Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

Graphene-Induced Growth of Co_3O_4 Nanoplates with Modulable Oxygen Vacancies for Improved OER Properties

Lei Qi,[a,b] Mei Wang,[a,b] and Xinheng Li [a,*]

[a] The State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, 730000, China.

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

Corresponding Author E-mail: xinhengli@licp.cas.cn

Experimental Methods

Preparation of pristine Co_3O_4

In a typical synthesis process, 2.19 g of $Co(NO_3)_2 \cdot 6H_2O$, 1.40 g of methenamine and 0.10 g of sodium laurylsulfonate were mixed with 200 mL ethylene glycol under vigorous magnetic stirring and reacted in a Teflon-lined stainless-steel autoclave for 24 h at 180 ^oC. The pink precipitation was obtained after rinsing several times with ethanol and purified water. The final product was collected by annealing at 500 ^oC for 2 h in air and denoted as pristine Co_3O_4.

Synthesis of $Co(OH)_2$ nanoplates

g-Co_3O_4 nanocomposite was synthesized via a facile hydrothermal reaction. 0.1 g of pristine Co_3O_4 and 0.15 g of $NaNO_3$ were added to 25mL of home-made graphene oxide solution(1mg/ml) and sonicated for 10 min. Then, 3 mL of NH_3 aqueous solution and 0.3 mL of hydrazine hydrate were added. Finally, the solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 ^oC for 3, 6, 9, 12 h respectively, denoted as g-Co_3O_4 3h, g-Co_3O_4 6h, g-Co_3O_4 9h, g-Co_3O_4 12h. While cooling to room temperature, the solid products were filtered and rinsed several times with ethanol and distilled water and dried for 12 h.

Materials Characterization:

Scanning electron microscopy (SEM) images were taken on a Hitachi S4800 scanning electron microscopy. Nitrogen adsorptio-desorption measurements were conducted using a Quantachrome NOVA4200e analyzer. X-Ray diffraction (XRD) measurements were conducted on a SmartLab diffractometer using Cu Ka1 radiation (λ = 0.15406 nm) at a scanning rate of 0.02 deg./ sec. X-Ray photoelectron spectroscopy (XPS) analysis was recorded on a thermo scientific NEXSA system, using monochromaticAl Ka radiation (1486.6 eV) operating at 25 W.

Electrochemical Measurement:

The electrochemical tests towards OER performance were conducted on an electrochemical workstation (CHI 760E) with a standard three-electrode cell at room temperature. The as-prepared samples as the working electrode, a Pt wire as the counter electrode, and a standard Ag/AgCl electrode with an additional salt bridge as the reference electrode were used in testing under 1 M KOH. All potentials were calibrated versus RHE, through the equation: E (RHE) = E(Ag/AgCl) + 0.197 + 0.059 × pH (the unit is volt). Linear sweeping voltammetry (LSV) was carried out at a scan rate of 5 mV s^{-1}, and 95% iR compensation. Tafel slopes were derived from corresponding OER polarization curves and fitted to the Tafel equation $\eta = b\log j + a$, where η is overpotential, j the current density, and b the Tafel slope. Electrochemical impedance spectroscopy (EIS) was performed over a frequency range from 100 kHz to 0.01 Hz with the potential of 1.6 V vs RHE. Electrochemical surface area (ECSA) was measured by cyclic voltammetry (CV) from 0.2V~0.3V.

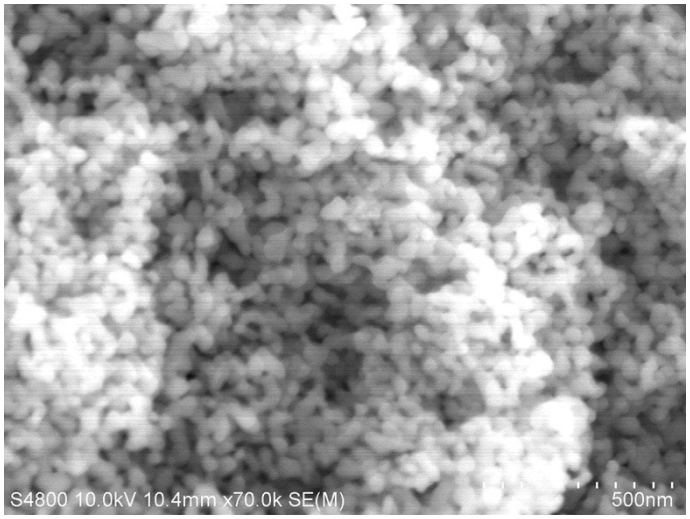

Fig. S1 SEM image of pristine Co_3O_4 spheres with good monodispersity. Scale bar is 500 nm.

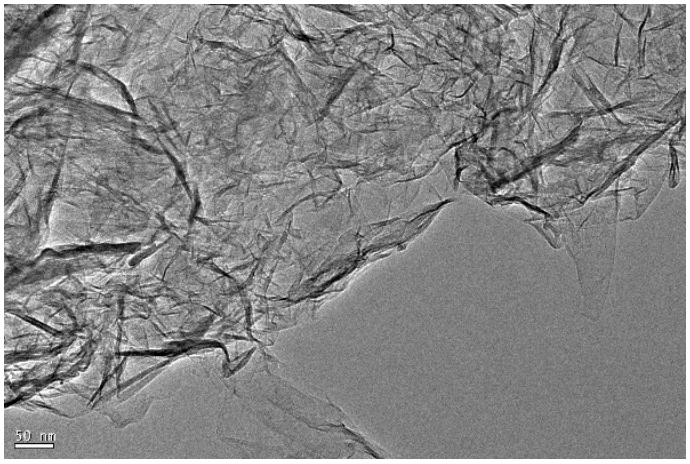

Fig. S2 TEM image of pristine home-made graphene.

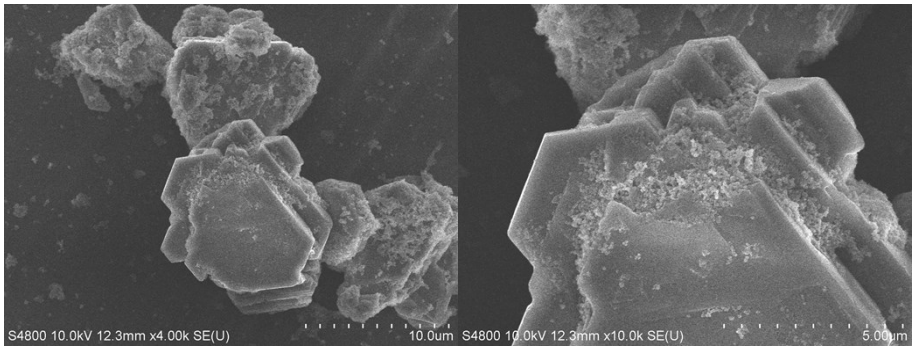

Fig. S3 SEM image of Co_3O_4 after hydrothermal treatment for 3h.

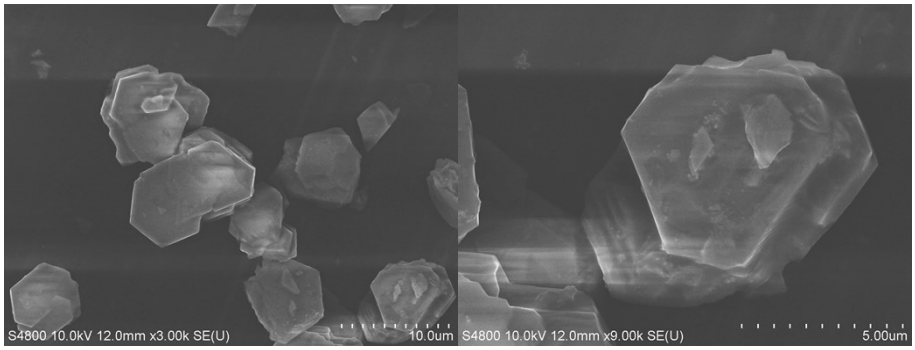

Fig. S4 SEM image of Co_3O_4 after hydrothermal treatment for 6h.

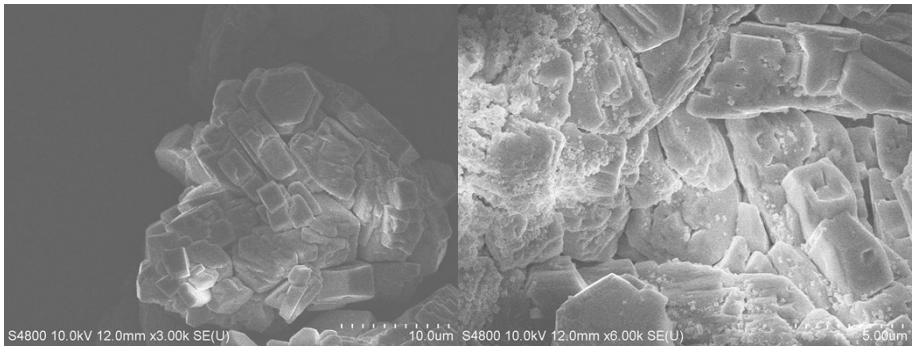

Fig. S5 SEM image of Co_3O_4 after hydrothermal treatment for 9h.

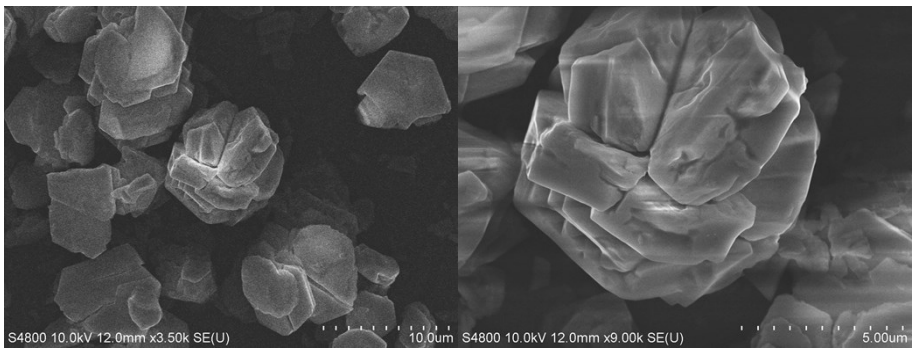

Fig. S6 SEM image of Co_3O_4 after hydrothermal treatment for 12h.

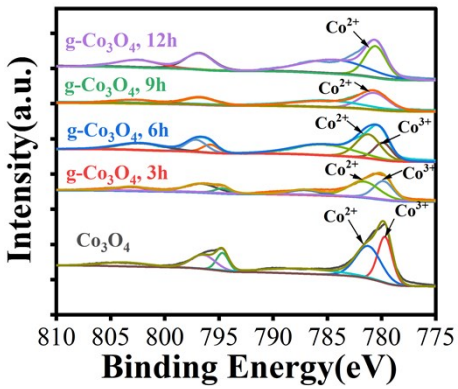

Fig. S7 XPS spectra of Co2p over pristine Co_3O_4 (black line) and g-Co_3O_4 with different hydrothermal reaction time: (red line) 3 h; (blue) 6 h; (green line) 9 h and (purple line) 12 h.

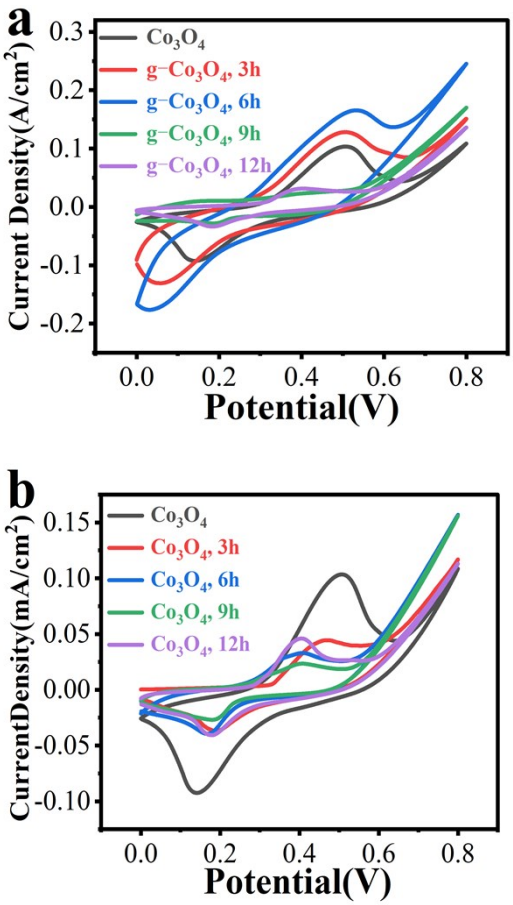

Fig. S8 CV curves of pristine Co_3O_4 and g-Co_3O_4 after hydrothermal treatment for 3 to 12h

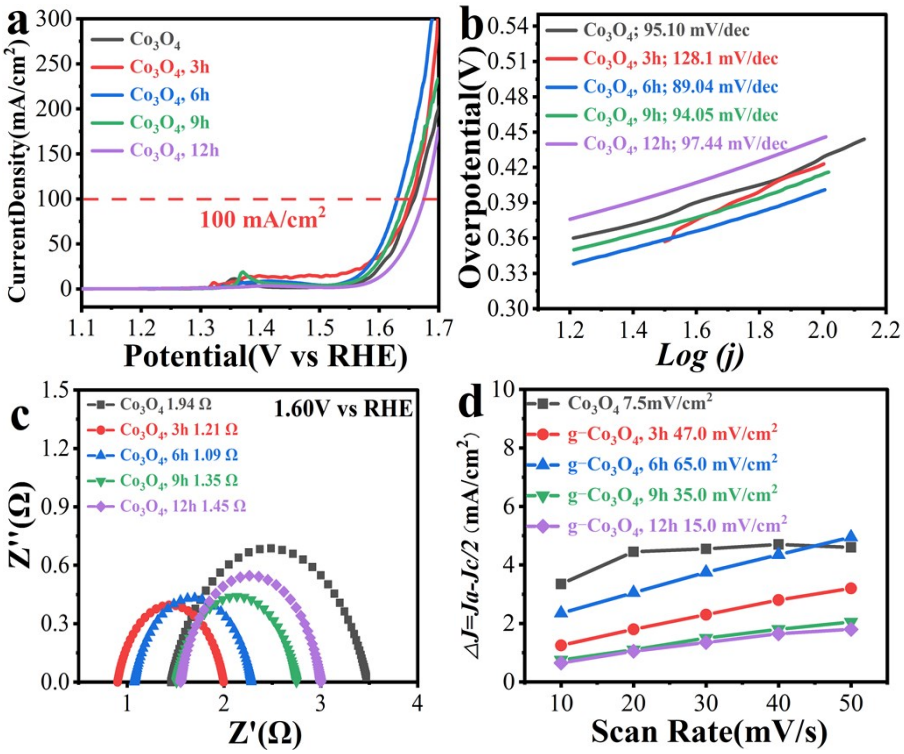

Fig. S9 (a) LSV curves of Co_3O_4 (black) and related g-Co_3O_4 with different hydrothermal reaction time: (red) 3 h; (blue) 6 h; (green) 9 h and (purple) 12 h; (b) related Tafel slope; (c) Nyquist plots of the samples and (d) Double layer capacitance