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Fabrication of homogeneously Cu^{2+}/La^{3+}-doped CeO_2 nanosheets and their application in CO oxidation

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Abstract

Nanosheets of coordination polymers (CPs) were synthesized via a facile and one-step complexing-coprecipitation (CC) method. Upon calcination, pure CeO_2 and homogeneously La^{3+}- or Cu^{2+}-doped CeO_2 products were fabricated by taking CPs as precursors. The final products not only retained stable nano-scaled sheet-shaped morphology of their CP precursors, but also possessed high catalytic activity towards CO oxidation. Superior to commercial ceria with negligible catalytic activity, the synthesized CeO_2 nanosheets exhibit high activity achieving CO conversion of 60% at the temperature of 360 °C. When doped with Cu^{2+}, remarkable improvement of catalysis is observed owing to the homogeneous incorporation of Cu^{2+} into CeO_2 lattice.

Introduction

Nano-scaled coordination polymers (nano-CPs) are an important class of materials created from various organic bridging ligands and inorganic metal ions or metal clusters. The advantages of highly tailored size, shape, structure and composition make nano-CPs excellent precursors towards nano-scaled metal oxides by high temperature annealing. Herein, we employ CPs as precursors to fabricate homogeneously La^{3+}- or Cu^{2+}-doped CeO_2 nanosheets. BTA not only controls the morphologies of oxides but also makes the doping metals homogeneously disperse in CeO_2 lattice, which significantly improves catalytic activity. Taking CO as model reaction, we carry out a systematic investigation to demonstrate the catalytic properties of final products.

Results and Discussion

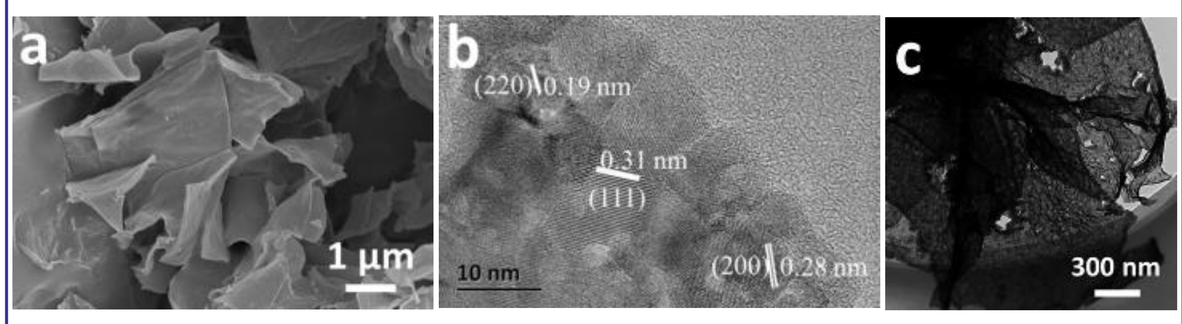


Figure 1. SEM (a), HRTEM (b) and TEM (c) images of $Cu_{0.1}Ce_{0.9}O_{2-\delta}$.

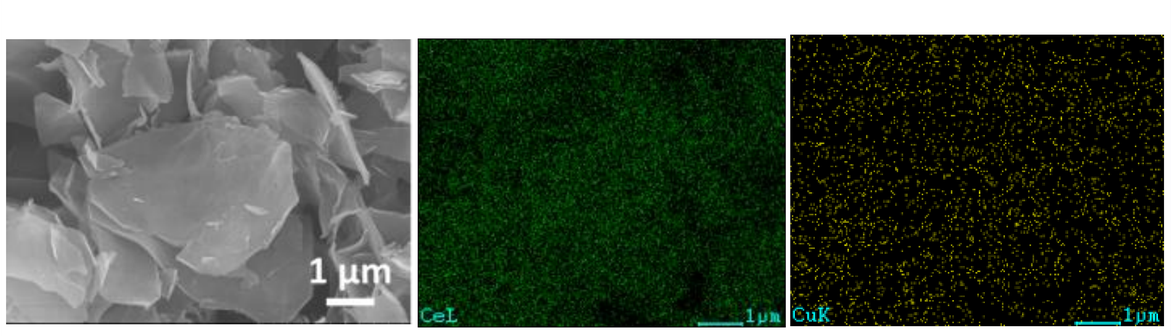


Figure 2. SEM image and the corresponding mapping patterns of $Cu_{0.1}Ce_{0.9}O_{2-\delta}$.

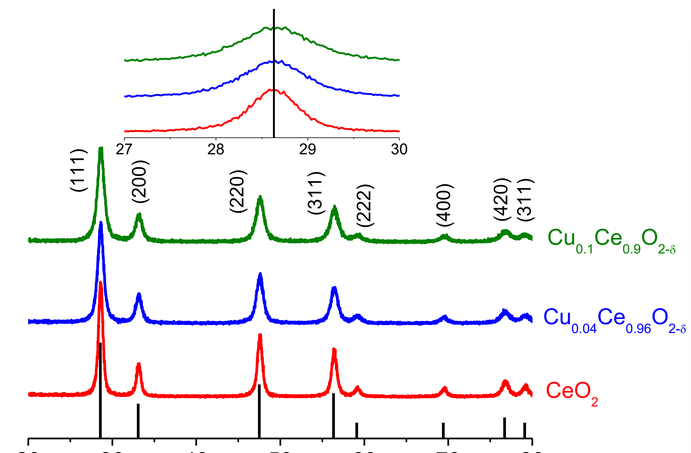


Figure 3. XRD patterns of Cu^{2+}-doped ceria.

With the increasing content of Cu^{2+}, the (111) reflection of samples slightly shifts to higher angles than that of pure CeO_2, suggesting the successful incorporation of the metal into the ceria lattice. The shift towards high angels, *i.e.* the shrinkage of ceria lattice, is ascribed to the substitution of larger Ce^{4+} (0.97 Å) with smaller Cu^{2+} cations (0.72 Å).

A broad band at ~570 cm^{-1} (α zone) of doped CeO_2 is accredited to the extrinsic oxygen vacancies after the substitution of Ce^{4+} with Cu^{2+}. Another new peak ~608 cm^{-1} (β zone) relates to intrinsic oxygen vacancies caused by the existence of Ce^{3+}.

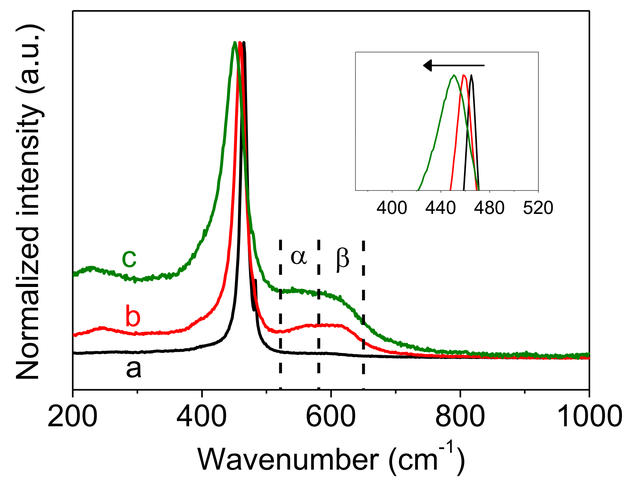


Figure 4. Raman spectra of CeO_2 (a), $Cu_{0.04}Ce_{0.96}O_{2-\delta}$ (b) and $Cu_{0.1}Ce_{0.9}O_{2-\delta}$ (c).

XPS spectra of Ce 3d can be deconvoluted into two series of peaks (u and v) corresponding to spin-orbital doublet peaks of $3d_{3/2}$ and $3d_{5/2}$. Two peaks labeled as v' (885 eV) and u' (902 eV) are related to $3d^{10}4f^1$ electronic state of Ce^{3+} ions, and the other six peaks marked as v (883 eV), v'' (889 eV), v''' (898 eV), u (901 eV), u'' (908 eV) and u''' (917 eV) are ascribed to $3d^{10}4f^0$ electronic state of Ce^{4+} ions.

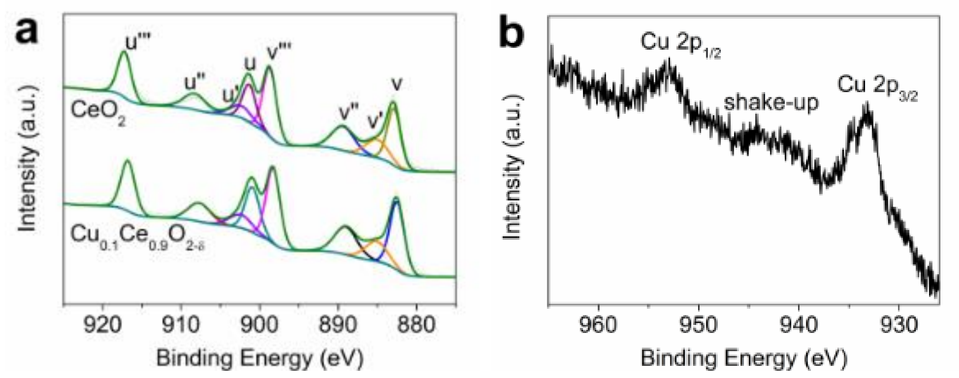
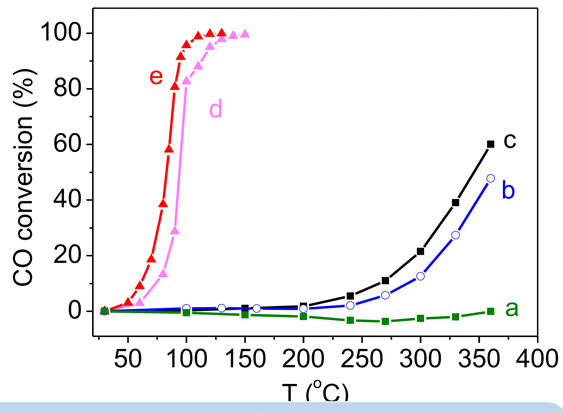


Figure 5. XPS spectra of Ce 3d (a) and Cu 2p (b) in $Cu_{0.1}Ce_{0.9}O_{2-\delta}$.

Figure 6. Profiles of CO conversion as a function of reaction temperature over commercially available CeO_2 powder (a), $La_{0.1}Ce_{0.9}O_{2-\delta}$(b), nano-sheet CeO_2 (c), $Cu_{0.04}Ce_{0.96}O_{2-\delta}$ (d) and $Cu_{0.1}Ce_{0.9}O_{2-\delta}$ (e).



Cu^{2+}-doped CeO_2 samples exhibit remarkable improvement of CO catalytic activity. The temperature with 50% CO conversion (T_{50}) are 83 and 95 °C for $Cu_{0.1}Ce_{0.9}O_{2-\delta}$ and $Cu_{0.04}Ce_{0.96}O_{2-\delta}$, respectively,

Conclusions

We demonstrate a facile and efficient strategy to fabricate pure ceria and cation-doped ceria nanosheets. After the preparation of BTA-Ce/cation precursors with nano-scaled sheet-shape, morphology-preserved CeO_2 and cation-doped CeO_2 are received by calcination at 650 °C. As BTA has high complexing capacities with metal ions, homogeneously La^{3+} and Cu^{2+}-doped ceria nanosheets are successfully prepared. The synthesized Cu^{2+}-doped CeO_2 ($Cu_{0.1}Ce_{0.9}O_{2-\delta}$) exhibits high catalytic activity in catalyzing CO oxidation, attributed to the uniform distribution of Cu^{2+} and enhanced interfacial interaction of Ce-O-Cu.

Acknowledgement

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References

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