Electronic Supplementary Material (ESI) for Nanoscale.

Controllable Dynamics of Oxygen Vacancies through Extrinsic Doping for Superior Catalytic Activities

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Supporting Information

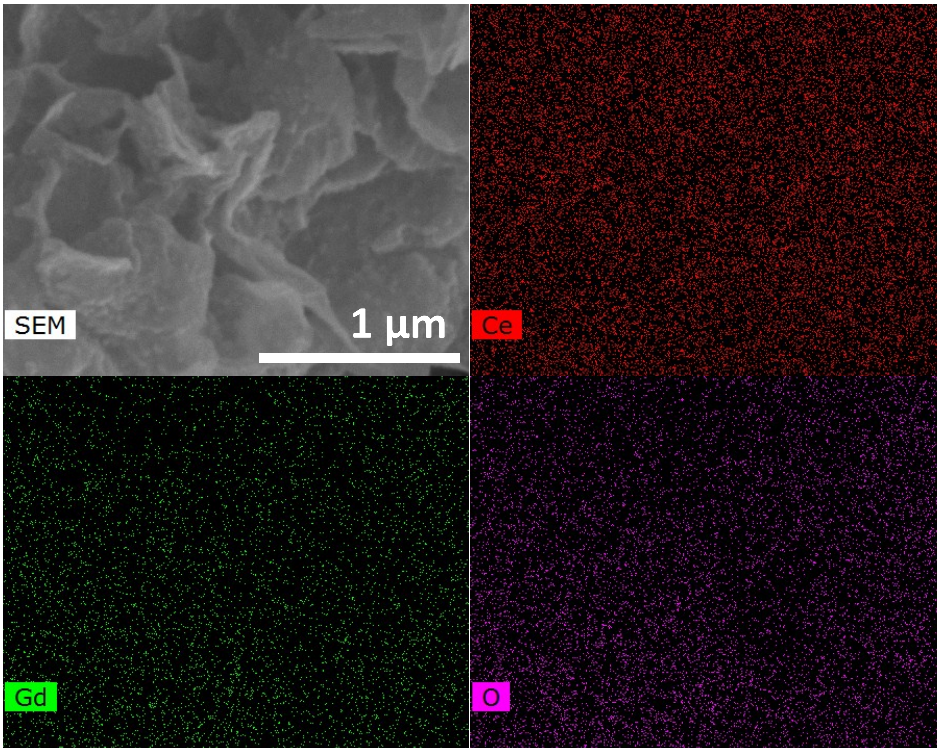

Figure S1: SEM-EDX mapping images of the GDC-15 sample, showing random distribution of Gd, Ce and O.

Sample Name	Ce Atom% (Set)	Gd (Atom% (Set)	Ce Atom% (EDS)	Gd (Atom% (EDS)
GDC-05	95	05	94.00	6.00
GDC-10	90	10	88.7	11.3
GDC-15	85	15	84.0	16.0
GDC-20	80	20	78.5	21.5
GDC-25	75	25	76.00	24.0
GDC-30	70	30	67.0	33.0

Table T1: The compositions of the as-prepared samples were determined by Energy Dispersive X-ray spectra. The results are generally consistent with the expected ratio between Ce and Gd.

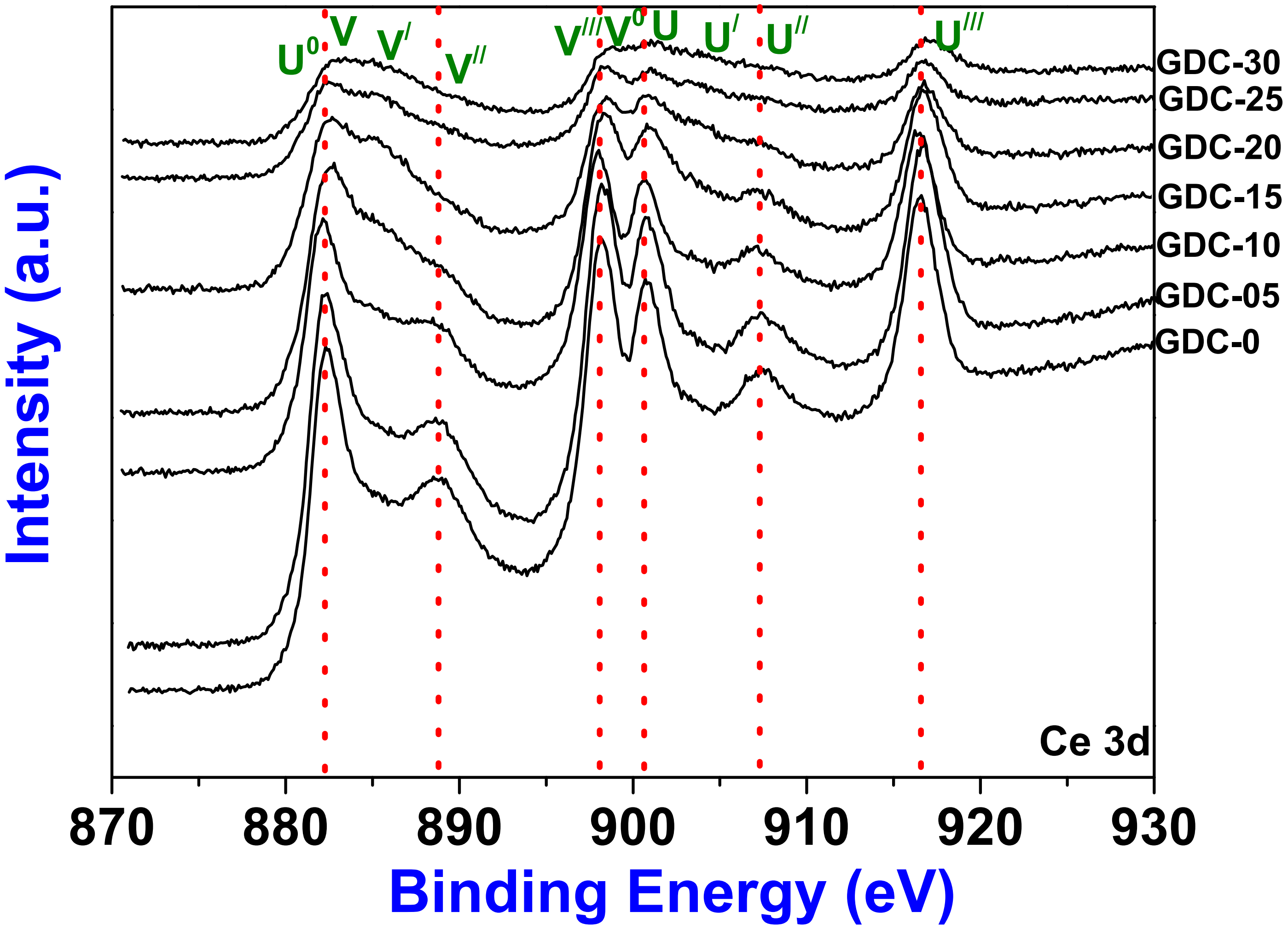

Figure S2: XPS spectra of Ce 3d of Gd-doped CeO_2 samples with different ratios of Ce:Gd.

UV−vis diffuse reflectance spectroscopy

To extract the surface coordination and oxidation states of metal ions (Ce ions) in as-prepared three samples (GDC-0, GDC-15 and GDC-30), UV−vis diffuse reflectance spectroscopy was carried out and the results are depicted in figure S3. The maxima appeared at 255 nm correspond to O^{2-} to Ce^{3+} charge transfer transitions, whereas the maximum at 285 nm and 340 nm may be due to O^{2-} to Ce^{4+} charge transfer and interband transitions[1]. The increased absorption intensity with Gd doping level indicates that the Ce^{4+} substitution with Gd^{3+} ions indeed facilitates the formation of Ce^{3+}, which generates more oxygen vacancies in the samples for charge compensation mechanism.

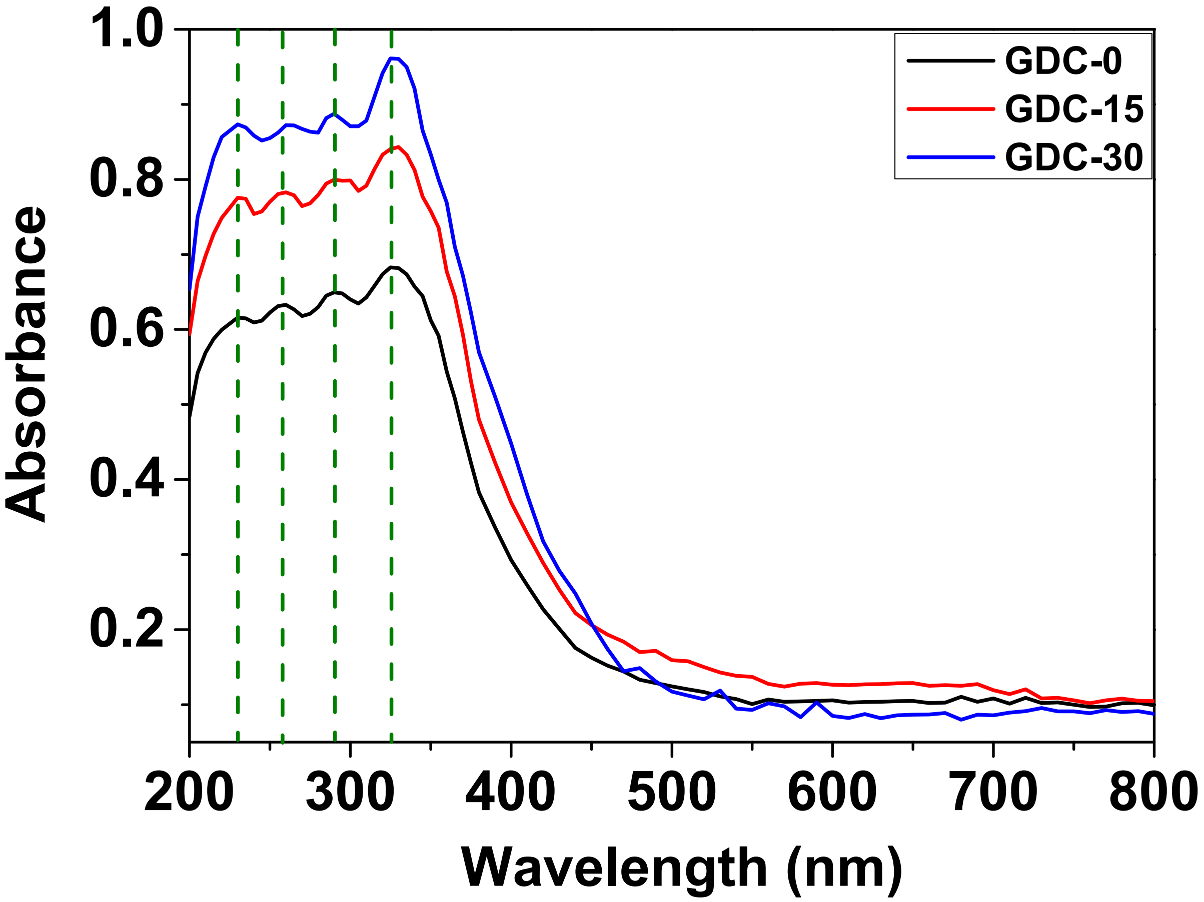

Figure S3: UV-vis diffuse reflectance spectra of GDC-O, GDC-15 and GDC-30 samples.

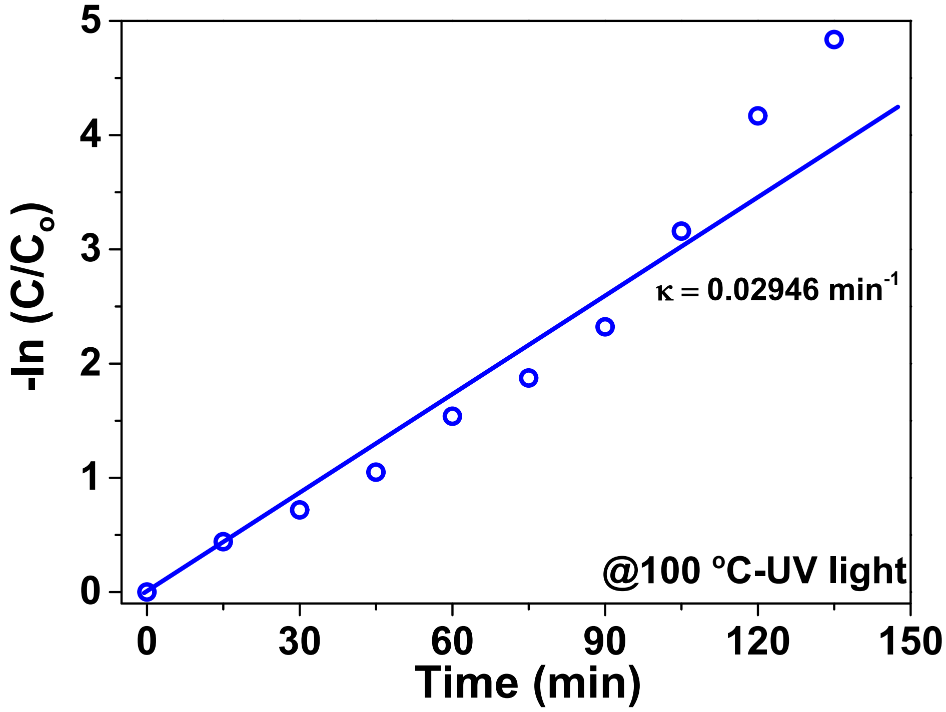

Figure S4: Plot of -ln (C/C_0) vs irradiation time for GDC-15 at 100 °C under UV light

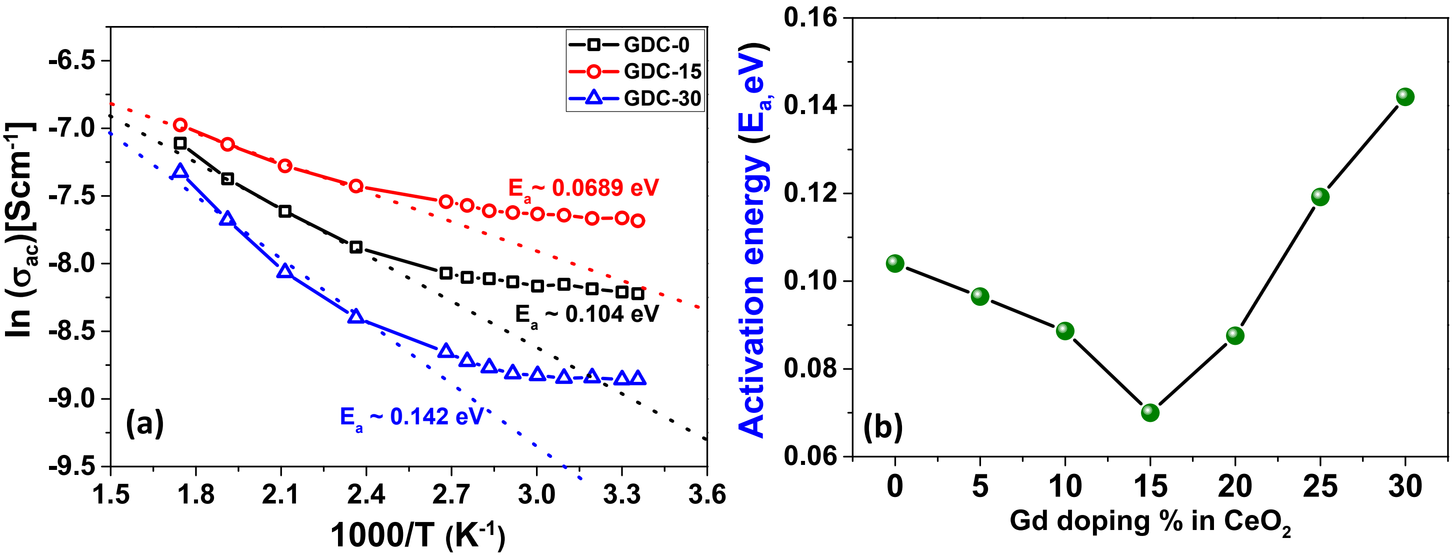

Figure S5: (a) Bulk ionic ac conductivity versus inverse temperature for GDC-0, GDC-15 and GDC-30 samples (b) Calculated activation energy values for all GDC-samples.

References:

1. Reddy, B.M., et al., *Structural Characterization and Catalytic Activity of Nanosized CexM1-xO2 (M = Zr and Hf) Mixed Oxides.* The Journal of Physical Chemistry C, 2008. **112**(31): p. 11729-11737.