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Cauliflower-like CeO₂-TiO₂ Hybrid Nanostructures with Extreme Photocatalytic and Self-Cleaning Properties

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In recent years, heterogenous photocatalysis gained an enormous interest due to increasing concerns about environmental pollution. Here we propose a facile approach to synthesize cauliflower-like CeO₂-TiO₂ hybrid structures by magnetron reactive sputtering, exhibiting an extremely high photocatalytic activity. While heating and air-quenching of sputter deposited TiO₂ thin film (first layer) triggered the formation of a nanocrack network, the second heat-treatment led to transformation of the CeO₂ film (second layer) into CeO₂ nanoclusters (NCs). We attribute the resulting high photocatalytic activity to the confined structure of the CeO₂ NCs and the CeO₂-TiO₂ interface, which allows Ce³⁺/Ce⁴⁺ dynamic shifting. In addition to high photocatalytic activity in an aqueous medium, the prepared CeO₂-TiO₂ hybrid structures exhibited a significant self-cleaning property in air (non-aqueous).

TiO₂ is an attractive material for a large number of applications including high-refractive-indexed optical films, high-density dynamic-memory devices, solar cells, supercapacitors, and photocatalytic processes.1-3 As the environmental pollution has become the focus of attention all over the world, the interest in heterogeneous photocatalysis involving TiO₂ has increased immensely at both fundamental science as well as application levels.4-6 Beside its various advantages such as low cost, earth abundance, and non-toxicity, high electron-hole recombination rate is one of the main drawbacks of TiO₂.6 In addition, low electron mobility and small diffusion length (for holes) limit the practical use of TiO₂ in heterogeneous photocatalytic applications.7

Doping or decorating TiO₂ with metallic elements is one of the common methods to improve its photocatalytic efficiency.8 Especially noble metals such as silver (Ag) and gold (Au) have been intensively used to extend the absorption to visible wavelengths and to enhance electron-hole separation.9,10 Alternatively, combining TiO₂ with rare-earth elements and their oxides has been shown to be an effective way to improve the conversion efficiency of TiO₂. Especially mixed oxides are of great interest due to superior catalytic properties owing to synergetic effects. Among various mixed oxides, CeO₂-TiO₂ combination attracts the attention of catalytic applications due to its novel physicochemical and electronic properties, which are totally different than their individual components.11

The redox couple Ce³⁺/Ce⁴⁺ with the ability of shifting between CeO₂ and Ce₂O₃ under oxidizing and reducing conditions make Ce based oxides exceptional in heterogeneous catalysis.12,13 In addition, the CeO₂ structure facilitates the formation of labile oxygen vacancies with relatively high mobility of bulk oxygen species. At CeO₂-TiO₂ hybrid structures, TiO₂ acts as chemical, thermal and mechanical stabilizer for achieving stable nanoscale CeO₂.14 Beside the role of TiO₂ as a simple support, similar to other oxides, the CeO₂-TiO₂ interface has been reported to exhibit unique chemical properties.15

Various wet chemical routes have been developed to synthesize hybrid CeO₂-TiO₂ structures with different morphology, size, and stoichiometry.16 Thanks to their high surface area CeO₂-TiO₂ hybrid nanoparticles have been shown to decompose various organic contaminants effectively in water; however, their practical use as slurry type suspensions is limited because of the difficulty of the separation of such small particles after the photocatalytic process. For outdoor (e.g. self-cleaning windows) as well as indoor applications (e.g. odor cleaning devices) immobilized, robust and highly adhering photocatalytic particles or films are needed. In general, suspended photocatalytic nanoparticles exhibit much higher activity (thanks to their high active surface area) in comparison to immobilized nanoparticles or thin films of the same material.17

Here, we prepared columnar TiO₂ structures decorated with CeO₂ nanoclusters (NCs) by a novel reactive sputtering process followed by the subsequent heat-treatment. In general, sputter deposited thin films offer high adherence and mechanical stability, but typically they are outperformed (due to lack of large surface area) in terms of photocatalytic properties by colloidal nanoparticles. Firstly, a 300 nm TiO₂ thin film was deposited on quartz and silicon substrates by magnetron reactive sputtering at a gas pressure (O₂:Ar, 10 sccm:250 sccm) of 2.9 Pa. We have previously shown that such a high working pressure led to the growth of isolated (poor interaction between adjacent structures) columnar structures (as schematically depicted in Fig. 1a).18,19 Afterwards by heating the sample at 650°C and air-quenching we induced nanocrack networks to enhance the active surface area (as schematically explained in Fig. 1a and Fig. 1b). Following the heat-treatment, a 6-8 nm thick CeO₂ layer was deposited on columnar TiO₂ structures and we subjected the CeO₂-TiO₂ bilayer to a second heat-treatment step at 650°C for 1 h to crystallize both oxides fully and to transform the ultra-thin non-continuous CeO₂ layer into CeO₂ NCs. Finally, we achieved cauliflower-like TiO₂ structures decorated with fine CeO₂ NCs (as schematically depicted in Fig. 1b).
Helium Ion Microscope (HIM) images of bare and CeO$_2$ NCs decorated TiO$_2$ films are shown in Fig. 1c-f (before and after heat-treatment). The columnar morphology of TiO$_2$ is typical for a sputter deposited film. Heat-treating and air-quenching induced thermal cracking which led to higher surface area (Fig. 1d). After second heat-treatment and air-quenching (following CeO$_2$ deposition) we observed the formation of CeO$_2$ NCs on top of former TiO$_2$ columnar structures (Fig. 1e and Fig. S1). The lattice mismatch between CeO$_2$ (cubic fluorite structure) and TiO$_2$ (anatase) seemed to generate a high stress, which might have caused the island-like re-organization of CeO$_2$ structures during heat-treatment. In the wet-chemical synthesis of TiO$_2$ supported CeO$_2$, structures tend to grow in the out-of-plane direction to minimize total added strain energy thereby limiting in-plane growth and triggering the island growth. We observed a similar morphology even after the deposition of the CeO$_2$ layer and such a morphology became more dominant after the heat-treatment (Fig. 1e and 1f). For details see Fig. S1 (Supplementary Information).

As expected, prior to heat-treatment the deposited TiO$_2$ film was amorphous (as demonstrated by selected-area electron diffraction (SAED) shown in Fig. S2). After heat-treatment and air-quenching, TiO$_2$ crystallizes to a polycrystalline mixture of mainly anatase and a small portion of brookite (Fig. 2a). In addition, we observed the contraction of the c-axis in the tetragonal unit cell of anatase from 9.51 Å to 9.14 Å. Such a contraction was detected in some crystallites by fast Fourier transformation (FFT) of corresponding HRTEM images (Fig. S3) as shown in Fig. S4. This contraction cannot be explained by the crystal-size below 20 nm as nanocrystalline samples typically show expansions of the unit cell. A more probable reason may be the oxygen deficiency induced by the heat-treatment. After heat-treatment and air-quenching we observed that hybrid structure consists of anatase and cubic CeO$_2$ phases (Fig. 2b). Here, the anatase structure was not distorted; the CeO$_2$ top layer seemed to prevent excessive oxygen-desorption from the anatase structure during heat-treatment. Cross-sectional (prepared by focused ion beam as described in Fig. S5) TEM-examination of deposited layer suggested that there is no interfacial correlation between anatase and cubic CeO$_2$ phases, rather CeO$_2$ crystals seem to be randomly oriented (Fig. S6 and S7).
In order to reveal the chemical state of prepared CeO$_2$-TiO$_2$ hybrid catalyst, the surface was investigated by XPS. The high-resolution spectra of C-1s, O-1s, Ti-2p, and Ce-3d were acquired for pure and hybrid catalysts. Charge referencing was done using adventitious carbon peak (C-1s) located at 285.0 eV.\(^\text{23}\) XPS spectra of Ce-3d for CeO$_2$ and CeO$_2$-TiO$_2$ are presented in Fig. 2c. In order to maximize visibility of the changes in Ce-3d, recorded spectra were normalized and plotted in an overlapped way. Peaks labeled as $u$ and $v$ are attributed to 3d$_{3/2}$ and 3d$_{5/2}$ spin-orbit states, respectively.\(^\text{23}\) The $u/v$, $u^2/v^2$, and $u^3/v^3$ doublets are attributed to 3d$^{10}$4f$^0$ initial electronic state corresponding to Ce$^{4+}$.

On the other hand, in the XPS spectrum of CeO$_2$-TiO$_2$ hybrid structures, we observed some slight changes. Although it is difficult to detect their presence due to persisting predominant Ce$^{4+}$ peaks, we believe that small peaks labeled with $u_1$ and $v_1$ indicate 3d$^{10}$4f$^1$ electronic state which corresponds to Ce$^{3+}$. Co-existence of both Ce$^{4+}$/Ce$^{3+}$ states is crucial for achieving high conversion efficiency. Moreover, the presence of Ce$^{3+}$ may inhibit the reduction of Ti$^{4+}$ because of the favorable electron compensation.\(^\text{24}\) As shown in Fig. 2d, we observed differences in binding energies of Ti-2p core level (Ti-2p$_{3/2}$ and Ti-2p$_{1/2}$ spin-orbit splitting) acquired for TiO$_2$ and CeO$_2$-TiO$_2$ hybrid structures. The position of Ti-2p$_{3/2}$ ($\sim$459.0 eV) confirms that Ti is in Ti$^{4+}$ state in the original TiO$_2$ thin film. On the other hand, there is a slight shift of binding energy towards higher value as well as the larger full width of half maximum of the Ti$_{2p}$ doublet. This can be interpreted by the formation of a very intimate composite between the two oxides that influences the structural environment of Ti$^{4+}$. Moreover, the formation of heterointerfaces between ceria and titania with different band bending, which can be a result of shown enhanced photocatalytic performance.\(^\text{11,25}\) Similarly we observed differences in oxygen binding energies of TiO$_2$ and CeO$_2$-TiO$_2$ as shown in Fig. 2e. In general, low binding energies given by O-1s peak confirm the presence of oxygen (O$_1$) in the lattice. In contrast, high oxygen binding energies (shifted by $\sim$2.5 eV) are related to the presence of a higher amount of oxygen vacancies (O$_2$). Moreover, the peak located at around 533.3 eV (O$_2$) for the hybrid film could be an indication for adsorbed oxygen. The relative high area ratio O$_2$/O$_1$ (0.38) in the CeO$_2$-TiO$_2$ O-1s spectrum in comparison to that of TiO$_2$ (0.16) could point to an increase of oxygen vacancies.\(^\text{24}\) Detailed deconvolution of O-1s core levels is shown in the supplementary information (Fig. S8).

The photocatalytic activity of the prepared CeO$_2$-TiO$_2$ hybrid catalyst was first evaluated by degrading Methylene Blue (MB) under ultra-violet (UV) light irradiation (in comparison to bare TiO$_2$) as shown in Fig. 3a. The degradation of MB was evaluated by observing the change in the absorption of the initial concentration ($C_0$) divided by the final concentration (C) of the dye as a function of irradiation time (t); the corresponding results are shown in Fig. 3a. By fitting a first-order kinetic model we calculated rate constants (Table S1). As-deposited TiO$_2$ film exhibited a very low photocatalytic efficiency ($k_1$=1.4x10$^{-4}$/s) and after the heat-treatment, there was only a slight improvement ($k_2$=1.5x10$^{-4}$/s). On the other hand, after depositing a 6-8 nm CeO$_2$ layer a significant increase ($k_3$=6.9x10$^{-4}$/s) has been observed.

Following the heat-treatment, CeO$_2$-TiO$_2$ hybrid structures exhibit an extremely high photocatalytic efficiency with a rate constant of $k_4$=3.4x10$^{-3}$/s. This extremely high difference in rate constants indicates that it is not simply the effect of mixed oxide induced dynamic charge flow and separation due to band leveling effects between the corresponding conduction bands of CeO$_2$ and TiO$_2$.

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** (a) Plot of ln($C/C_0$) versus reaction time for photocatalytic degradation of MB and (b) optical image of MB coated CeO$_2$-TiO$_2$ deposited quartz glass before and after 5 min UV irradiation.

It is believed that the confined structure of CeO$_2$ (on TiO$_2$ structures) and the CeO$_2$-TiO$_2$ interface are key factors for achieving such a high activity. For instance, when we increased the thickness of the CeO$_2$ deposit we achieved activities similar to bare TiO$_2$ (Fig. S9). Therefore, we believe that the coexistence of both Ce$^{3+}$/Ce$^{4+}$ states is important for the observed high activity. In other words, the fluorite structure probably plays a role in the behavior of reduced Ce and/or oxygen vacancy sites. This in accordance with studies which reported that oxygen vacancies alter their electron-capturing properties as a function of their isolated or associated nature, and basically such nature is a function of the CeO$_2$ primary particle size and other morphological variables.\(^\text{26}\) The CeO$_2$-TiO$_2$ interface seems to stabilize electron-capturing oxygen-vacancy-related centers.\(^\text{27}\)

In addition to analysis of the photocatalytic performance of CeO$_2$-TiO$_2$ by monitoring MB bleaching in aqueous solution, we verified the capability of photocatalytic bleaching in a non-aqueous environment. First, a thin MB layer was spin-coated
onto a CeO$_2$-TiO$_2$ deposited quartz substrate. Prior to the spin-coating, we prepared a diluted MB solution using de-ionized (DI) water. Following the ultrasonication, the MB solution was mixed by a magnetic stirrer operating for 3h. Before the spin coating, the solution was filtered to eliminate any undissolved or agglomerated solid particles. Fig. 3b shows the optical images of MB coated CeO$_2$-TiO$_2$ deposited quartz glass before and after 5 min irradiation. It is clearly seen that the MB layer was quickly decomposed by highly active CeO$_2$-TiO$_2$ structures. This indicates that such hybrid structures may be applicable for outdoor applications such as photocatalytic windows.

To reveal the self-cleaning property of prepared CeO$_2$-TiO$_2$ hybrid structures, we treated the sample surface with oleic acid (as a model for organic contaminants) and afterward we monitored its photocatalytic decomposition by measuring the decrease in water contact angle (WCA) during UV irradiation. A diluted oleic acid solution in acetone (50 µL, 10 mmol/L) was prepared and drop-casted onto test samples. While a WCA of 30° was observed on CeO$_2$-TiO$_2$ hybrid structures; after oleic acid deposition, the WCA changed to 75° (Fig. 4a). This clearly indicated the contamination of the surface.

The oleic acid treated CeO$_2$-TiO$_2$ hybrid structures were exposed to UV light and, as a result, the WCA decreased gradually from 75° to 26° during 60 min irradiation time. The decrease in WCA after UV irradiation confirms the photocatalytic degradation of oleic acid by CeO$_2$-TiO$_2$ hybrid structures. On the other hand, WCAs of oleic acid on as-deposited and heat treated TiO$_2$, and as-deposited CeO$_2$-TiO$_2$ did not decrease during the same irradiation time. The self-cleaning ability of prepared samples was visualized by observing the change in the optical appearance of oleic acid residues after UV irradiation. As one can see in Fig. 4b while the residue left after oleic acid treatment on CeO$_2$-TiO$_2$ hybrid structures vanished totally within 60 min of UV irradiation, residues on other samples persisted.

Conclusions

We fabricated cauliflower-like CeO$_2$-TiO$_2$ hybrid structures by a simple reactive sputtering method followed by heating and air-quenching. The heat-treatment induced the formation of nanocrack networks between well-separated columnar TiO$_2$ structures, enhancing the active surface area. Due to the lattice mismatch between CeO$_2$ (cubic fluorite structure) and TiO$_2$ (anatase), island-like re-organization of the CeO$_2$ layer during heat-treatment led to the formation of fine CeO$_2$ NCs. The formation of such fine clusters and the CeO$_2$-TiO$_2$ interface seems to stabilize electron-capturing oxygen-vacancy-related centers. Therefore, the prepared surfaces exhibit an extreme photocatalytic performance. Besides the high photocatalytic performance in an aqueous test medium, we showed that the same CeO$_2$-TiO$_2$ hybrid structures are able to effectively decompose non-aqueous organic contaminants (MB and oleic acid) within a few minutes. CeO$_2$-TiO$_2$ hybrid structures are
promising for photocatalytic and self-cleaning outdoor and indoor applications.

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