Supporting Information

Towards a highly dispersed and more thermal stable Ru/OCNTs catalyst +

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Experimental Section

Purification and oxidation of CNTs

PR24-LHT carbon nanotubes were purchased from Pyrograf Products Inc. (Ohio, USA). Concentrated hydrochloric acid was used to remove impurities (iron element especially) at room temperature under mechanically stirring conditions for 24 h. CNTs functionalization was carried in an 8 M H₂SO₄-HNO₃ mixture at 55 °C for 2 h by sonication under reflux conditions, which would result in a high density of functional groups such as carboxyl, hydroxyl, and carbonyl group on CNTs.¹⁻³

Preparation of Ru/OCNTs-IP sample

The as-prepared OCNTs (450 mg) and RuCl₃•xH₂O (24.168 mg) were mixed in ethanol (120 ml) through sonification for 1 h and followed by evaporation at 50 °C. The sample was then dried in the vacuum and reduced in 25% H₂ mixed with Ar under a total flow rate of 80 mL min⁻¹ at 200 °C. This sample obtained through impregnation method was denoted as Ru/OCNTs-IP.

Preparation of Ru/OCNTs-EG sample

Ru/OCNTs-EG was synthetized by an ethylene glycol (EG) reduction method as follows. An RuCl₃•nH₂O EG solution was added dropwise into OCNTs suspended in EG under magnetic stirring for 4 h. The pH of the synthetic solution was adjust to above 13 by adding 1.0 M NaOH in EG and then was heated at 160 °C for 3 h under flowing Ar gas to ensure that Ru was completely reduced. After cooling to room temperature, the pH of the mixture was adjusted to below 3.0 using 2 M hydrochloric acid and stirred magnetically for 3 h to separate the Ru NPs as a precipitate deposited on OCNTs from ethylene glycol solvent. Subsequently, the Ru/OCNTs-EG sample was filtered and dried.

Thermal treatment

These as-obtained samples were annealed in tubular furnace under flowing He gas conditions, from room temperature (RT) *via* 350 °C for 30 min to 600 °C for 20 min, respectively, in order to investigate the thermal stability of Ru NPs supported on OCNTs. As a comparison, Ru/OCNTs-EG sample was chosen to observe real-timely by employing an *in-situ* TEM with special heating holder along the above

temperature function treatment.

Characterization

A FEI Tecnai G2 F20 microscope equipped with HAADF and EDAX detectors was employed to acquire the HRTEM, STEM images and energy-dispersive X-ray (EDX) spectra under 200 keV. The XRD patterns of the products were obtained using a D/MAX-2500 PC X-ray diffractometer with monochromatized Cu Ka radiation ($\lambda = 1.54$ Å). The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) ESCALAB 250 setup equipped with a monochromatic Al Ka X-ray source (1486.6 eV; anode operating at 15 kV and 20 mA).



Fig. S1 Obvious sintering particles on some OCNTs with large particle formation and poor morphology in Ru/OCNTs-IP sample.



Fig. S2 STEM-EDX elemental maps of Ru/OCNTs-IP before heating.



Fig. S3 TEM and STEM images of Ru/OCNTs-EG sample before heating.



Fig. S4 STEM-EDX elemental maps of Ru/OCNTs-EG before heating.



Fig. S5 XPS survey (a) and O1s (b) spectra of OCNTs.

Oxygen species introduced onto CNTs through functionalization can be analyzed with O1s XPS (Fig. S5). The oxygen content determined by XPS is 5.42 at% (Fig. S5a). The XP O1s core level spectra shown in Fig. S5b have been deconvoluted by introduction of four contributions with peak maxima as follows: O1 (C=O), 531.1 ± 0.1 ; O2 (Hydroxyls, ethers and C=O in esters), 532.3 ± 0.1 ; O3 (C-O in esters and anhydrides), 533.3 ± 0.1 ; O4 (Carboxylic groups), $534.2\pm0.1.^4$ With the presence of high-density surface functional groups, CNTs treated by H₂SO₄-HNO₃ show much better dispersibility in water, ethanol and other solvents compared with the raw nanotube material. These oxygen functional groups can act as active components of nucleation sites for a well dispersed deposition Ru NPs on the surface of OCNTs.⁵



Fig. S6 Typical TEM images of Ru/OCNTs-EG sample annealed by in-situ heating TEM holder at RT

(a), 350 °C (b), 600 °C (c) and STEM image after heating (d).



Fig. S7 STEM-EDX elemental maps of Ru/OCNTs-EG after annealing from RT to 600 °C by heating TEM holder.



Fig. S8 Typical TEM images of Ru/OCNTs-IP sample treated by *in-situ* TEM heating holder at RT (a), 350 °C (b), 600 °C (c) and STEM image after heating (d).



Fig. S9 Schematic diagrams of part of impregnation process (a) and EG reduction process (b).

References

- L. Shao, B. Zhang, W. Zhang, S. Y. Hong, R. Schlögl and D. S. Su, Angewandte Chemie International Edition, 2013, 52, 2114-2117.
- 2. L. Shao, W. Zhang, M. Armbrüster, D. Teschner, F. Girgsdies, B. Zhang, O. Timpe, M. Friedrich, R. Schlögl and D. S. Su, *Angewandte Chemie International Edition*, 2011, **50**, 10231-10235.
- 3. B. Zhang, W. Zhang, L. Shao and D. S. Su, *ChemCatChem*, 2013, 5, 2586-2590.
- 4. J. L. Figueiredo and M. F. R. Pereira, Catalysis Today, 2010, 150, 2-7.
- R. Arrigo, M. Havecker, S. Wrabetz, R. Blume, M. Lerch, J. McGregor, E. P. J. Parrott, J. A. Zeitler, L. F. Gladden, A. Knop-Gericke, R. Schlogl and D. S. Su, *Journal of the American Chemical Society*, 2010, **132**, 9616-9630.