Supplementary information

Role of the redox state of cerium oxide on glycine adsorption: an experimental and theoretical study

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S1. The resonant enhancements D(Ce^{4+}) and D(Ce^{3+}) in cerium oxide

The RPES technique was applied to estimate the relative amount of Ce^{3+} and Ce^{4+} ions in the surface layers of CeO_2 using the Ce 4d→4f transition. The Ce^{3+} resonance occurs due to super Coster-Kronig decay, when photon energy of 121.4 eV is used, and appears at binding energy of 1.4 eV (Fig. S1). The Ce^{4+} resonance occurs due to electron emission from Ce 4f - O 2p hybridized states at photon energy 124.8 eV. It is observed as a feature located at binding energy ~4 eV (Fig. S1). [1] The resonant enhancements of Ce^{3+} and Ce^{4+} ions were determined from the spectra as a difference between intensity values of on- and off-resonance (photon energy 115 eV) spectra at corresponding binding energies, shown in Figure S1 as D(Ce^{3+}) and D(Ce^{4+}), respectively. The resonance enhancement ratio RER was calculated as the ratio between D(Ce^{3+}) and D(Ce^{4+}).

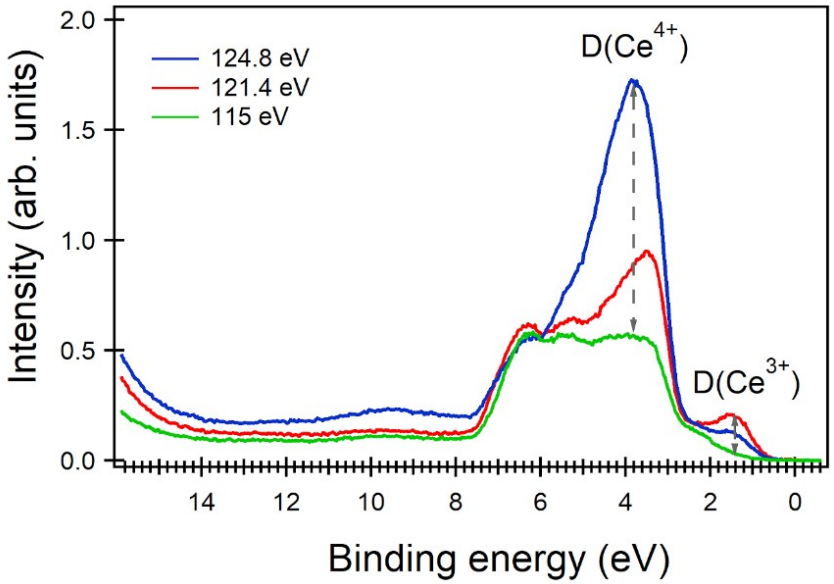

Fig. S1. The valence band spectra of CeO_2 film with glycine adlayer after the annealing at 75 °C. The spectra were taken with photon energy of 124.8 eV (blue, top curve), 121.4 eV (red, middle curve), and 115 eV (green, bottom curve). The arrows show the resonant enhancements D(Ce^{4+}) and D(Ce^{3+}).

S2. Ce 3d core level spectra

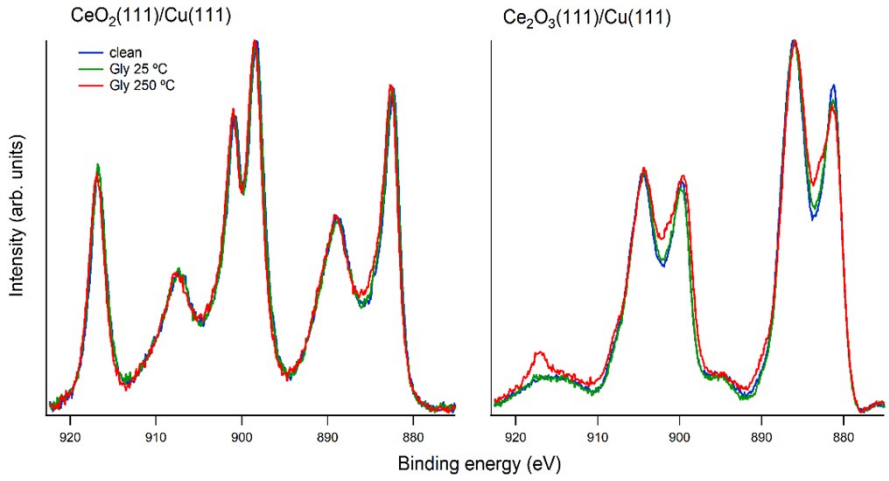

Fig. S2. Ce 3d spectra of glycine adsorbed on CeO_2 (left) and Ce_2O_3 (right) surfaces. Photon energy 1486.6 eV.

S3. Estimation of glycine coverage on cerium oxide surfaces.

The coverage of glycine on cerium oxide surfaces was estimated by analyzing the ratio of the N 1s intensity to the topmost surface contribution of the Ce 3d signal from the clean oxide film. Both spectra were acquired with photon energy of 1486.6 eV. The idea was to relate the number of nitrogen atoms to the number of cerium cations on the surface. The coverage was evaluated for each system after glycine adlayer annealing at 75 °C. The topmost surface ($Ce\ 3d_{clean})_{surf}$ signal, which accounts for the photoelectrons from the first O–Ce–O trilayer of thickness 3 Å, was derived from the Ce 3d peak area by taking into account the value of the IMFP (Inelastic Mean Free Path) of Ce 3d photoelectrons in cerium oxide (11.67 Å) and the layered structure of the oxide film. [2]

The integrated intensity of the N 1s spectrum acquired from the adsorbed molecules is considered to be proportional to the glycine coverage θ (see Fig. S3). The surface component $I(Ce\ 3d_{clean})_{surf}$ accounts for the photoelectrons escaping from uncovered oxide $(1-\theta)$ and from the surface underneath the molecular adlayer $\theta \times exp(-4/\lambda)$ (Fig. S3). The intensity ratio can be presented by the following equation:

$$\frac{I(N\ 1s)}{I(Ce\ 3d_{clean})_{surf}} = \frac{\theta}{((1-\theta)+\theta \times exp(-4/\lambda))},$$

where 4 Å is the estimated size of the glycine molecule according to Ref. [3]; λ is the IMFP of Ce 3d photoelectrons in glycine calculated from the equation for organic materials [2] and equals 16.60 Å. The estimated values of glycine coverage on the oxide surfaces are presented in Table 1 of the main text.

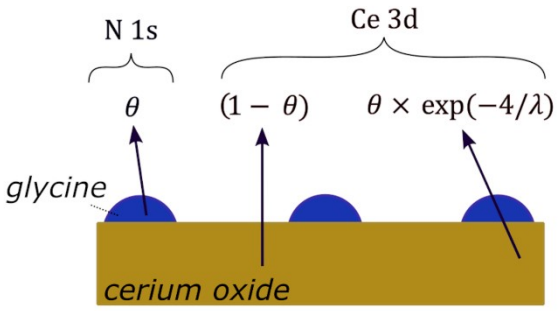

Fig. S3. Schematic diagram of the coverage estimation of glycine molecules adsorbed on the cerium oxide film.

References:

1 V. Matolín, I. Matolínová, L. Sedlácek, K. C. Prince and T. Skála, A resonant photoemission applied to cerium oxide based nanocrystals., *Nanotechnology*, 2009, **20**, 215706.

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