Nanoceria as acid-base catalyst for hydrolysis of sulfonamides, sulfonylureas and other emerging pollutants

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Significance and Relevance
Nanoceria can be used as an efficient acid-base heterogeneous catalyst for the hydrolytic decomposition of various ester compounds including emerging water pollutants such as organophosphate pesticides. In recent works, we have shown that many other environmentally relevant compounds such as sulfonamide antibiotics or bisphenol-S can also be spontaneously decomposed at ambient conditions using nanoceria. We propose that the cleavage of other important bonds in biologically and environmentally important organic molecules can be achieved using a carefully designed and prepared ceria catalyst.

Preferred and 2nd choice for the topic: Water treatment, photocatalysis
Preferred presentation: (Oral preferred or Short Oral)

Introduction and Motivations

Degradation of various environmental pollutants in water and air using nanomaterials is an attractive way to remove many micropollutants and contaminants of emerging concern (CEC) including pesticides, industrial chemicals or antibiotics. Several transition metal oxides (TMO) show extraordinary surface reactivity, catalytic, photocatalytic and electrocatalytic activities that can be used in various water and air treating systems.

Nanoceria is a promising reducible metal oxide with exceptional redox and acid/base properties, with many industrial and emerging applications including VOC oxidation in three-way catalyst, fuel cells, or water-gas shift reaction.[1] In addition, it can also spontaneously degrade phosphate (and other) esters,[2] enabling the decontamination of organophosphate pesticides or nerve agents.[3] However, its hydrolytic activity can extend far beyond dephosphorylation reactions and can be useful for many other environmentally and biologically relevant catalytic reactions.[4]

Materials and Methods

Various nanoceria samples with the different structural and surface chemical properties were prepared by several water-based precipitation methods using cerium nitrate hexahydrate as starting compound. The synthesis details are available elsewhere.[5] One of the precipitation methods was also used to prepare ceria/graphene oxide composites.[6] The kinetics and mechanism of hydrolytic and photocatalytic degradation of several environmental pollutants (sulfonamide antibiotics, bisphenols) on the ceria surfaces were studied by HPLC/DAD, LC/MS-MS and NMR spectroscopy.

Results and Discussion

In our recent study[5], it was experimentally demonstrated for the first time that CeO_2 nanostructures show extraordinary reactivity toward sulfonamide drugs (sulfadimethoxine, sulfamerazine, and sulfapyridine) in aqueous solution without any illumination, activation, or pH adjustment. Hydrolytic cleavage of various bonds, including S–N, C–N, and C–S, was proposed as the main reaction mechanism and was indicated by the formation of various reaction products, namely, sulfanilic acid, sulfanilamide, and aniline, which were identified by HPLC-DAD, LC-MS/MS, and NMR spectroscopy (Figure 1). The degradation efficiency was strongly dependent on the structure of the sulfonamide molecule and physicochemical properties of nanoceria. However, not all tested sulfonamide drugs were spontaneously decomposed (e.g., sulfomethoxazole), indicating an urgent need for further elucidation of the reactivity of cerium along with identification of active sites and other key parameters that control the decomposition reactions on the ceria surfaces.

Furthermore, the composites based on CeO_2 nanoparticles grown in situ on graphene oxide (GO) sheets were prepared by a low-temperature water-based method and used for the removal of bisphenols from water.[6] It has been demonstrated that ceria-based nanomaterials can also spontaneously decompose bisphenol-S (BPS) containing a sulfonyl functional group by hydrolytic cleavage upon its adsorption, while bisphenol-A (BPA) and F (BPF) can be efficiently decomposed by simulated solar light using CeO_2/GO composites as photocatalysts.

Based on these results, further tests are underway with other pollutants (e.g., sulfonylurea herbicides) and molecules with ester (or other) bonds that can undergo hydrolysis on the surface of nanoceria. It can be assumed that these reactions can find application in heterogeneous catalysis and environmentally significant degradation reactions and may be relevant for other nanocrystalline transition metal oxides.

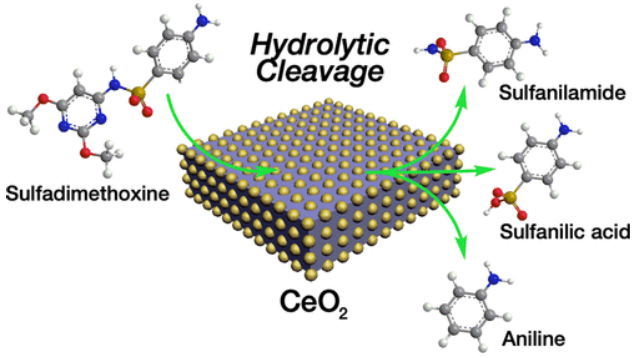

Figure 1 Nanoceria can decompose various sulfonamide antibiotics (e.g., sulfadimethoxine) on their surface by hydrolytic cleavage under ambient conditions to form various degradation products such as sulfanilamide, sulfanilic acid, or aniline.

References

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