Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Cauliflower-like CeO_2-TiO_2 Hybrid Nanoclusters with Extreme Photocatalytic and Self-Cleaning Properties

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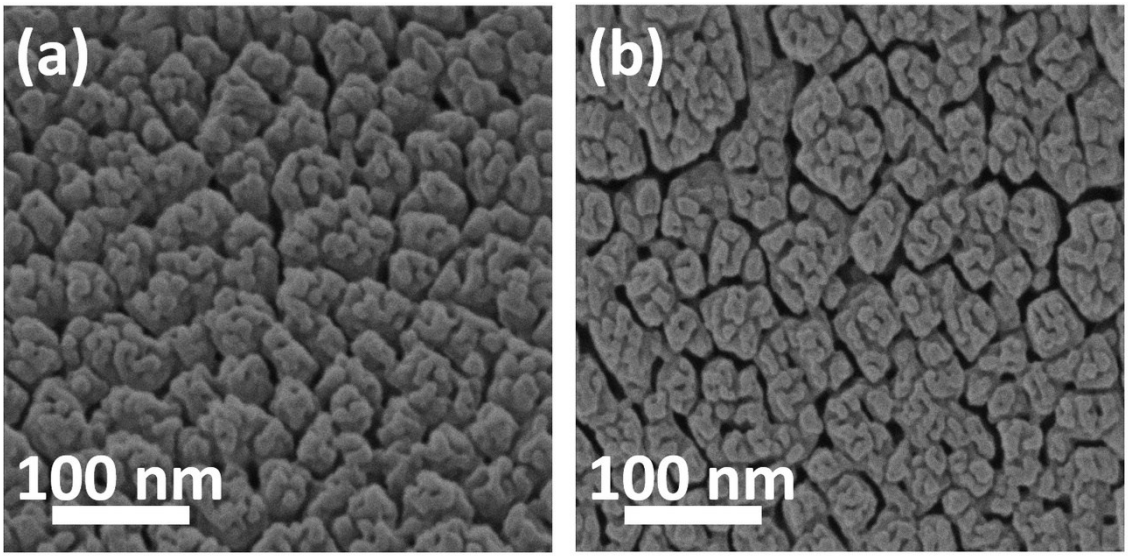

Fig S1. HIM images of heat-treated CeO_2-TiO_2 at different angles **(a)** 30^0 and **(b)** 0^0.

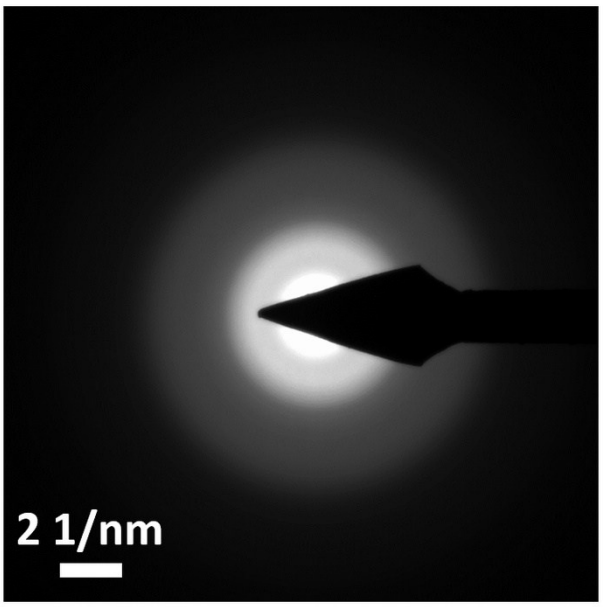

Fig S2. Selected-area electron diffraction (SAED) of as-deposited TiO_2.

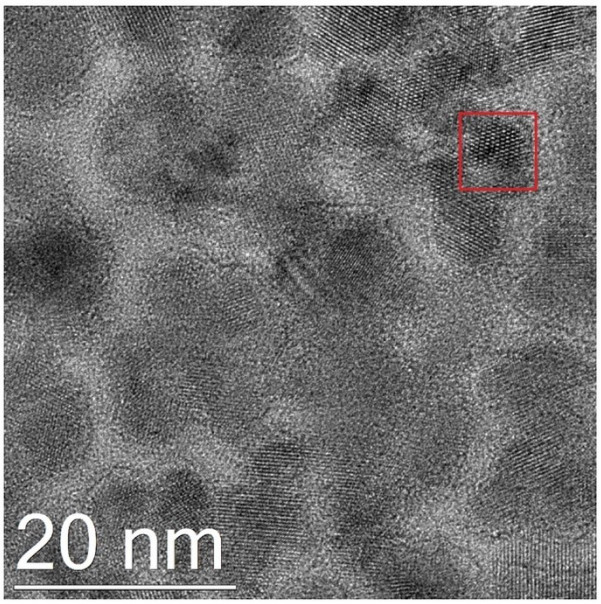

Fig S3. The high-resolution transmission electron microscopy (HRTEM) image of heat-treated CeO_2-TiO_2.

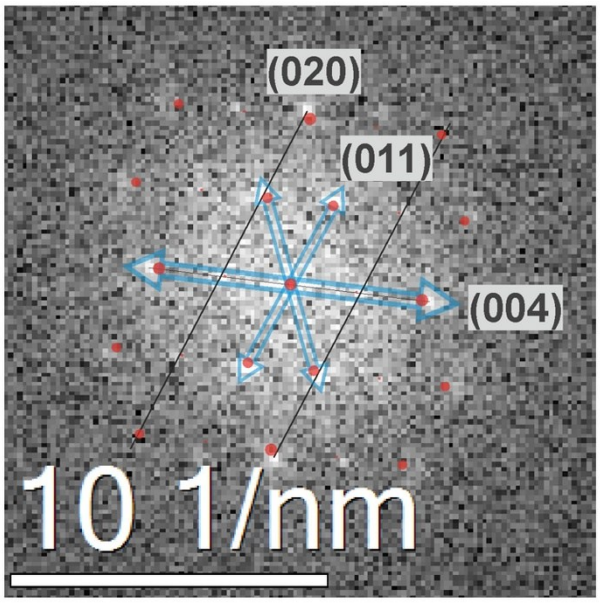

Fig S4. Fast Fourier transform (FTT) analysis of heat-treated TiO_2 structure.

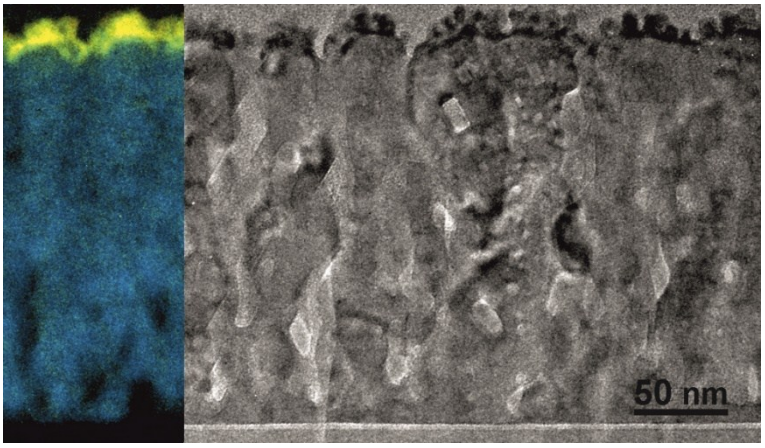

Fig. S5. High-resolution transmission electron microscopy (HRTEM) image of the bi-layer (cross-section) prepared by focused ion beam (FIB). (The colored image on the left side is an energy filtered TEM-micrograph where yellow and turquoise represent cerium (Ce) and titanium (Ti) elements, respectively).

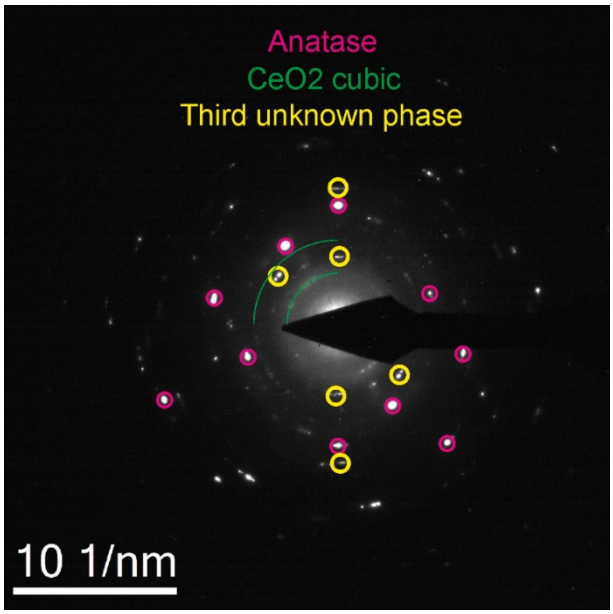

Fig. S6. Selected-area electron diffraction (SAED) of the cross-section of heat-treated CeO_2-TiO_2.

The reflections clearly demonstrated the presence of both anatase and cubic CeO_2 phases. The anatase seems to be not epitaxially grown on Si-substrate. Additionally, we observed a third phase with d-spacings of 2.05 Å and 2.40 Å which might be attributed to either cubic TiO or a mixed oxide composed of one-third CeO_2 and two-third TiO_2.

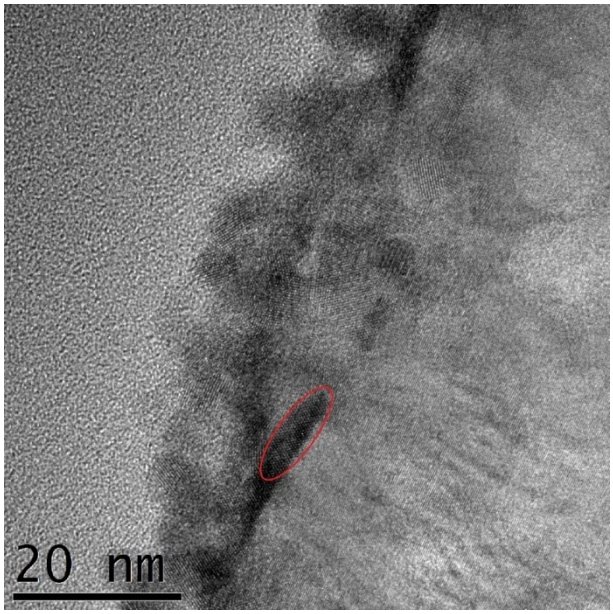

Fig. S7. The high-resolution transmission electron microscopy (HRTEM) image of the cross-section of heat-treated CeO_2-TiO_2.

In HRTEM analysis we observed a different phase, which was neither a CeO_2 nor a TiO_2 phase, at CeO_2-TiO_2 interface, too. Only in few cases we could observe a clear interface between CeO_2 and this

third phase (area marked by red color shown in Fig. S7). Here 5-nm-thick CeO_2 crystals were essentially randomly arranged as it can be seen in Fig. S5 and S7.

On the other hand, this third phase was neither observed in top-view HRTEM nor SAED. This might be due to a special texture of this third phase; or mostly probably FIB-preparation might have induced a structural artifact.

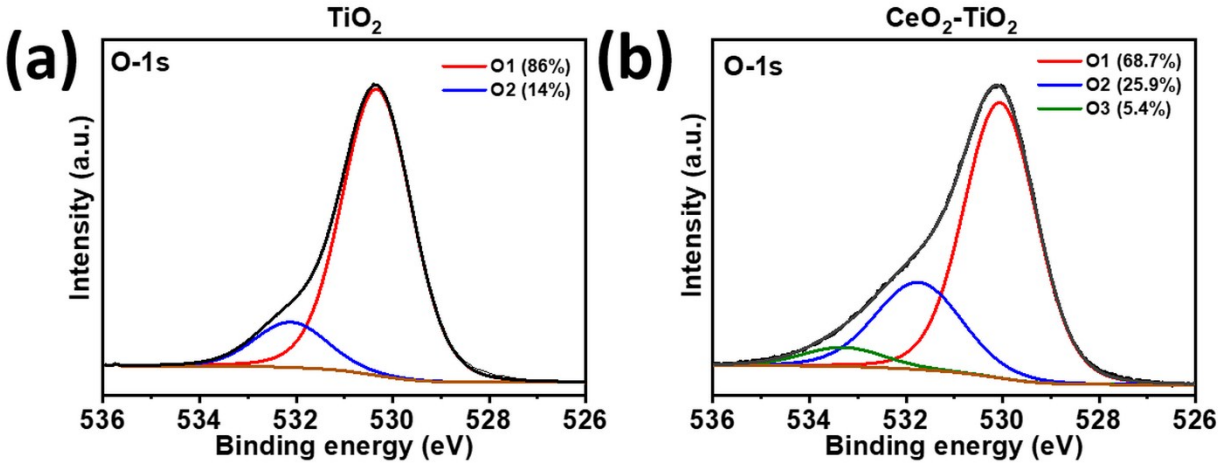

Fig. S8. Detailed deconvolution of a high-resolution XPS O-1s for: **(a)** TiO_2 and **(b)** CeO_2-TiO_2 hybrid structure.

Table S1. Kinetics rate constants (k) for photocatalytic degradation of MB by prepared thin film photocatalysts. **(Kinetics rate constants (k) were calculated according to *$ln(C/C_0)=k.t$*)**

Photocatalysts	Rate Constant (s^{-1})
as-deposited TiO_2	-0.14×10^{-3}
heat-treated TiO_2	-0.15×10^{-3}
as-deposited CeO_2 - TiO_2	-0.69×10^{-3}
heat-treated CeO_2 - TiO_2	-3.40×10^{-3}

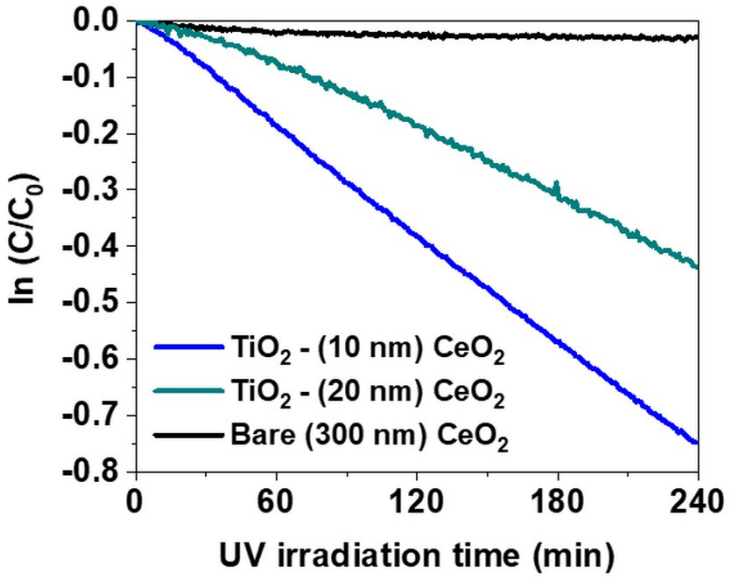

Fig S9. The plot of $\ln(C/C_0)$ versus reaction time for photocatalytic degradation of methylene blue (MB) at different CeO_2 thicknesses.