Template-free fabrication of fractal porous Y₂O₃ monolithic foam and its functional modification by Ni-doping

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Hierarchically porous materials have attracted growing interest due to their great potential in catalysis, separation, and biomedical systems [1–6]. Tremendous efforts have been devoted to the rational design and synthesis of advanced porous materials with fascinating synergetic properties or multifunctions originating from their special porous structures [7–13]. Generally, hierarchical porous structures can be created through hard or soft templates, or combination of soft and hard templates [14,15]. However, disadvantages related to high cost or tedious synthetic steps have been impeding the scale-up of these synthesis routes for practical applications. A template-free coordination polymer precursor method was reported to fabricate lanthanide oxide monolith with hierarchical or aligned meso-macropores, and the following process was driven by Oswald Ripening, and this pore formation mechanism offered a facile route toward the hierarchical porous materials. [16]

Fractals, as described by Mandelbrot [17], were “exactly the same at every scale or nearly the same at different scales”. Fractals are ubiquitous and exist extensively in nature, such as human lungs and the surface of human brains, clouds and snowflakes, coastlines and leaves. Complicated and fascinating fractal patterns are very important in science, engineering, mathematics and aesthetics, and scientists have been struggling to understand, explore and build fractal structures. Fractal structures such as macromolecular or supramolecular dendrimers built by divergent or convergent approach have been reported [18,19]. Recently, Shang *et al.* [20,21] succeeded in fabrication of Sierpiński triangles by the spontaneous

self-assembly of small building blocks at cryogenic temperatures. In materials science, although some fractal-related studies have been reported, most of them are focused on developing hierarchical branched architectures, such as silica aerogels [22], leaf-like metals [23, 24], graphene [25], silica [26] and titanium dioxide [27]. To the best of our knowledge, there is hardly any report on the synthesis of hierarchical metal oxide with fractal porous structure through a template free method. Furthermore, because the general methods are hardly applicable to create fractal porous structures, fabrication of multi-scaled and self-similar fractal porous metal oxide has not been discussed and remains a challenge. Herein, we report the template-free fabrication of fractal porous Y₂O₃ monolithic foam and its functional modification by Ni-doping.

In the first step of synthesis, an asparagine yttrium coordination polymer (denoted as AYCP) was synthesized through a hydrothermal process (details see Supplementary information). Typically, yttrium nitrate (Y(NO₃)₃·6H₂O) was added into an asparagine solution under stirring to obtain a transparent solution. After the transparent solution was hydrothermally treated at 200°C for 24 h, the obtained AYCP was a brown monolith (Fig. 1a) with an amorphous structure (Fig. S1). The AYCP exhibited an interesting porous structure (Fig. S2) which was inherited in the oxide obtained after calcination. Based on the thermogravimetry and differential thermal analysis (TG-DTA) results of AYCP (shown in Fig. S3), the AYCP precursor monolith was calcined in air at 750°C for 3 h to obtain Y₂O₃ (denoted as FP-Y₂O₃). As

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Figure 1 Photographs of YACP (a) and its corresponding oxide FP- Y_2O_3 (b). (c, d) SEM observation of the first and secondary pores shown in FP- Y_2O_3 oxide. (e, f) TEM images of tertiary and quaternary pores shown in FP- Y_2O_3 oxide. The inset in (d) is an image of simulated fractal structure.

shown in Fig. 1b, an obvious shrinkage occurred, which was due to the mass loss of organic species during the calcination.

As shown in Fig. 1c, Y_2O_3 displays a multi-cellular foam-like morphology with a cellular size about 10–50 μm . At a higher magnification (shown in Fig. 1d), it can be clearly seen that the wall of the cell is composed of secondary macropores with a pore diameter around 1 μm . Interestingly, the pore-wall of this secondary pore is also composed of a sub-level self-similar nanoscale porous structure. A detailed porous structure of this interconnected porous wall was further examined by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Fig. 1e presents a representative TEM image of the nanoscale pore-wall with a fractal feature; this image confirms that the secondary pore-wall consists of tertiary nanopores, with a pore diameter ranging from 30 to 100 nm. The HRTEM image (Fig. 1f) shows that the wall of the tertiary nanopores is composed of interconnected nanoparticles, with mesopores (2–10 nm) between these nanoparticles. The observed fringe spacing in the HRTEM image shown in Fig. 1f further indicates the well crystallized structure of Y_2O_3 . In

the N_2 adsorption-desorption isotherm of the fractal porous Y_2O_3 (Fig. S4), the H2 hysteresis loop indicated the ink-bottle type of pores, corresponding to the nanopores shown in Fig. 1e. The Brunauer-Emmett-Teller (BET) surface area of the Y_2O_3 was $38 \text{ m}^2 \text{ g}^{-1}$.

A schematic diagram showing the consecutive steps for the formation of fractal porous structure starting from amino acid and metal ions, is illustrated in Scheme 1. In the initial stage of the synthesis, *L*-asparagine in the solution as a chelating agent was employed to coordinate with Y^{3+} , and during the following hydrothermal treatment, asparagine- Y coordination spheres with different sizes were formed, as shown in scanning electron microscopy (SEM) observation (Fig. S5a). With the extension of hydrothermal reaction, the coordination polymer spheres gradually aggregate and merge together (Fig. S5b). During the merging process, the small spheres would preferably accumulate in the space between large coordination spheres. Meanwhile, the space between small spheres would be filled by even smaller spheres. In this way, during the hydrothermal reaction, a coordination polymer monolith was constructed, which consists of merged spheres whose sizes are in different levels of hierarchy. On the basis of our previous work, it is proposed that for the lanthanide-organic coordination polymer spheres, an Ostwald ripening process took place during the hydrothermal treatment and gave rise to the hollow interiors of the coordination polymer spheres by an inner-dissolving and outer-growth process [13]. Accordingly, here the accumulated coordination spheres would undergo Ostwald ripening during further hydrothermal reaction, and as a result the accumulated asparagine- Y coordination polymer spheres with different sizes would become hollow (Fig. S5c, d). After the hollowing process, a fractal porous structured coordination polymer monolith is formed (Fig. S5e, f). After calcination, the FP-

Scheme 1 Schematic synthesis of Y_2O_3 fractal porous monolith through a coordination based self-assembly way. HT means hydrothermal treatment. CP means coordination polymer.

Y_2O_3 can be obtained. Though lanthanide oxide foams were reported previously [13], those materials contained only one level of macroporous structure. In contrast, the FP- Y_2O_3 contains multiple levels of fractal porous structures, ranging from micrometer to nanometer.

For the synthesis of a second-metal-doped fractal porous Y_2O_3 , a second metal nitrate can be added together with $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to the Y-asparagine solution before the hydrothermal treatment. All the obtained metal-doped Y_2O_3 exhibited a perfect fractal porous structure, as shown in Figs S6 and S7. For example, for nickel oxide stabilized in FP- Y_2O_3 , both $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to the asparagine solution together, and then the solution was subjected to hydrothermal treatment and calcination. As shown in Fig. 2a, after NiO doping into FP- Y_2O_3 , the color of the oxide monolith changed to dark grey. SEM images shown in Fig. 2b and c demonstrate the well maintenance of the monolith-shape and fractal porous structure of NiO-doped FP- Y_2O_3 . Fig. 2d and e show the TEM and annular dark-field scanning TEM (ADF-STEM) images which display the sub-level pores in the fractal porous FP-Ni@ Y_2O_3 . It can be clearly seen that FP-Ni@ Y_2O_3 retained the three dimensional hierarchical fractal porous structure. Energy dispersive X-ray spectroscopy (EDS)-based elemental mapping associated with ADF-STEM was used as an effective examination approach to characterizing the NiO-doped FP- Y_2O_3 . EDS-mapping shown in Fig. 2f was obtained from the same area in the ADF-STEM image in Fig. 2e, showing an overview of the joint of interconnected wall. Fig. 2f shows an overlay of yttrium (blue), oxygen (red) and nickel (green) elemental distributions extracted from the EDS mapping analysis, which effectively demonstrates that NiO nanoparticles are embedded within the Y_2O_3 matrix, and agglomeration sintering does

Figure 2 Photograph (a), SEM images (b, c), TEM image (d) ADF-STEM image (e) of FP-Ni@ Y_2O_3 . (f) Elemental mapping of FP-Ni@ Y_2O_3 : yttrium (blue), oxygen (red) and nickel (green).

not occur even under high temperature calcination at 750°C.

Hydrogen production from renewable resources has been attracting intense research interest due to its promising potential as a source of clean energy. Because of its high content of hydrogen (13.6 wt%), ethanol is regarded as a good resource for the hydrogen production. Furthermore, CO_2 generated from ethanol-to-hydrogen process can be consumed in biomass growth, and this process could be nearly CO_2 neutral in carbon circulation [28–31]. Among the catalysts reported to be active for ethanol steam reforming (ESR) for hydrogen, Ni-based catalysts have been considered as promising candidates because of their low costs and high selectivities compared with the catalysts based on precious metals. One issue in Ni-based catalysts is that isolated nickel oxide in the catalysts tends to induce carbon deposition, which can further deactivate the catalysts [32,33].

Here the FP-Ni@ Y_2O_3 was preliminarily tested as a catalyst in the ESR reaction. *In-situ* H_2 -temperature program reduction (TPR) XRD patterns of FP-Ni@ Y_2O_3 are shown in Fig. 3. Before reduction, the XRD pattern of FP-Ni@ Y_2O_3 exhibited cubic phase Y_2O_3 combined with cubic phase NiO. The NiO diffraction peaks at 7.6° and 12.5° remained unchanged till 265°C, and then after the embedded NiO started to be reduced, diffraction peaks of metallic Ni appeared at 9.0° and 10.3°. It should be noted that the reduction temperature of 265°C for the embedded NiO in FP-Ni@ Y_2O_3 is much lower than the re-

Figure 3 *In-situ* XRD patterns of FP-Ni@ Y_2O_3 being reduced in H_2 , indicating phase evolution of NiO to metallic Ni during the TPR. All other diffraction peaks correspond to Y_2O_3 .

ported value of pure NiO (about 360°C) in Ref. [34].

For comparison, a conventional supported NiO/Y₂O₃ catalyst was also prepared by the deposition-precipitation method (described in Supplementary information). The commercial Y₂O₃ nanoparticles were used as a carrier to support the precipitated NiO nanoparticles, named as Ni/CYO. TEM and STEM images (Fig. S8) show that in Ni/CYO, NiO nanoparticles are not well dispersed. *In situ* H₂-TPR XRD patterns indicated that the onset reduction temperature for NiO in Ni/CYO was 350°C (Fig. S9), confirming that the confinement effect in fractal porous Y₂O₃ can lower the reduction temperature of the NiO nanoparticles.

Before reaction, the catalyst was firstly pre-reduced by H₂, and the ESR activity was evaluated in the temperature range from 250 to 450°C over Ni/CYO and FP-Ni@Y₂O₃, respectively (Fig. 4). The temperature program consisted of 5 min ramps and 60 min plateaus for steady-state measurements at each temperature. During the ESR on FP-Ni@Y₂O₃, substantial conversion of ethanol was observed at 250°C, and a complete conversion was achieved at 350°C. For comparison, the Ni/CYO catalyst was not active for ESR at low temperature and converted a negligible amount of ethanol at 300°C. A small amount of ethanol was consumed as the temperature was raised to 350°C and a complete conversion of ethanol could only be achieved at about 450°C. By *in-situ* XRD measurements performed during the ESR reaction, the state of Ni species in the catalyst can be monitored. As shown in Fig. S10, the pre-reduced metallic Ni was gradually re-oxidized by the flow of ethanol/H₂O at elevated temperature for both FP-Ni@Y₂O₃ and Ni/CYO. It is obvious that the metallic Ni in FP-Ni@Y₂O₃ is much more stable than that in Ni/CYO, and the residual stable metallic Ni

would be responsible for the better activity of FP-Ni@Y₂O₃ at relatively low temperature (Fig. 4).

After the ESR reaction, both Ni/CYO and FP-Ni@Y₂O₃ catalysts were characterized by TEM. As shown in Fig. S11, after the reaction in ethanol steam, there was no carbon deposited on FP-Ni@Y₂O₃, which retained the fractal porous structure. While for Ni/CYO after steam reforming, carbon nanotubes were found (Fig. S11b). As shown in a higher magnification image of a selected particle in Ni/CYO (Fig. S11c, d), carbon deposition occurred on a NiO particle. The hierarchically fractal porous feature of FP-Ni@Y₂O₃ is beneficial to the diffusion of reactants and products, and thus may be helpful to prevent the carbon deposition process.

In summary, Y₂O₃ monolith with unique hierarchically fractal porous structure was fabricated from the precursor of coordination polymer. The hierarchical accumulation and merging of coordination spheres with different sizes, and further hollowing effect by Ostwald ripening give rise to a fractal porous feature. By Ni-doping, fractal porous NiO/Y₂O₃ was prepared, which exhibited enhanced activity in ESR compared with a common supported NiO catalyst. More exploration of other functional fractal porous oxides and their applications are expected.

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Figure 4 Ethanol conversions over FP-Ni@Y₂O₃ (red line) and Ni/CYO (black line) as the temperature and time evolution for ESR.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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无模板法合成分形孔结构 Y_2O_3 泡沫单块及其镍掺杂功能化

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摘要 自相似的分形结构如云、树、雪花、闪电、人类循环系统等广泛存在于自然界中, 然而自然界中自发形成的分形结构很难用常规的实验室合成方法得到. 本文利用一种无模板的、基于金属-小分子配位聚合作用的自组装方法, 制备了具有分形孔结构的整体钇-氨基酸配合物材料, 并通过焙烧得到分形孔结构 Y_2O_3 . 材料的孔尺度分布范围从微米到纳米尺度, 最为有趣的是, 这种孔结构表现出自相似特征的结构, 即任意一级的大孔的孔壁都是由次级尺度范围的二级小孔孔结构组成. 整体配合物由几十微米的微米孔构筑而成, 微米孔的孔壁由尺度更小的次级微米孔组成, 次级微米孔的孔壁继续由100 nm左右的纳米孔组成. 继续放大后可以看到纳米孔的孔壁包含由纳米晶粒堆积而成的更小的介孔(2–10 nm). 通过在合成中引入其他金属阳离子(Ni^{2+} , Bi^{3+} , Ce^{3+} , Eu^{3+}), 可以得到分形孔包裹镶嵌的掺杂型分形孔混合氧化物. 以 Ni^{2+} 为例, 分散的NiO纳米颗粒嵌入 Y_2O_3 泡沫分形孔结构中. 在乙醇水蒸气重整制氢反应中, 与常规的负载型Ni催化剂相比, 被分形孔 Y_2O_3 封装的Ni催化剂表现出更优的低温催化活性.