Electronic Supplementary Information

In situ synthesis of noble metal nanoparticles on onion-like carbon with enhanced electrochemical and supercapacitor performance

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Preparation of OLC

The OLC used in this work was produced from oxidized detonation nanodiamond (ND). As nanodiamond soot (purchased from Henan Union Abrasives, China) contains much disordered carbon and graphitic layers on the surface of diamond nanoparticles, we first purified the pristine ND by mixed concentrated acid (H_2SO_4:HNO_3=3:1) under 160 ℃ refluxing for 24 h. After washed several times by deionized water and dried at 60 ℃ under vacuum we can get the ND. Then onion-like-carbon can be obtained by annealing as-received ND soot under argon atmosphere as following procedure. First we raised the temperature of the furnace to 200 ℃ from room temperature in twenty minutes and kept for ten minutes. Then we raised the temperature to 1500 ℃ by rate of 10 ℃/min and held for 2 h. After naturally cooled to room temperature we got the powder of pristine OLC. Finally, the pristine OLC was oxidized by mixed concentrated acid (H_2SO_4:HNO_3=3:1) under 80 ℃ refluxing for 2 h. After washed to neutral by deionized water and dried at 60 ℃ under vacuum we obtained the final hydroxylated OLC powder.

Preparation of noble metal nanoparticles-OLC

In a typical procedure for Pt-OLC, OLC obtained above was dispersed in water (36 ml) under ultra-sonic at 0.3 mg/mL. After 1h, we dropped 110 μL chloroplatinic acid ($H_2PtCl_6.6H_2O$, Aldrich, 0.1 M) into the OLC solution with pipette. Finally, hydrothermal treatment of the mixed solution was carried out at 200 ℃ in autoclave

with a Teflon liner for two days. After the autoclave was naturally cooled to room temperature, the final product was obtained by centrifugation, washed several times with deionized water and absolute ethanol, and dried in a vacuum at 60 ℃ for 12 h. The procedure for Pd-OLC, Au-OLC and Ag-OLC was the same as that for Pt-OLC except that sodium palladium(II) chloride (Na_2PdCl_4, Aldrich), chloroauric acid ($HAuCl_4$, Aldrich), and silver nitrate ($AgNO_3$, Aldrich) were used as noble metal precursor, respectively.

Preparation of O_2-OLC and Ar-OLC

O_2-OLC was obtained by the same synthesis of Pt-OLC just without adding the chloroplatinic acid (0.1 M). Before the hydrothermal treatment to get O_2-OLC, we through argon into the OLC solution for 10 min to remove the oxygen. Then we got Ar-OLC sample after two days under 200 ℃.

Sample characterization and XAFS data analysis

Transmission electron microscopy (TEM) images were obtained by a transmission electron microscope (JEOL JEM2010). X-ray diffraction (XRD) patterns of samples were recorded on a D8-Advance power diffractometer with a Cu - Kα radiation source (λ = 1.54178 Å).

The mass fraction of noble metal nanoparticles were obtained by Plasma Atomic Emission Spectrograph (Optima 7300 DV). Fourier Transform Infrared Spectroscopy (FTIR spectrum) was got from the Fourier Transform Infrared Spectrometer (Nicolet 8700). X-ray Photoemission spectroscopy (XPS) experiments were performed at the Photoemission Endstation at the BL10B beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The Pt L_3-edge XAFS measurements were made in the transmission mode at the beamline 14W1 in Shanghai Synchrotron Radiation Facility (SSRF). The X-ray was monochromatized by a double-crystal Si(111) monochromator, and the energy were calibrated using a platinum metal foil for Pt L_3-edge. The monochromator was detuned to reject higher harmonics. XAFS

data was analyzed with the WinXAS3.1 program.[1] The energy thresholds were determined as the maxima of the first derivative. Absorption curves were normalized to 1, and the EXAFS signals $\chi(k)$ were obtained after the removal the pre-edge and post-edge background. The Fourier transform (FT) spectra were obtained as $k^3\chi(k)$ with a Bessel window in the range 3-12.5 $Å^{-1}$ for Pt L_3-edge. Theoretical amplitudes and phase-shift functions of Pt-Pt were calculated with the FEFF8.2 code[2] using the crystal structural parameters of the Pt foil.[3] The S_0^2 values were found to be 0.97.

Electrochemical measurements

Electrochemical properties of as-prepared products were performed on a CHI660D electrochemical workstation using a three-electrode configuration comprised of the samples-prepared as the working electrodes, carbon rod as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. The working electrode was prepared by coating a small amount of sample ink on glassy carbon electrode. Briefly, 2.0 mg noble metal nanoparticles-OLC sample was dispersed into a solution containing water (750 μL), isopropyl alcohol (250 μL) and Nafion solution (5 wt.%, 30 μL), followed by ultra-sonic treatment for 1h. Then, the resultant suspension (5 μL) was pipetted onto the GC electrode and dried at 60 ℃ for 2 h. As reference, the electrochemical performance of commercial 20% Pt/C was also conducted.

The Tafel plots were linear fitted by the Tafel equation $\eta = b*\log(-i) + a$, where $b = 2.3RT/(\alpha F)$ is the Tafel slop, $a = -2.3RT/(\alpha F)*\log(-i_0)$ and i is the exchange current density.

The electrocatalytic activity of the prepared samples towards the HER was studied in a 0.5 M H_2SO_4 aqueous solution using linear sweep voltammetry (LSV) at 0.005 V/s. The supercapacitive properties of cyclic voltammetry (CV) curves were tested from -0.1 V to 0.5 V at 0.1 V/s. The galvanotastic charge/discharge tests were performed from 0 to 1 V at 1 A/g in the aqueous electrolyte of 1 M H_2SO_4.

The specific capacitance from galvanotastic charge/discharge curves was calculated by using the formula $C = I*\Delta t/(m*\Delta V)$, where I is the constant discharge current, Δt is the discharge time and ΔV is the voltage drop upon discharge time.
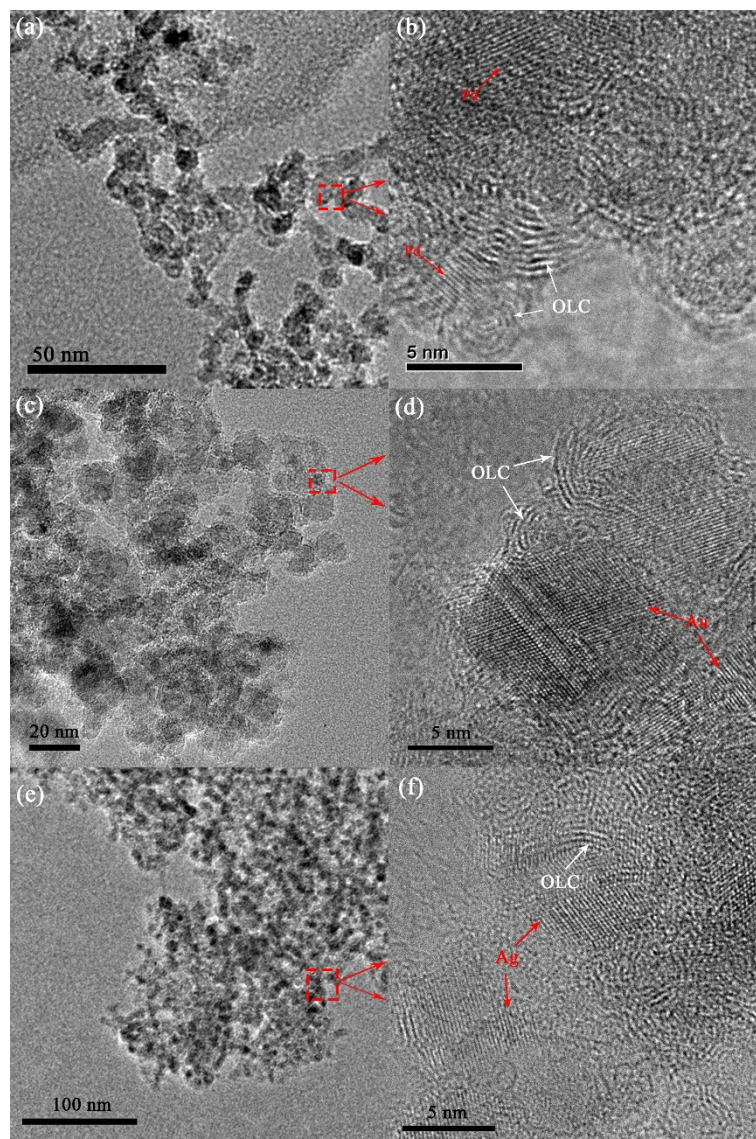
Figure S1. TEM images of Pd-OLC (a), Au-OLC (c), Ag-OLC (e), and their high-resolution TEM (b), (d) and (f).
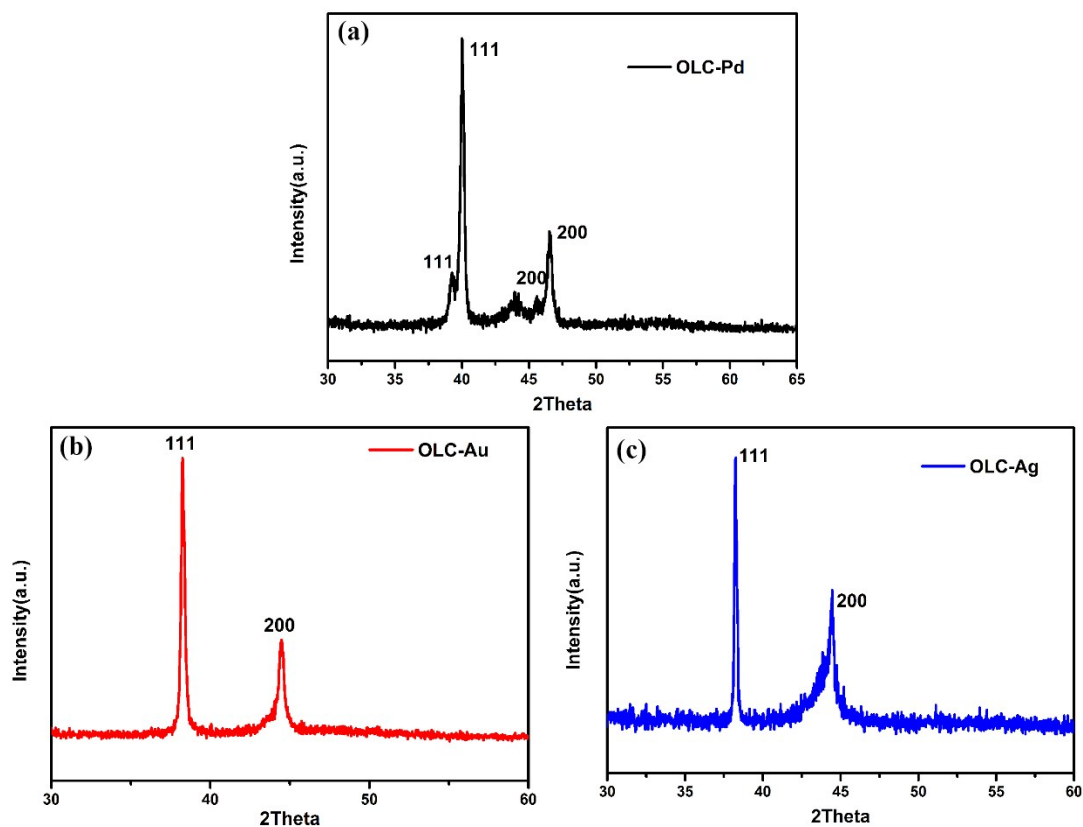
Figure S2. X-ray diffraction patterns of Pd-OLC (a), Au-OLC (b) and Ag-OLC (c).
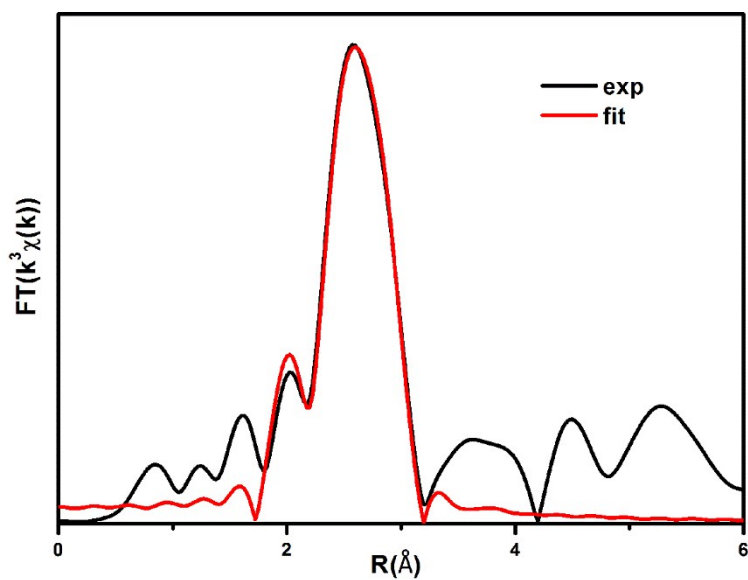

Figure S3. Comparison between experimental data and the fitting curves of Pt-OLC.

Table S1. Corresponding fit parameters for Pt foil and Pt-CNO

Sample	Bond	R(Å)	N	$\sigma^2(\times 10^{-3})$
Pt foil	Pt-Pt	2.77	12	4.6
Pt-OLC	Pt-Pt	2.75	6.6	4.4

R, bond distance; N, coordination number; σ^2, Debye-Waller factor; Error bounds (accuracies) were estimated as R, ±1%, N, ±5%; σ^2, ±1%.
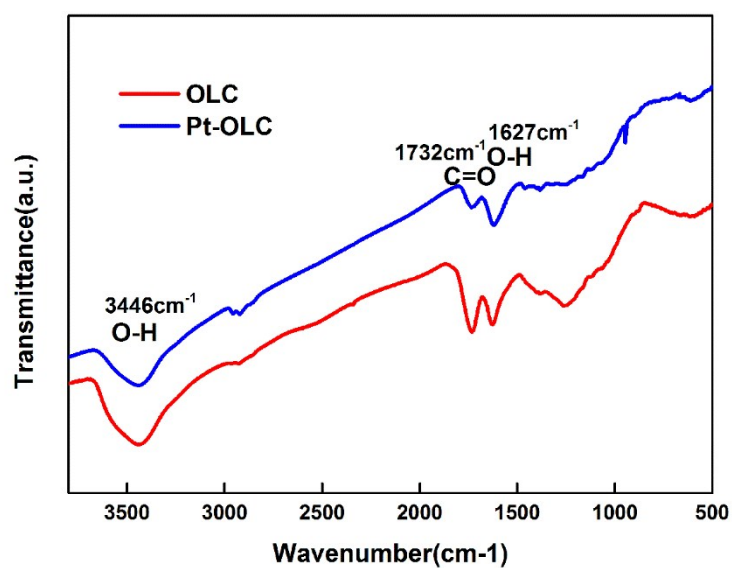

Figure S4. Fourier Transform Infrared Spectroscopy (FTIR) of OLC (red) and Pt-OLC (blue).
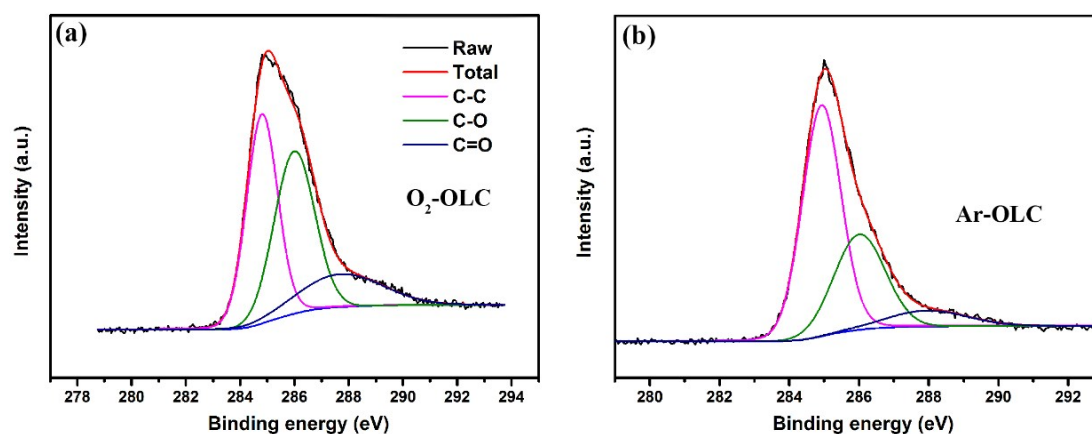
Figure S5. The high-resolution C1s XPS spectra of O_2-OLC (a), Ar-OLC (b).

Table S2. Summary of XPS Peak Analysis on OLC, Pt-CNO, O_2-OLC and Ar-OLC.

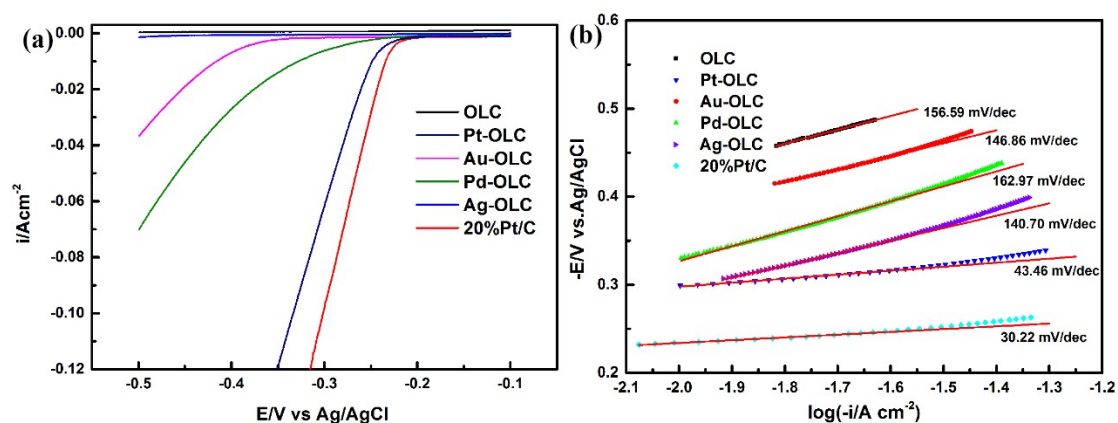| Sample	Compound type	B.E. (eV)	Peak area	Fraction (%)
OLC	**C1s**			
	C-C	284.6	185532	31
	C-O	285.7	285193	48
	C=O	288.6	119900	21
Pt-OLC	**C1s**			
	C-C	284.7	241200	35
	C-O	286.0	301226	44
	C=O	287.9	135248	21
O_2-OLC	**C1s**			
	C-C	284.8	128827	41
	C-O	285.9	125818	40
	C=O	287.7	52465	19
Ar-OLC	**C1s**			
	C-C	284.9	129221	60
	C-O	286.0	67857	31
	C=O	287.9	17310	9

Figure S6. (a) Polarization curves for HER in 0.5 M H$_2$SO$_4$ of OLC, Pt-OLC, 20% Pt/C, Pd-OLC, Au-OLC and Ag-OLC at the scan rate of 5 mV/s. (b) Corresponding Tafel plots derived from (a).
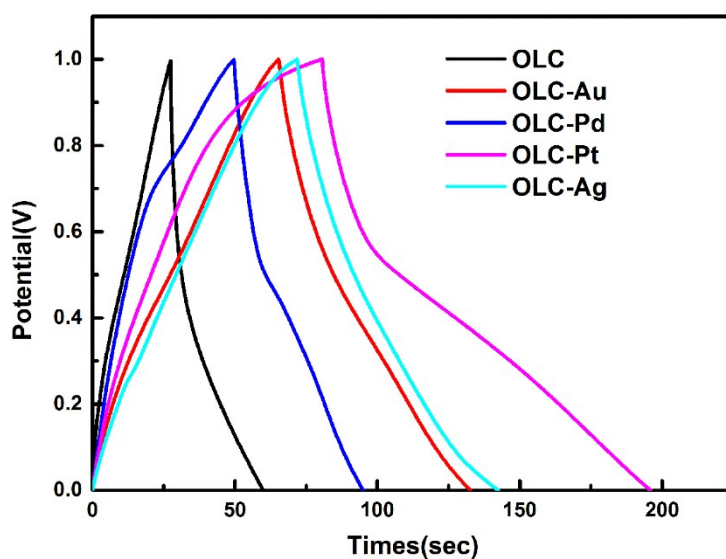

Figure S7. Galvanostatic charge/discharge curves of OLC, Pt-OLC, Pd-OLC, Au-OLC and Ag-OLC at 1 A/g.

Supplementary References:

1   T. J. J. Ressler, Journal of synchrotron radiation, 1998, 5, 118-122.
2   A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, Phys. Rev. B, 1998, 58, 7565-7576.
3   J. Häglund, A. F. Guillermet and G. K. r. Grimvall, M., Phys. Rev. B, 1993, 48, 11685-11691.