.