



Communication

An unexpected generation of magnetically separable Se/Fe₃O₄ for catalytic degradation of polyene contaminants with molecular oxygen



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ABSTRACT

Selenization of Fe₂O₃ with NaHSe led to Se/Fe₃O₄. The unexpected generation of Fe₃O₄ attributed to the reduction conditions of the reaction, and the resulted magnetic features of the material facilitated its separation in practical applications. Owing to the synergistic effect of Se with Fe, the material was especially active to catalyze the oxidative C=C scission using O₂ as mild oxidant. The technique has been successfully applied in polyene degradation project, which is of profound practical values for the treatment of the polyene pigment pollution and may be applied in the food and pharmaceutical industry.

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Chalcogen-containing materials are comprehensively used owing to their unique chemical- and bio-activities [1–11]. In the field, Se-containing catalytic materials [12–16] began to draw attention with the rise of Se catalysis [17–21], which, as a distinctive catalytic technique, was in line with the developing trend of transition metal-free catalysis unfolding in the new centenary [22–31]. Investigations on Se catalysis are in rapid progress. However, the magnetically separable Se catalyst, which is easily recoverable, has never been invented yet. Although there has been a variety of reported references on magnetic materials, the tedious fabrication procedures enhance their costs for large scale applications [32,33]. Thus, developing concise method to prepare magnetically separable Se catalyst is of good practical meanings.

On the other hand, polyenes are widely contained in natural products and are also applied as the pigments in food and pharmaceutical industry [34–36]. They are usually in bright colors for the conjugated C=C systems and the pollutions of these molecules are of potential risks for animals and human beings for their bioactivities [37]. Polyene degradation is a promising subject with application significances. Recent progresses in Se catalysis

have successfully achieved the oxidative C=C scission by using homogeneous or heterogeneous Se catalysts [12,38,39]. It was also reported that the relay catalysis of Se with ion salt could utilize molecular oxygen (O₂) as the mild oxidant instead of the conventionally employed H₂O₂ [40]. Inspired by these findings, we recently tried to achieve the polyene degradation with O₂ by using selenized Fe₂O₃ catalyst. Surprisingly, the starting Fe₂O₃ was found to be converted into Fe₃O₄ in the material after selenization with NaHSe, leading to a facile access to the magnetically separable Se/Fe₃O₄ catalyst. Herein, we wish to report our findings.

Se was introduced into the starting Fe₂O₃ via the selenization reaction with the selenization reagent of NaHSe [41], which was generated through the reduction of Se powder by NaBH₄ (Eq. 1). The experimental details were given in supplementary material for reference.



The as-prepared material was in black color (Fig. 1a). Interestingly, although the Fourier transform infrared (IR) spectra (Fig. 1b) of the selenized and unselenized materials were similar, they possessed quite different appearances (Figs. 1a and c). Moreover, the selenized Fe₂O₃ could be picked up by magnet, and its saturation magnetization, residual magnetic field strength and coercive force were 74.8 emu/g, 10.2 emu/g and 127.1 Oe respectively (Fig. 1d). The powder X-ray diffraction (XRD) spectrum demonstrated that partial of the starting Fe₂O₃ was converted into

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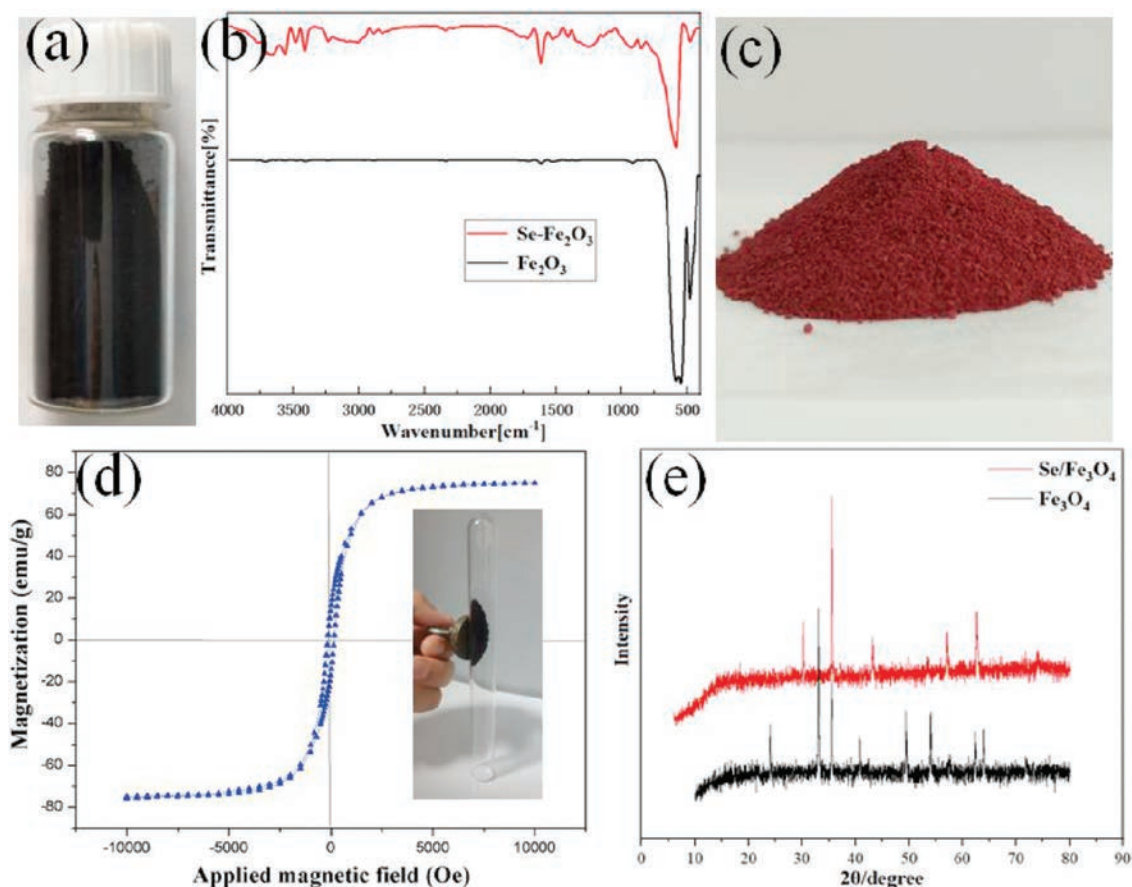


Fig. 1. Photographs and characterizations of the materials: (a) Photograph of the selenized Fe_2O_3 ; (b) IR spectra of the selenized and unselenized Fe_2O_3 ; (c) Photograph of the starting Fe_2O_3 ; (d) Magnetometer hysteresis loops of the selenized Fe_2O_3 ; (e) XRD patterns of the selenized material ($\text{Se}/\text{Fe}_3\text{O}_4$) and Fe_3O_4 .

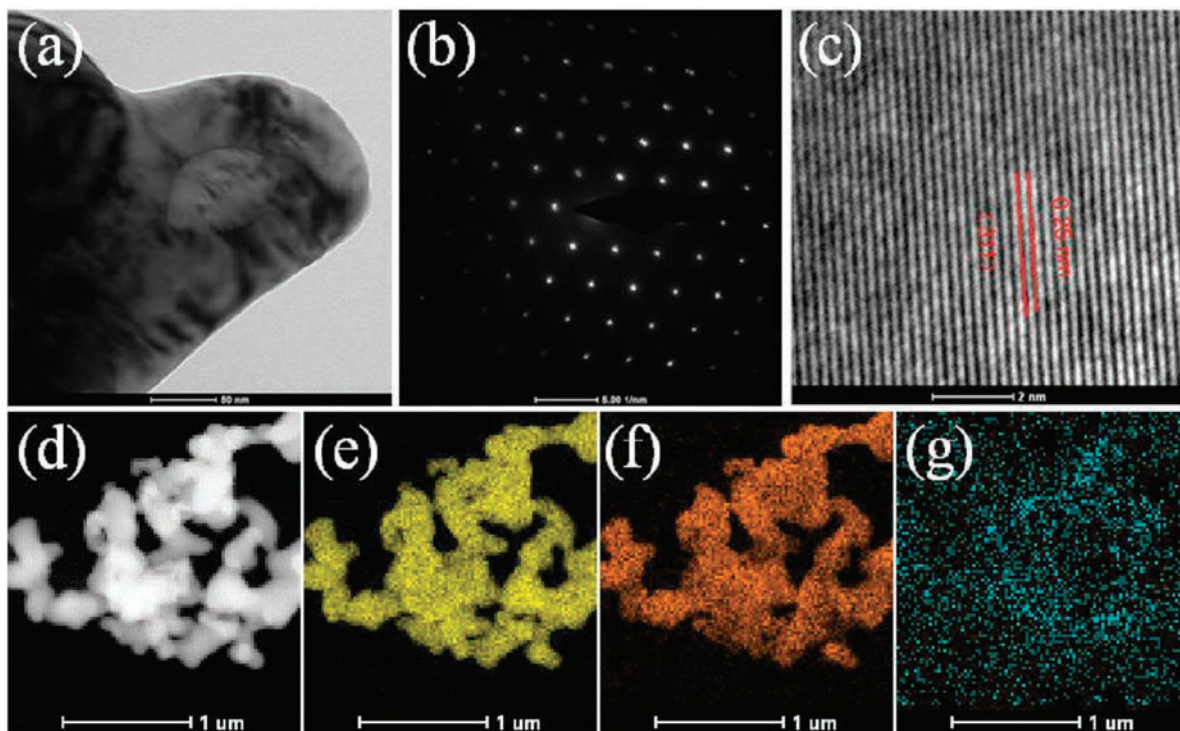


Fig. 2. Composition analysis of $\text{Se}/\text{Fe}_3\text{O}_4$: (a) TEM image; (b) Electron diffraction pattern; (c) HR-TEM image; (d) HAADF-STEM image, (e-g) elemental mapping images of (e) Fe, (f) O and (g) Se.

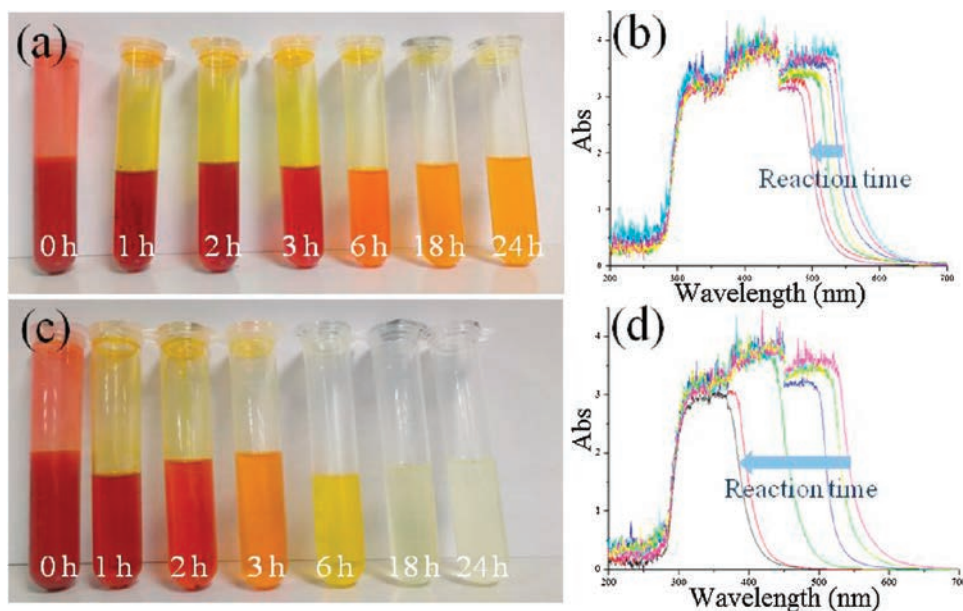


Fig. 3. (a) Photographs and (b) UV-vis spectra of β -carotene degradation reactions with Fe_3O_4 . (c) Photographs and (d) UV-vis spectra of $\text{Se}/\text{Fe}_3\text{O}_4$.

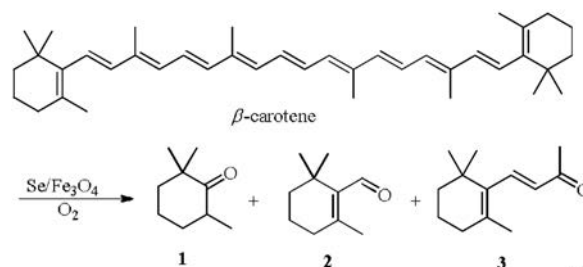
Fe_3O_4 , as the characterization peaks agreed well with the standard Fe_3O_4 (cubic phase) XRD pattern (Fig. 1e, JCPDS No. 89-0688) [42]. The phenomenon was probably caused by the reduction conditions of the selenization reaction, in which the selenization agent NaHSe and the excess NaBH_4 were strong reductants and might reduced partial Fe^{3+} to generate the stable Fe_3O_4 species after calcination. The hypothesis was further confirmed by the X-ray photoelectron spectroscopy (XPS) analysis, which showed that Se existed as the low-valent Se^0 and Se^{2-} species, while Fe was formed by Fe^{2+} (64.7%) and Fe^{3+} (35.3%) (Figs. S1 and S2 in Supporting information). Se^{2-} might exist in iron salt form (FeSe), while Se^0 diffused in the material. Strong reducibility of the selenization step led to much higher Fe^{2+} ratio of the material (64.7%) than normal Fe_3O_4 (33.33%). The selenized material was marked as $\text{Se}/\text{Fe}_3\text{O}_4$ in the following discussions.

Transmission electron microscope (TEM) image showed that the material did not contain hollow structures (Fig. 2a), while its electron diffraction pattern illustrated the existing of crystallines (Fig. 2b). High-resolution transmission electron microscope (HR-TEM) image of the material reflected the primary $\{311\}$ facet exposure of Fe_3O_4 and the $d_{(311)}$ spacing was *ca.* 0.25 nm (Fig. 2c) [43]. Inductively coupled plasma mass spectrometry (ICP-MS) analysis indicated that the weight content of Se in the material was very low (*ca.* 0.17%). Elemental mapping analysis was performed to confirm the constituent of the material and the results were illustrated in Figs. 2d–g. First, high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image as Z-contrast image is highly sensitive to variations in the atomic number of atoms in the sample, and the Z contrast intensity is proportional to the square of the atomic number [44]. Therefore, the bright area may attribute to the heavy elements in the HAADF-STEM image of $\text{Se}/\text{Fe}_3\text{O}_4$ (Fig. 2d). Elemental mapping images shows that the material is majorly constituted by Fe and O (Fig. 2e and f), while the dispersion of Se on the Fe–O frameworks is in consistent with the bright area of the HAADF-STEM image (Figs. 2g and d). The Se element was also detected to be dispersed out of the major Fe–O frameworks for the existing of a few fragments in the materials (Fig. 2g).

The material was then used as catalyst for polyene contaminants degradation and β -carotene was chosen as the model sample for its bright color easy to judge. In a blank reaction using

simple Fe_3O_4 as catalyst, the sample did not fade after blowing O_2 for 24 h (Fig. 3a), and the blue-shift in UV-vis spectra was weak (Fig. 3b). In contrast, using $\text{Se}/\text{Fe}_3\text{O}_4$ as catalyst, the sample faded within 18 h (Fig. 3c), and an obvious blue-shift were observed in UV-vis spectra, reflecting the destruction of C=C conjugation system (Fig. 3d). The catalytic activity of $\text{Se}/\text{Fe}_3\text{O}_4$ attributed to the synergistic effect of Se with Fe [40], and the Fe_3O_4 catalyst prepared by reducing Fe_2O_3 with NaBH_4 or selenium powder showed poor catalytic activity in β -carotene degradation.

Moreover, the gas chromatography-mass spectrometry (GC-MS) analysis demonstrated that in the oxidation reaction catalyzed by $\text{Se}/\text{Fe}_3\text{O}_4$, β -carotene decomposed into a variety of fragments, such as the 2,2,6-trimethylcyclohexan-1-one (**1**), 2,6,6-trimethylcyclohex-1-ene-1-carbaldehyde (**2**), (*E*)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-one (**3**), etc. (Scheme 1, for detailed mass spectra of the products, please see the Supporting information). Compound **3** was the major product of the reaction and it could be isolated in 62% yield. β -carotene was observed in the GC-MS spectra, showing that the chemical was completely converted. These results attested that the fade of β -carotene was caused by the complete C–C scission leading to small molecules other than the epoxidation or dihydrogelation reactions, which might also destroy the conjugation system of color rendering [38]. The strong catalytic activity of $\text{Se}/\text{Fe}_3\text{O}_4$ leading to the oxidative C–C scission might attribute to the synergistic effect of Se with Fe, which has been reported by our group previously [40]. As a magnetical material, $\text{Se}/\text{Fe}_3\text{O}_4$ was easily recovered and could be reused for at least five times in β -carotene degradation.



Scheme 1. Detecting the β -carotene degradation products by GC-MS.

In conclusion, Se/Fe₃O₄ was unexpectedly generated during the selenization process of Fe₂O₃. Conversion of Fe₂O₃ to Fe₃O₄ attributed to the strong reduction conditions of the reaction. In the reaction, Se acted as the oxygen carrier catalyst [45], while synergistic effect of Se with Fe endowed the material strong catalytic activity for oxidation reactions to degrade the polyenes. As a magnetical separable material, Se/Fe₃O₄ is easily recyclable and may serve as an efficient catalyst for industrial application as well as the environment protection. Investigations of the novel Se-containing materials and their applications are still ongoing in our laboratory [46,47].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2020.07.031>.

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