

## Supporting Information

### Morphological effects of the nanostructured ceria support on the activity and stability of CuO/CeO<sub>2</sub> catalysts for the water-gas shift reaction

S.Y. Yao,<sup>a,b</sup> W.Q. Xu,<sup>b</sup> A.C. Johnston-Peck,<sup>c</sup> F.Z. Zhao,<sup>b</sup> Z.Y. Liu,<sup>b,e</sup> S. Luo,<sup>b,e</sup> S.D. Senanayake,<sup>b</sup> A. Martínez-Arias,<sup>d</sup> W.J. Liu\*<sup>a</sup> and J.A. Rodríguez\*<sup>b,e</sup>

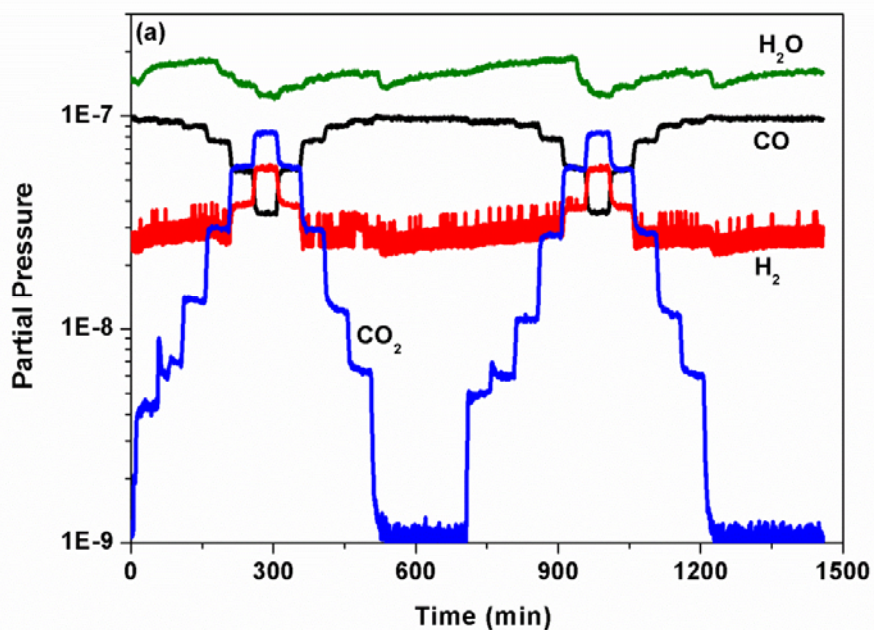
<sup>a</sup> Center for Computational Science & Engineering and Green Chemistry Center, Peking University, Beijing 100871, China.

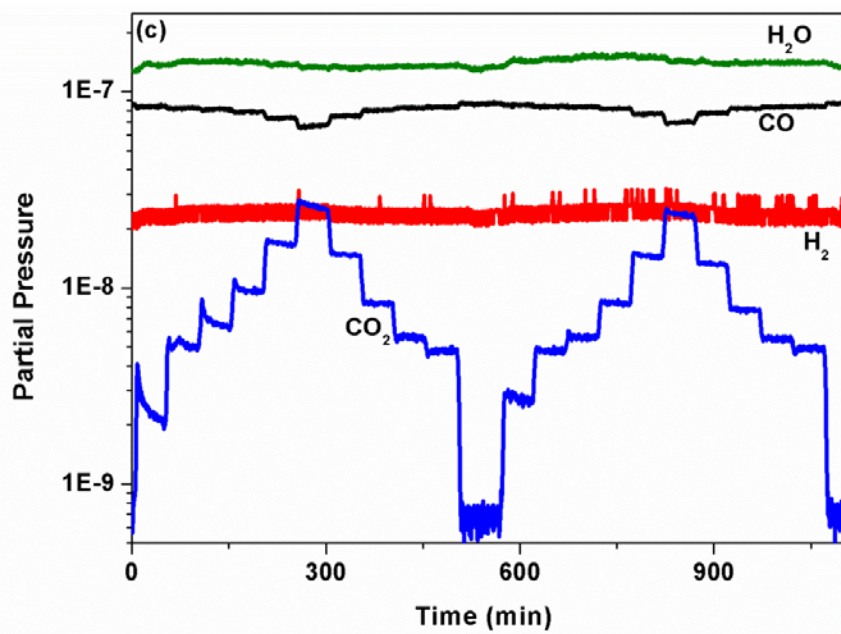
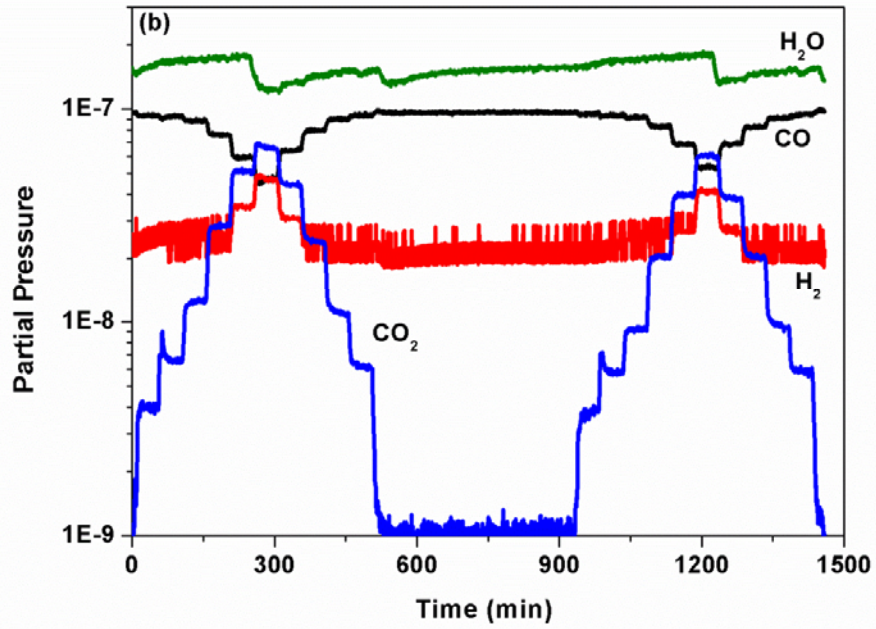
<sup>b</sup> Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA.

<sup>c</sup> Center of Functional Nanomaterial, Brookhaven National Laboratory, Upton, NY 11973, USA.

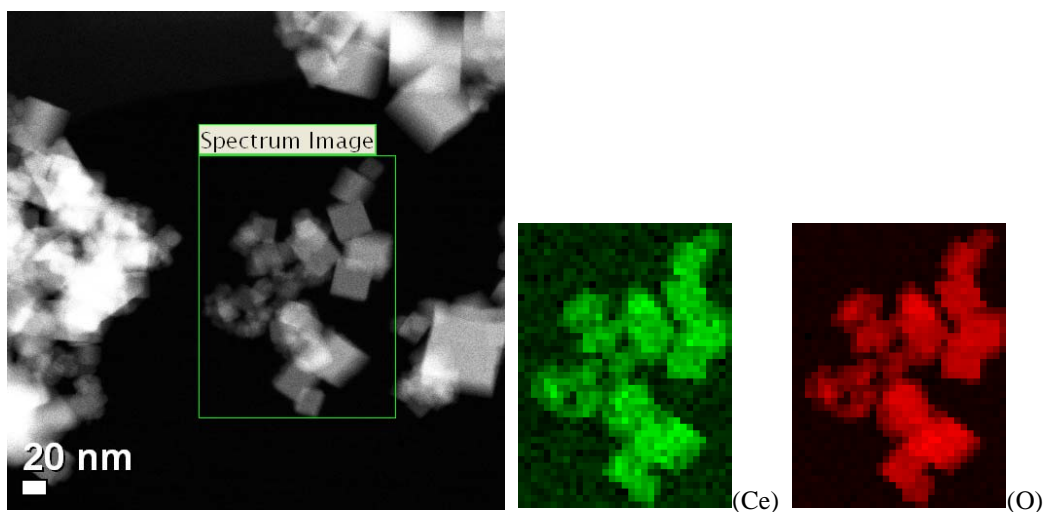
<sup>d</sup> Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas (ICP-CSIC), E-28049 Madrid, Spain.

<sup>e</sup> Department of Chemistry, State University of New York (SUNY), Stony Brook, NY 11749, USA.

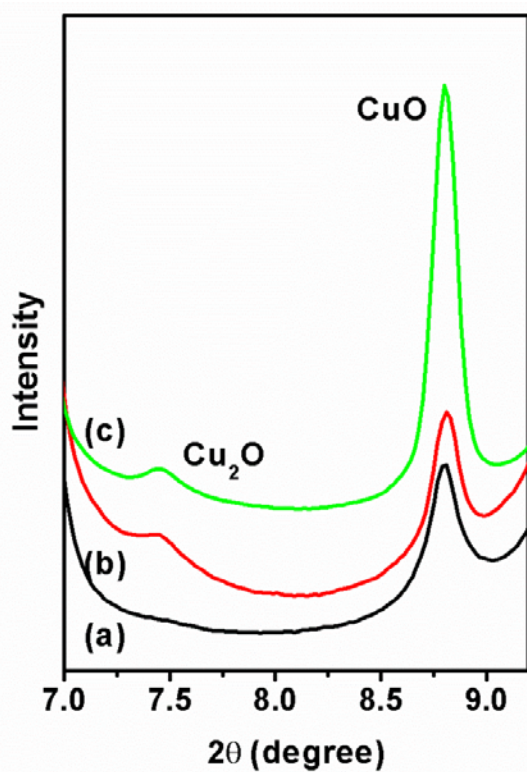




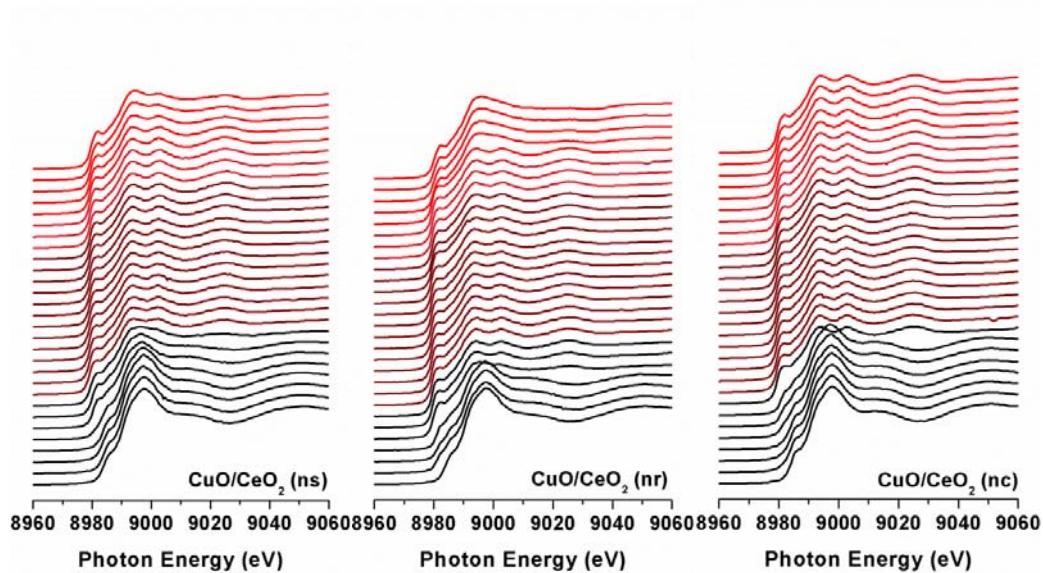
**Figure S1.** The RGA MS signals of three CuO/CeO<sub>2</sub> catalysts during 2-cycle WGS reaction. (a) CuO/CeO<sub>2</sub> (ns), (b) CuO/CeO<sub>2</sub> (nr) and (c) CuO/CeO<sub>2</sub> (nc).



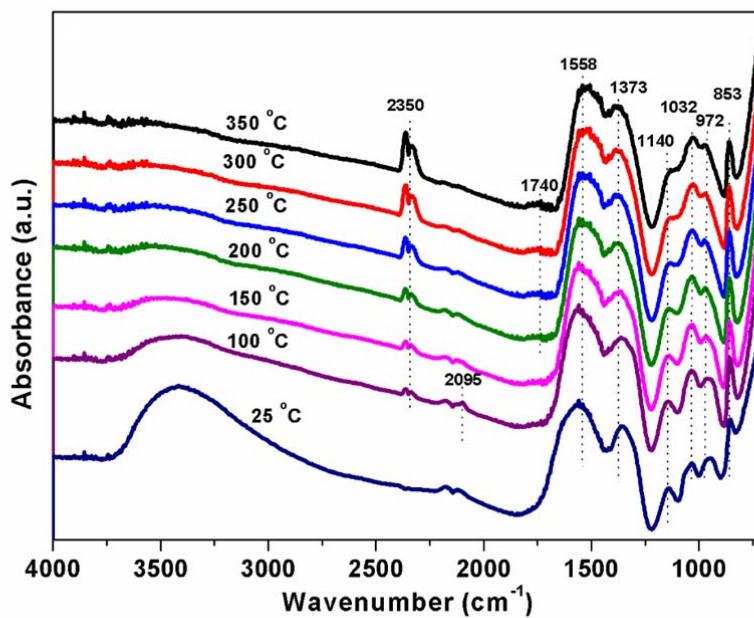
**Figure S2.** EELS Mapping of CuO/CeO<sub>2</sub> (nc) catalyst as an example. No signal of copper was observed.

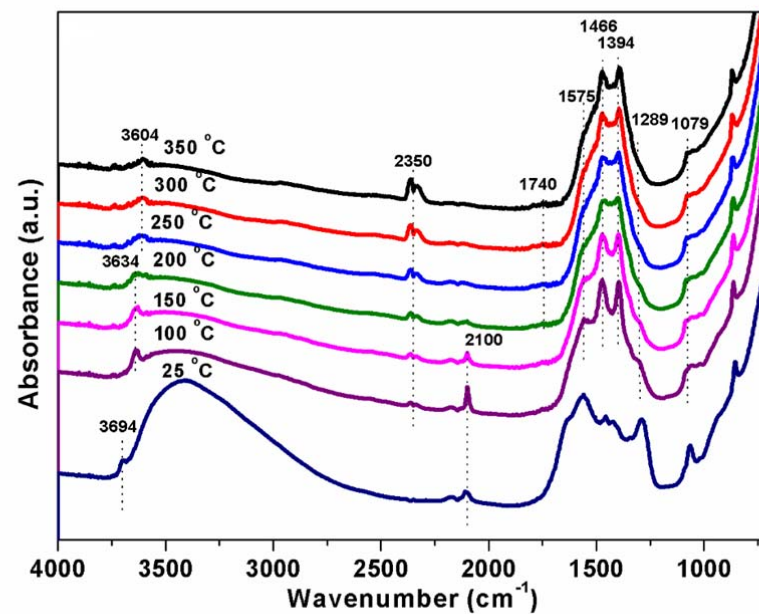
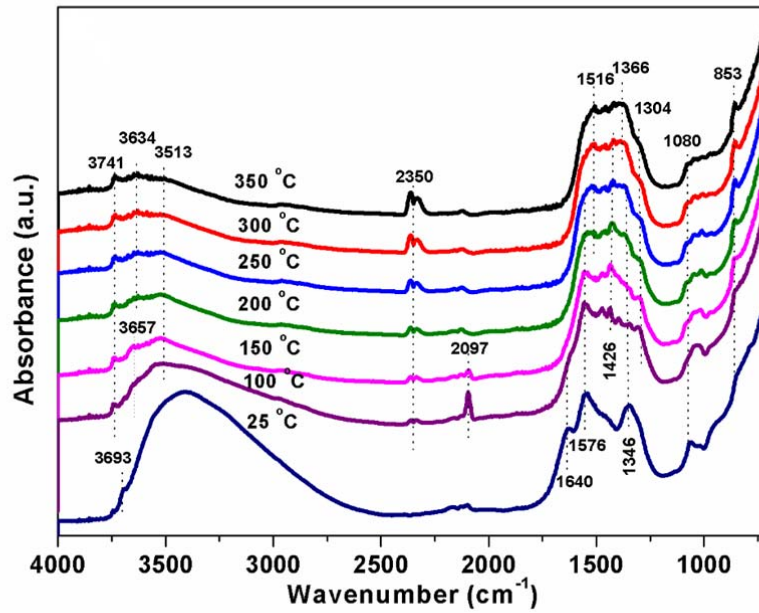


**Figure S3.** XRD pattern of three CuO/CeO<sub>2</sub> catalysts at room temperature between two WGS reaction cycle. (a) CuO/CeO<sub>2</sub> (ns)\*4, (b) CuO/CeO<sub>2</sub> (nr)\*4 and (c) CuO/CeO<sub>2</sub> (nc). The estimated weight percent of Cu<sub>2</sub>O by Rietveld refinement is: smaller than the limit of estimation for CuO/CeO<sub>2</sub> (ns); 1.2 % for CuO/CeO<sub>2</sub> (nr) and 0.8 % CuO/CeO<sub>2</sub> (nc).



**Figure S4.** Cu K edge XANES spectra of three catalysts in first WGS cycle reaction from room temperature heating to 350 °C and then cooling back to room temperature. (black to red)





**Figure S5.** *In-situ* DRIFTS spectra collected during the WGS reaction over CuO/CeO<sub>2</sub> (ns) (up), CuO/CeO<sub>2</sub> (nr) (middle) and CuO/CeO<sub>2</sub> (nc) (bottom) catalyst at different temperatures during cooling periods.