Electronic Supplementary Material (ESI) for Biomaterials Science.

Electronic Supplementary Information

Antioxidant Properties of ALD Grown Nanoceria Films with Tunable Valency

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Analysis of X-ray photoelectron spectroscopy (XPS) data: The Ce (3d) spectra are fitted with 5 sets of spin-orbit split doublets of Ce 3d ($3d_{5/2}$ and $3d_{3/2}$) with a Gaussian-Lorentzian peak shape after the subtraction of an offset Shirley-type background (blending Shirley and Linear Background). To ensure proper peak fitting, the area ratio of 3d spin-orbit split doublets, their splits, as well as peak positions and their FWHMs from the reference spectra were considered. In addition, spectra were analyzed using an automated incremental peak deconvolution program which varied the peak height within an envelope over a complete range to determine the best fit, checked by using the X-squared value to the actual data. With this method, the percent concentration of surface Ce^{3+} (or Ce^{4+}) ions in the film was calculated from the ratio of sum of the integrated areas of the XPS 3d peaks related to Ce^{3+} (or Ce^{4+}) to the total integral area for the whole Ce 3d region. Similarly, O (1s) and Si (2p) spectra are fitted using a Gaussian-Lorentzian peak shape after the background separation.

Optimization of number of Ce precursor pulse for ALD CeO_x film deposition: The first sample was deposited with 1 pulse of Ce precursor of 2.5 sec for 200 cycles during the inception period. The existence of color gradient on the sample between the pump-in and pump-out locations provided the first evidence of non-uniform deposition. This was further confirmed by the Raman spectroscopy and thin film XRD. Peaks of Si appeared in the Raman and XRD spectrum for location closer to the pump-out location. On the other hand, Si peaks were absent for location closer to the pump-in location. The obtained spectra confirmed the presence of CeO_2 in the films at 275°C but indicated the insufficient concentration of Ce precursor in the reaction chamber. The concentration of Ce precursor in the reaction chamber can be increased by two ways, i.e. (i) increase the pulse time and (ii) increasing the number of pulses. The second approach of increasing the number of pulses to 2 was adopted for further experiments. We hypothesized that a concentration gradient will exist for longer pulse time that will prevent the Ce precursor molecule to diffuse/reach to the other end of the reaction chamber. Two consecutive pulses of Ce precursor can lower the probability of existence of concentration gradient because a N_2 purge between two Ce pulses will clean the chamber. Secondly, absence of -OH groups at the adsorbed Ce precursor monolayer will not pose any chemical reactivity towards freshly pumped Ce precursor in the chamber, thus allow Ce molecules to adsorb on the freshly available surface. With this hypothesis, another sample was deposited for 200 cycles using 2 consecutive Ce precursor pulses at 275 ^{o}C. The resulting deposited sample was uniform in color and appearance. Raman and XRD spectrum only showed the evidence of CeO_2 presence throughout the sample, no Si peaks appeared. Furthermore, uniform thickness was measured using XRR on the sample providing the evidence of surface saturation with two consecutive pulses of Ce precursor. Based on this finding, CeO_x films of different thickness were grown by varying the number of ALD cycles from 50 to 1000.

Figure S1. Broader view of XRD spectrum of CeO_x films between 2theta 43-53°.

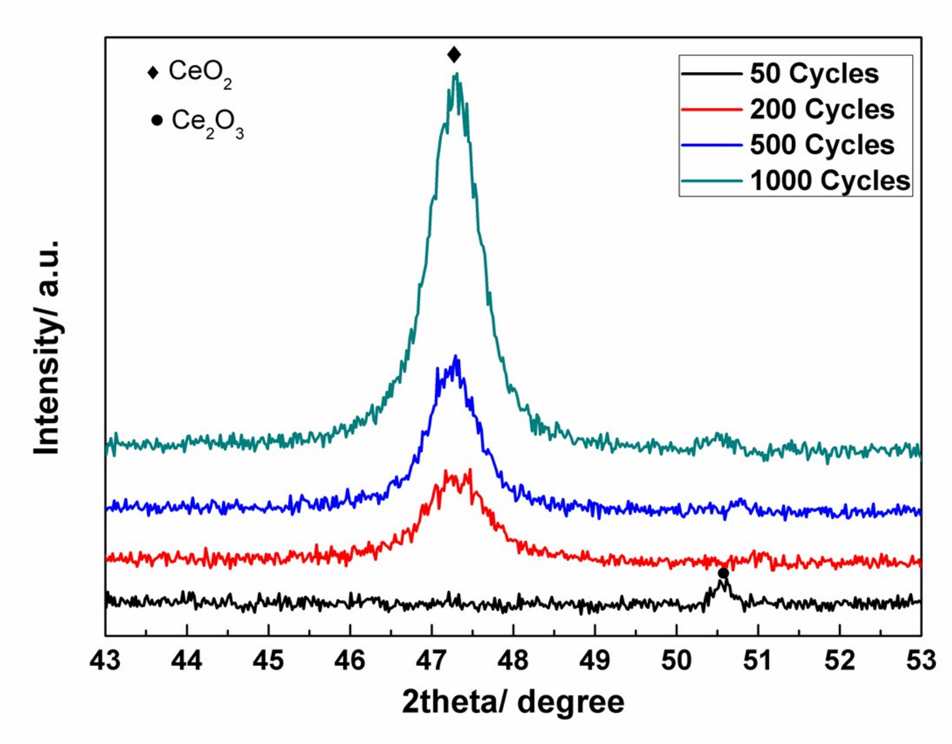

Figure S2. Fast-Fourier Transform (FFT) of (a) ALD CeO_x, (b) amorphous SiO_2, and (e) Si (100) substrate regions taken from the bright-field TEM micrograph shown in Figure 7a. Atomic model of silicon single crystal (c), and simulated diffraction pattern (d) of (c) with [100] zone axis. Experimental diffraction pattern (e) matches with the simulated diffraction pattern (d) validate the 100 orientation of Si substrate. Absence of ring pattern in FFT (e) taken from Si (100) region confirm that the substrate is composed of single crystal.

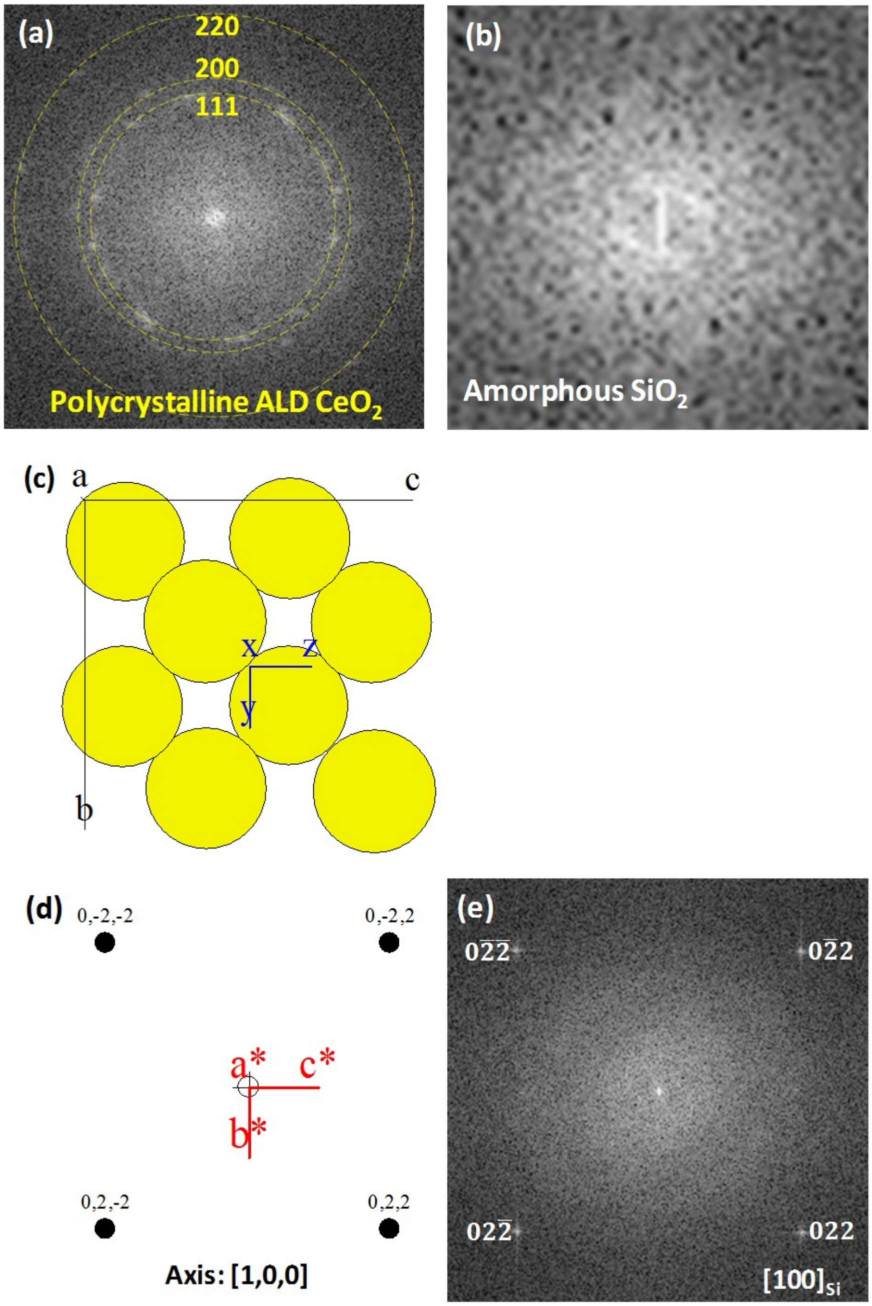

Figure S3. Inverse Fast-Fourier Transformation (FFT) images constructed from HRTEM of the ALD CeO_x film used for grain size measurement. The different colors of the grains correspond to the various FFT spots of the CeO_2 lattice spacings.

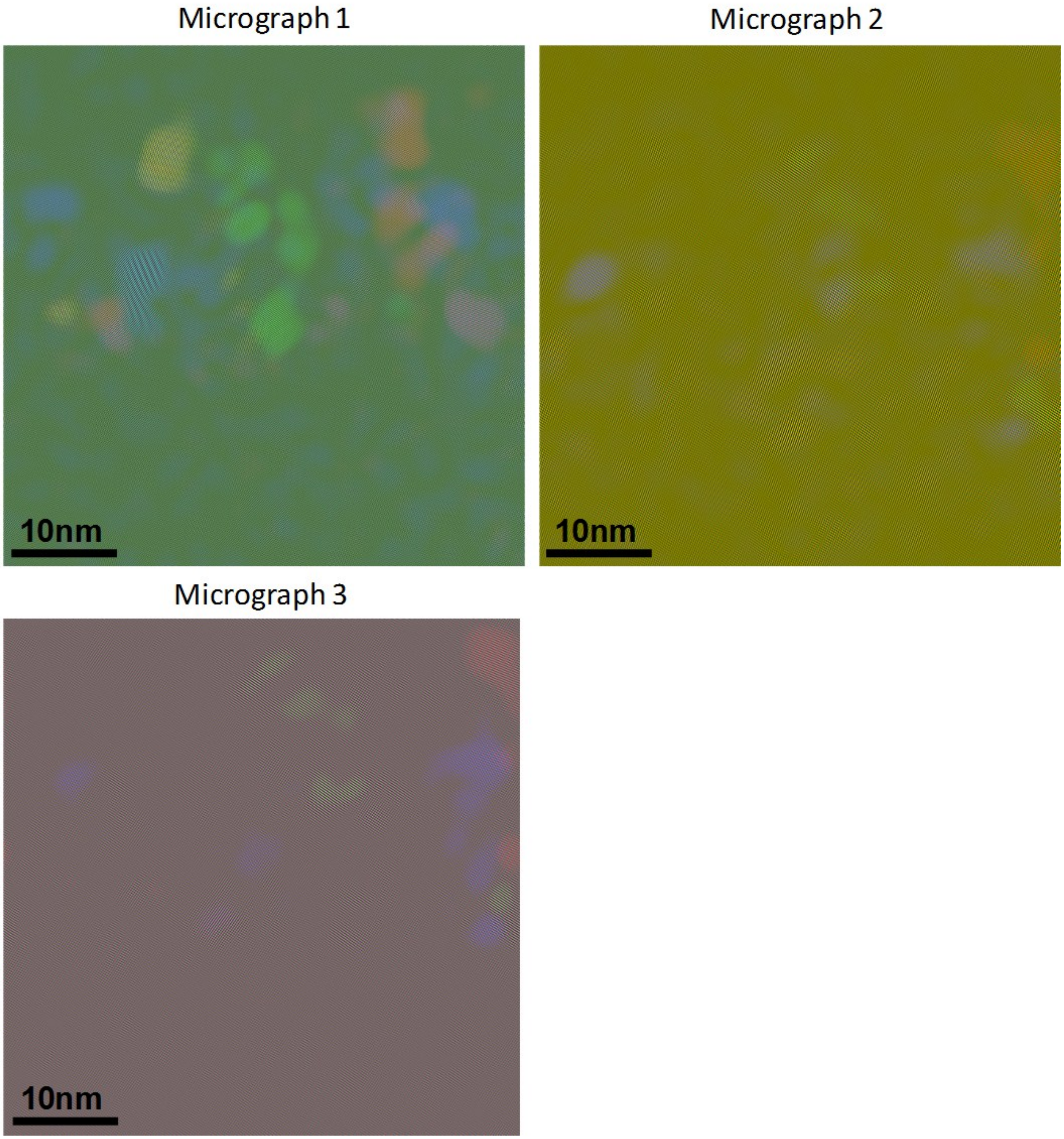

Figure S4. X-ray photoelectron spectroscopy (XPS) survey of ALD CeO_x films deposited for different cycles.

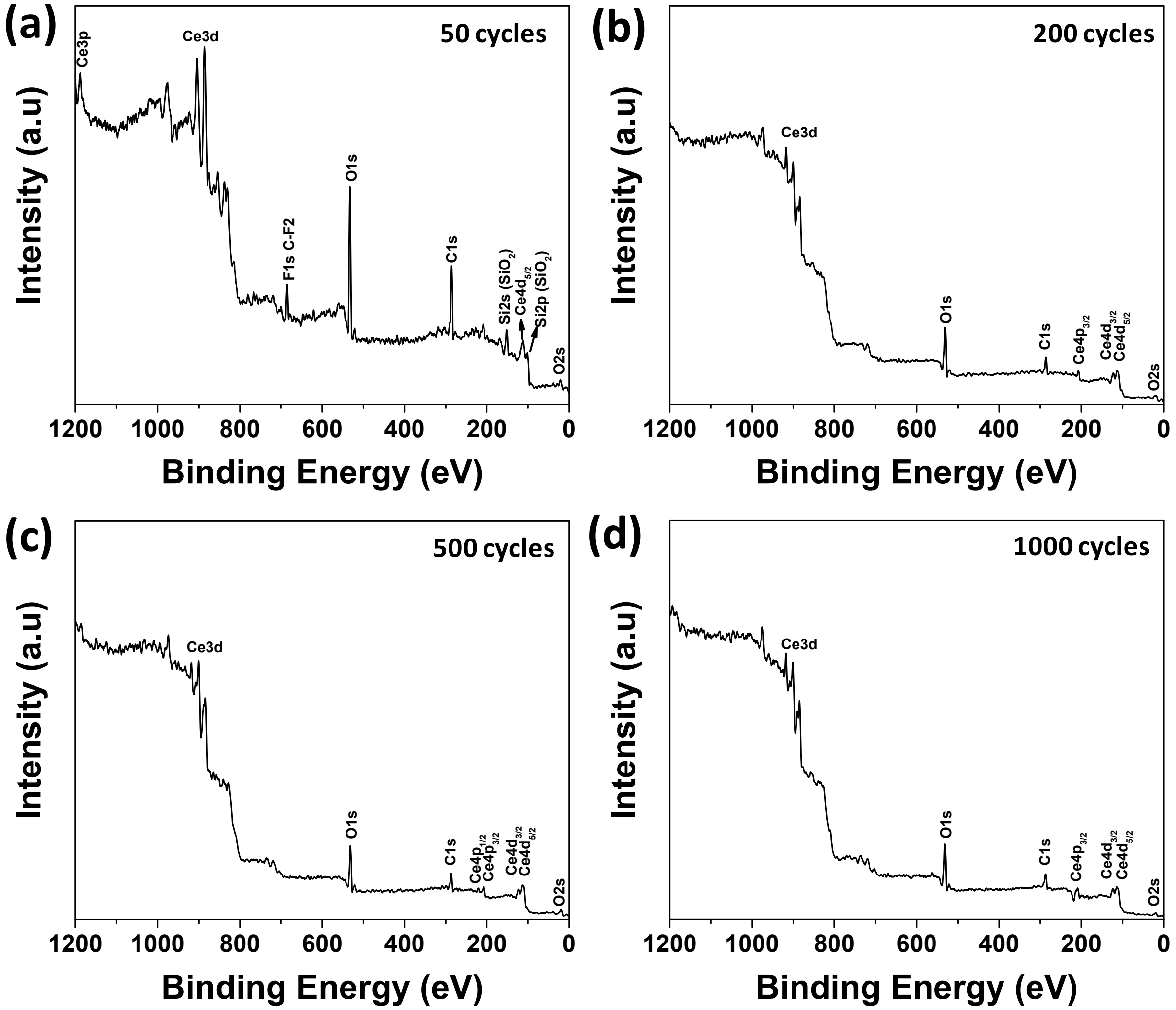

Figure S5. XPS spectrum of Si (2p) taken from ALD CeO_x films deposited for different cycles. No Si peaks are visible for higher thickness ALD CeO_x films.

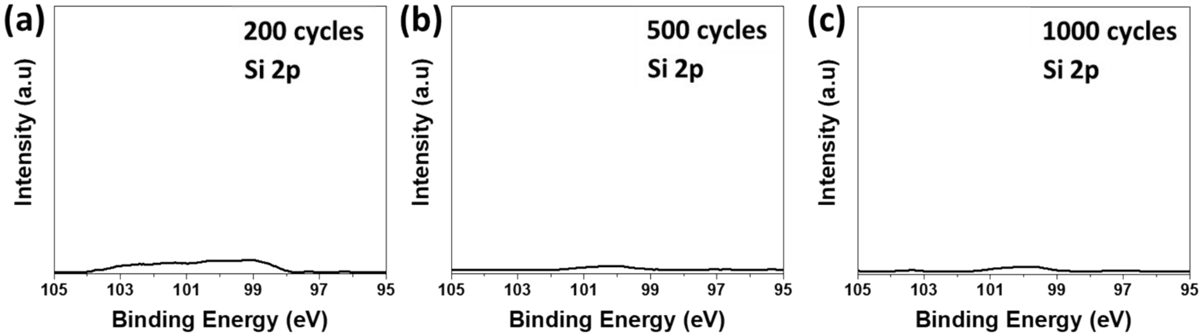

Figure S6. FTIR spectra of CeO_x deposited for different ALD cycles.

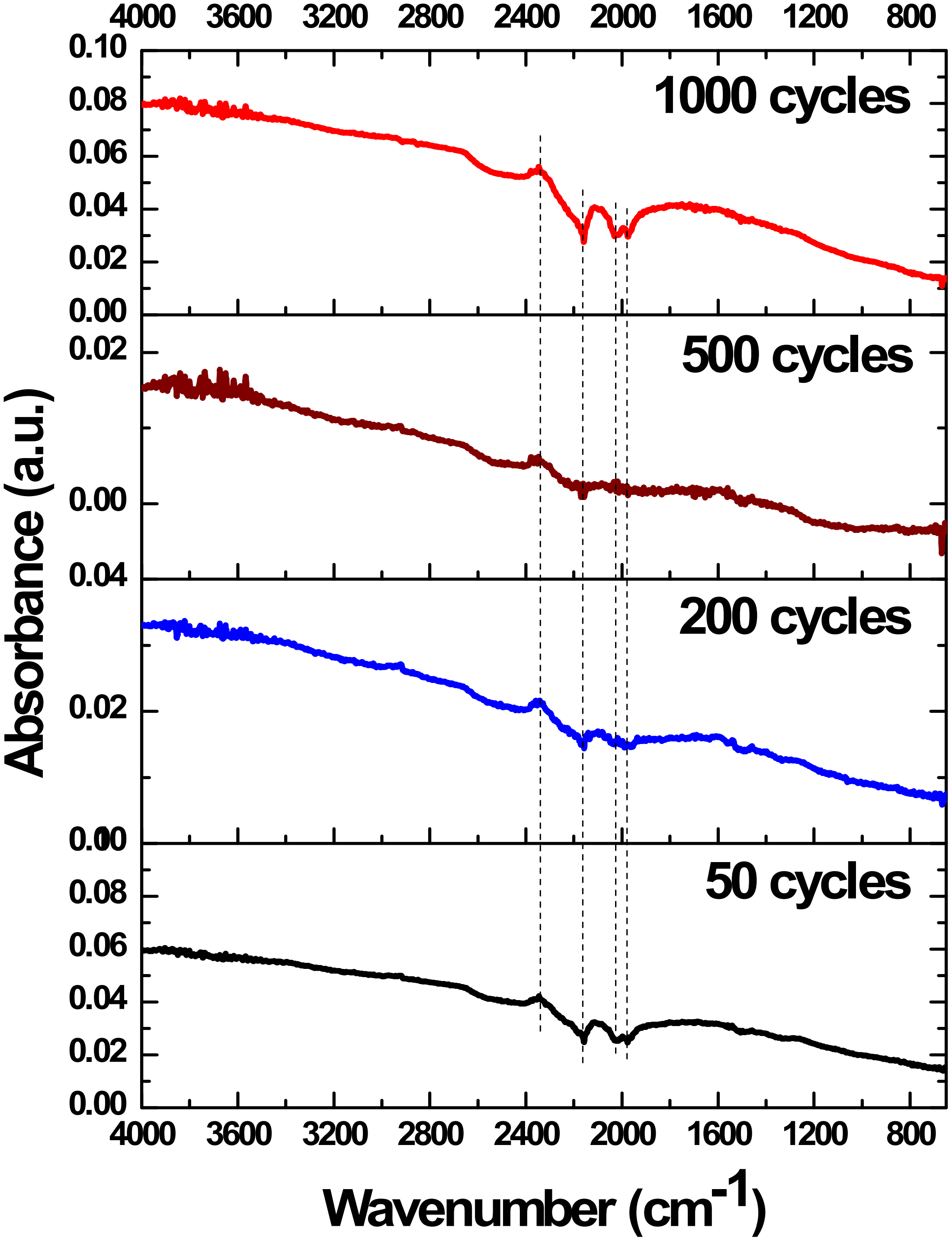

Figure S7. Quantification of intracellular ROS scavenging properties of different cycle ALD CeO_x films using fluorescence spectroscopy.

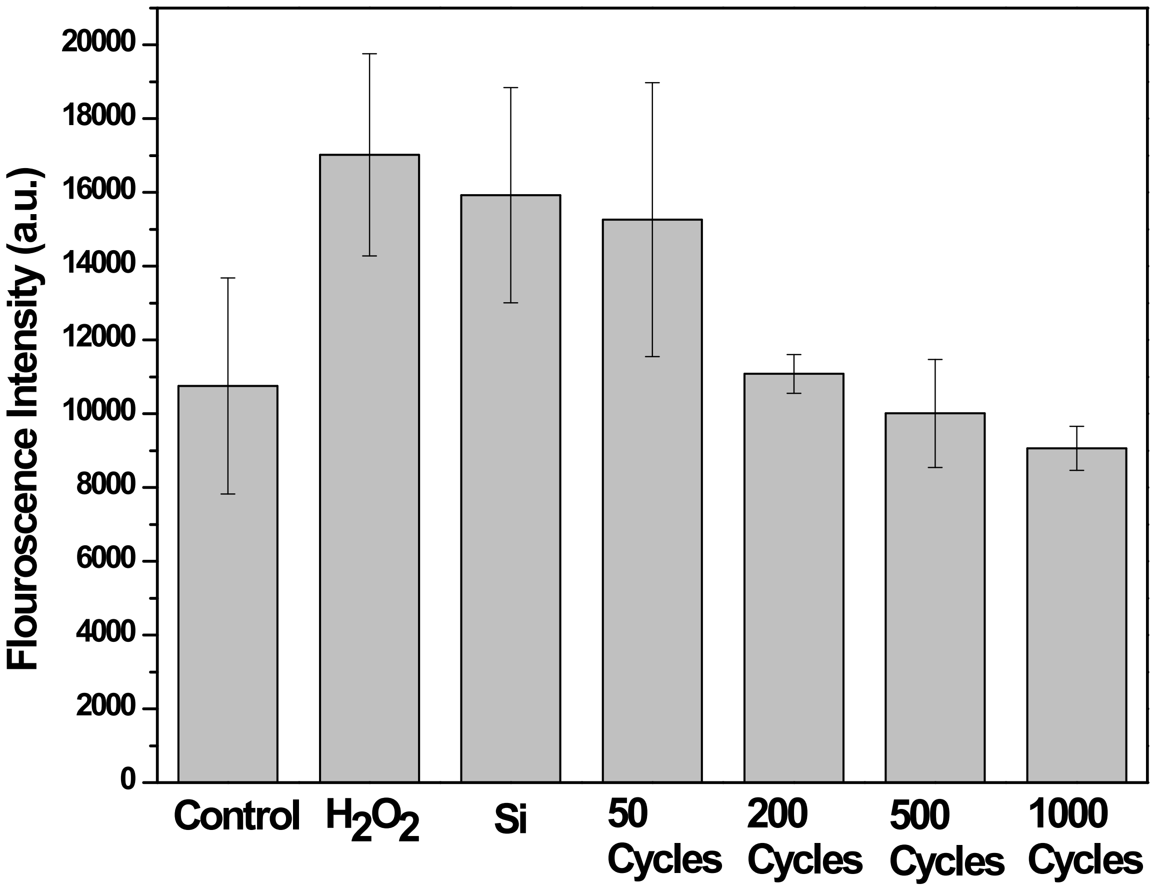

Figure S8. Cyclic voltammograms response of 200 cycle deposited ALD CeO_x electrode in [10 m_M PBS and 100 μ_M H_2O_2] with varying scan rate.