Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Tuning the morphology and composition of ultrathin cobalt oxide film via atomic layer deposition

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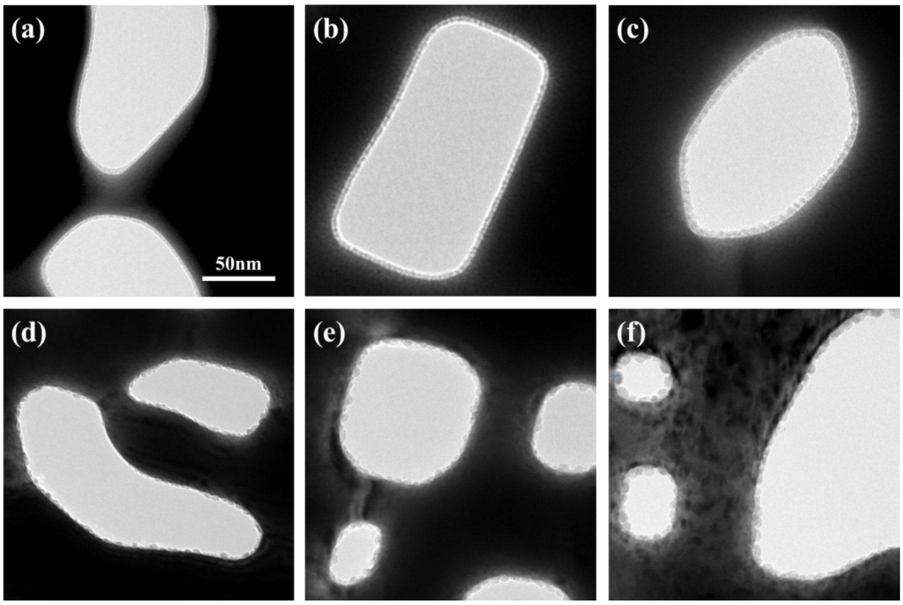

Fig. S1. TEM characterization of cobalt oxide coated nanoporous gold for 50, 100 and 200cycles at (a-c) 150°C and (d-f) 250°C.

To verify the effect of the nucleation sites, Si samples with piranha treatment was chosen considering the initial growth process can be facilitated by more precursor adsorption. It is well known that the surface becomes more hydrophilic after piranha clean due to the increase of surface hydroxyl groups. Compared with the bare Si wafer, the piranha cleaned Si wafer can provide larger density of chemisorption sites for cobalt precursor, leading to a rapid coverage of the whole surface. The increased nucleation sites would promote the growth of small nuclei and hinder the growth of large individual islands. Fig. S2 shows the AFM images as well as the surface morphology line scan of films deposited on bare silicon and piranha cleaning silicon substrates under 250 °C. After 150 ALD cycles the film grown on untreated Si substrate is still discontinuous with large height fluctuation. In contrast, the surface of Si cleaned by piranha process is fully occupied by cobalt oxide with a relatively large islands density. The roughness of films grown on piranha cleaned substrate is ideally smaller than these on untreated substrate, demonstrating the improved nucleation process. This result indicates that it is possible to manipulate the film microstructure by controlling the surface condition of substrates.

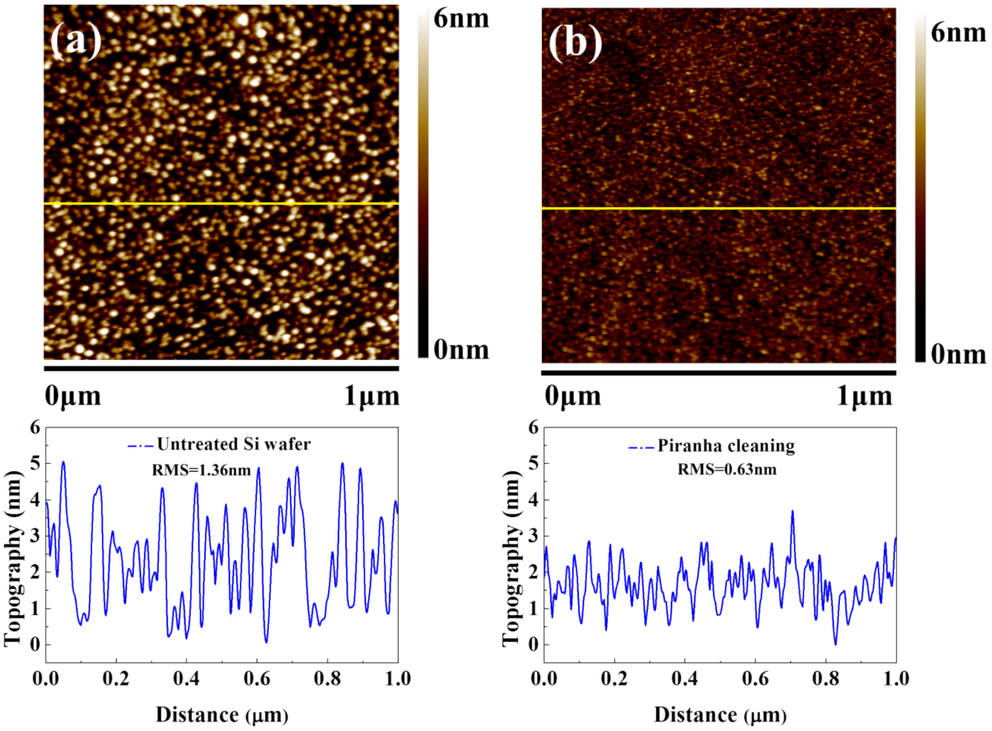

Fig. S2. AFM surface comparison for cobalt oxide deposited at 250 °C for 150 cycles on (a) untreated Si wafer, (b) piranha cleaned Si wafer

In order to test the substrate effect to AFM analyses, we have carried out experiment to treat bare Si wafer at elevated temperatures (150°C, 200°C and 250°C) in vacuum (500 Pa) conditions. Then the treated Si wafer was used as reference surface to test the substrate effect during AFM analysis. For both conditions, the morphology of Si surface is stable before and after the treatment (Fig S3). The surface of Si is very flat with RMS ~0.3-0.4nm, which has little influence to analyze the surface morphology after cobalt oxide deposited, especially for rough surface of cobalt oxide deposited at 250°C.

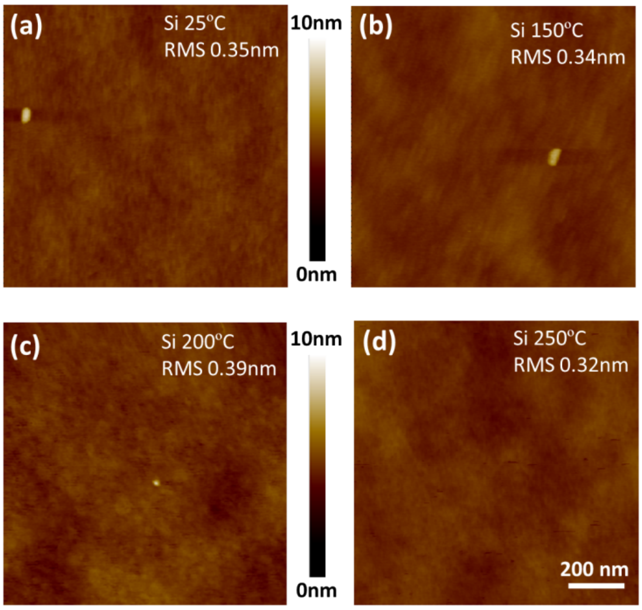

Fig S3. AFM images of Si wafer treated at vacuum conditions with elevated temperature at (a) 25°C, (b) 150°C, (c) 200°C and (d) 250 °C

Controlled experiments were carried out to probe the influence of surface morphology effect to CO oxidation. Three kinds of samples are fabricated including (1) 9nm cobalt oxide film prepared at 150°C, (2) 9nm cobalt oxide film prepared at 250°C and (3) 9nm cobalt oxide film prepared at 250°C with oxidative treatment at 150°C with ozone flow. The surface morphology of 250°C prepared samples before and after oxidative treatment are obtained by AFM. Figure S4 shows that there is nearly no change after oxidative treatment.

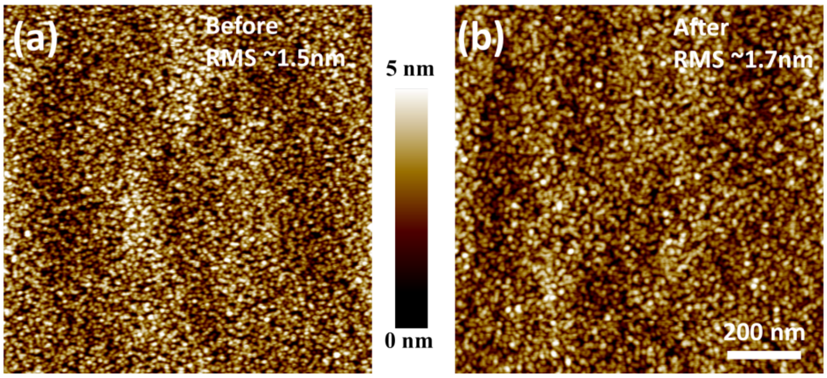

Fig S4. AFM surface morphology of samples prepared at 250°C (a) before and (b) after oxidative treatment.

The Co 2p spectra obtained from sample after oxidative treatment shows no satellite peak (Figure S5). Reveal that after such oxidative treatment, CoO has been converted to Co_3O_4 for the sample prepared 250°C and the chemical state of cobalt oxide is the same as sample prepared at 150°C.

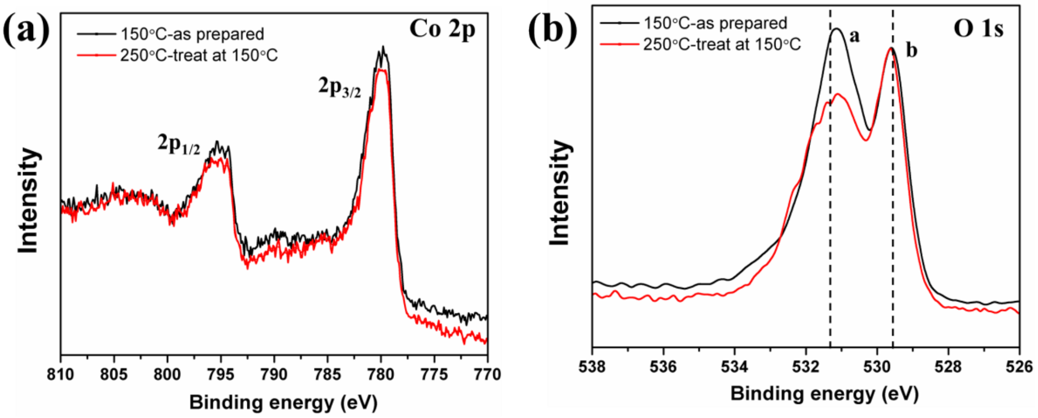

Fig S5. (a) Co 2p and (b) O 1s spectra of sample prepared at 250°C after oxidative treatment at 150 °C.

Then the CO oxidation performance of the three kinds of samples is compared (designated as $T_{150\ ^{\circ}\mathrm{C}}$, $T_{250\ ^{\circ}\mathrm{C}}$ and $T_{250\ ^{\circ}\mathrm{C\text{-}oxidative\ treat}}$). The result illustrated at Figure S6 indicates that the tendency that the catalytic ability $T_{220\ ^{\circ}\mathrm{C\text{-}oxidative\ treat}} > T_{250\ ^{\circ}\mathrm{C}}$, which means that after oxidative treatment, catalytic activity has been increased due to the increased amount of Co_3O_4. However this activity is still slightly lower than sample prepared at 150°C. Surface oxygen could be another reason. As shown in Figure S5(b), although chemical composition of cobalt oxide is similar, the amount of chemisorbed oxygen species to oxygen vacancies (peak a, 531.4eV) is less than sample prepared at 150°C after oxidative treatment. This may lead to the lower catalytic activity than the sample prepared at 150°C.

From the results, we can infer that both surface oxygen and cobalt oxide composition play an important role in catalytic performance.

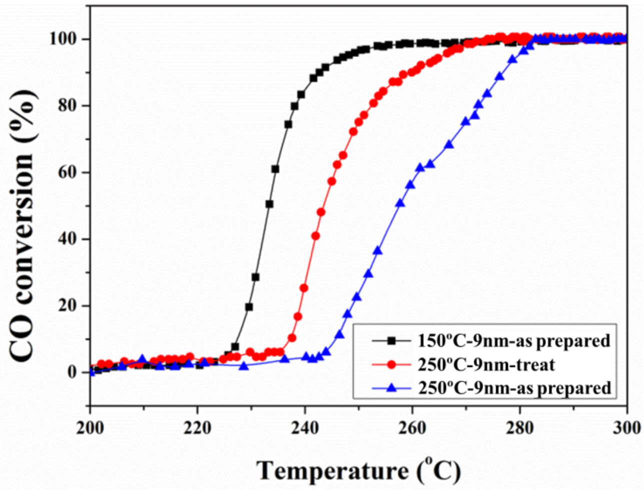

Fig S6. CO oxidation light curves of cobalt oxide thin film prepared under different condition