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Morphology modulated photocatalytic activity of CeO2 nanostructures for selective oxidation of biobased alphaPinene to oxygenates

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Abstract

The effective Ce3+/Ce4+ redox and oxygen mobility of CeO2 induced by tunable nanostructure morphology has attracted a great interest in photocatalytic organic synthesis. Herein, we report on the microwave-assisted synthesis of CeO2 with nanoparticles (NPs), nanorods (NRs) and nanocubes (NCs) morphologies. The optical-electronic properties of the nanostructure CeO2 catalysts varied relatively with the respective morphologies. Ce-NPs catalyst showed a significant blue shift while a red shift was observed for Ce-NCs and a slight blue shift for Ce-NRs. The Ce-NRs and Ce-NPs showed high charge recombination suppression, which was due to the formation of surface defects associated with dislocations, steps and oxygen vacancies (Vo) as elucidated from the photolumiscence, X-ray photoelectron spectroscopy and electron paramagnetic resonance results. The surface oxygen defects populated with reactive superoxide oxygens of Ce-NRs and its high surface showed better photocatalytic activity for oxidation of alpha-pinene to pinene oxide, verbenol and verbenone as major products. A pinene conversion of 33.6 % to pinene oxide with the selectivity of 54.3 % was achieved with Ce-NRs. The effective photocatalytic activity of the Ce-NRs was attributed to its enhanced efficient charge recombination suppression and oxygen vacancies. Ce-NRs catalyst was recyclable without any significant loss of its initial photoactivity.