Hierarchical Fe$_2$O$_3$ @mesoporous silica for catalytic activity enhancement to Fenton-like reaction

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Abstract: The hierarchical Fe$_2$O$_3$ was coated by mesoporous silica to form Fe$_2$O$_3$@mesoporous silica composite with core/shell structure through a simple solution-based method with the assistance of Fe$_2$O$_3$ precursor. When used as catalyst for Fenton-like reaction to the degradation of Methylene Blue, the Fe$_2$O$_3$@mesoporous silica composite was much more active than the bare flowerlike Fe$_2$O$_3$, which suggest that the catalytic activity of the flowerlike Fe$_2$O$_3$ to Fenton-like reaction was dramatically enhanced by the mesoporous silica coating.

Keywords: mesoporous silica, Fenton-like reaction, hierarchical Fe$_2$O$_3$.

1. Introduction (11-point boldface)

Fenton reaction based on the generation of hydroxyl radicals from the decomposition of hydrogen peroxide in the presence of ferrous ions at acidic condition is one of the most cost-effective methodologies to treat waste water. Heterogeneous catalysts for Fenton-like reaction is attracting more and more research attention due to the advantage of allowing easier separation from the effluent and reuse without activity loss. Iron-based materials are promising catalysts for practical application as they are low cost and storable. However, the heterogeneous Fenton-like activities of these catalysts were relatively low in normal reaction conditions without any external energy input such as light irradiation. Therefore, to design and develop heterogeneous catalysts with high activity and high durability is most important for Fenton-like reaction. Hierarchical structured Fe$_2$O$_3$ is promising catalyst for Fenton-like reaction as their nano-sized building blocks could provide large specific surface area, more catalytically active sites and facile mass transportation pathways while their micro-metered entire size was favourable for the catalyst recovery. However, the application of hierarchical structured Fe$_2$O$_3$ in Fenton-like reaction was rarely reported. In this report, a flowerlike Fe$_2$O$_3$ with hierarchical structure was prepared through a simple hydrothermal method. Then the flowerlike Fe$_2$O$_3$ was coated by mesoporous silica to form Fe$_2$O$_3$@mesoporous silica (Fe$_2$O$_3$@meso-SiO$_2$) composite with core/shell structure. The flowerlike Fe$_2$O$_3$ and the Fe$_2$O$_3$@meso-SiO$_2$ composite was both used as catalyst for Fenton-like reaction to the degradation of MB.

2. Experimental (or Theoretical)

Fe$_2$O$_3$ precursor (0.2 g) was dispersed in 70 mL mixture solution of H$_2$O and EtOH (4:3, V/V). Then 0.14 g CTAB, 0.56 g NH$_3$·H$_2$O was added to the solution. Finally, 0.2 mL TEOS was added to the solution under stirring and reacted for 6 h. The precipitate was collected by centrifugation and washed with ethanol four times. The solid was calcined in air at 500 °C for 2 h to obtain Fe$_2$O$_3$@meso-SiO$_2$ composite.

3. Results and discussion

The Fe$_2$O$_3$@meso-SiO$_2$ composite has the same XRD pattern as the flowerlike Fe$_2$O$_3$, indicating that the crystal structure of the flowerlike Fe$_2$O$_3$ was not changed after the mesoporous silica coating. After the mesoporous silica coating, the Fe$_2$O$_3$@meso-SiO$_2$ composite has almost the same morphology as the flowerlike Fe$_2$O$_3$ except that the width of the petals of the flower became a litter thicker due to the mesoporous silica coating (Figure 1a). TEM image of the Fe$_2$O$_3$@meso-SiO$_2$ composite further prove that the mesoporous silica coating did not change the morphology of the flowerlike Fe$_2$O$_3$ (Figure 1b). The core/shell structure of the Fe$_2$O$_3$@meso-SiO$_2$ composite was also demonstrated by the TEM image. The dividing line between the Fe$_2$O$_3$ core and the mesoporous silica shell is visible (Figure 1c). Mesoporous silica hollow flowers with replica morphologies were then obtained when the metal oxide cores were
removed (Figure 1d), which suggests that the mesoporous silica coating on the flowerlike Fe$_2$O$_3$ was integrity and fully covered on the surface of crystalline Fe$_2$O$_3$.

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**Figure 1.** SEM (a) and TEM (b) image of flowerlike Fe$_2$O$_3$@meso-SiO$_2$ composite, respectively, (c) is the enlarged TEM image of the selected area of (b) in red circle; (d) is the TEM image of the outer meso-SiO$_2$ coating of the flowerlike Fe$_2$O$_3$@meso-SiO$_2$ composite after the removal of the Fe$_2$O$_3$ core; (e) Fenton-like degradation of MB as a function of time using different catalyst.

Fenton-like reactions were carried out for MB degradation to test the activities of flowerlike Fe$_2$O$_3$ and the flowerlike Fe$_2$O$_3$@meso-SiO$_2$ composites (Figure 1e). The Fe$_2$O$_3$@meso-SiO$_2$ composite showed active and enhanced activity in the Fenton-like reactions than bare Fe$_2$O$_3$ and mesoporous silica. The MB solution was fully decolorized in 120 min by the Fe$_2$O$_3$@meso-SiO$_2$ composite catalyst. The outstanding activity of the catalyst was attributed to the specific hierarchical structure of the flowerlike Fe$_2$O$_3$ core and the mesoporous silica shell of the Fe$_2$O$_3$@meso-SiO$_2$ composite. In the case of flowerlike Fe$_2$O$_3$ the nano-sized building blocks of the flowerlike Fe$_2$O$_3$ provide large surface area for contacting and sufficient active sites for the decomposition of H$_2$O$_2$ to produce ·OH radicals in Fenton-like reaction. In the Fe$_2$O$_3$@meso-SiO$_2$ composite, the mesoporous shell of the Fe$_2$O$_3$@meso-SiO$_2$ composite can adsorb the MB molecules from the bulk solution and enrich them on the surface of the flowerlike Fe$_2$O$_3$ core, while ·OH radicals generated on the surface of the flowerlike Fe$_2$O$_3$ core were also trapped by the mesoporous silica shell, resulting in higher reactant concentration on the surface of flowerlike Fe$_2$O$_3$. The degrading reactions were confined within mesoporous pores, where the Fe$_2$O$_3$ core was more accessible than bare flowerlike Fe$_2$O$_3$ in bulk solution. Moreover, the contacting opportunities between MB molecules and hydroxyl radicals was also increased in Fe$_2$O$_3$@meso-SiO$_2$ composite compared with the bare flowerlike Fe$_2$O$_3$ due to the mesoporous silica coating. Thus, the catalytic activity of the flowerlike Fe$_2$O$_3$ was enhanced by the mesoporous silica coating.

### 4. Conclusions

The flowerlike Fe$_2$O$_3$ with hierarchical structure was synthesized through a simple hydrothermal method. The flowerlike Fe$_2$O$_3$ was coated by mesoporous silica to form Fe$_2$O$_3$@meso-SiO$_2$ composite in aqueous media. SEM and TEM images demonstrated that in the Fe$_2$O$_3$@meso-SiO$_2$ composite mesoporous silica was coated uniformly and completely on the surface of the flowerlike Fe$_2$O$_3$ core. When used as catalyst for the Fenton-like reaction to the degradation of MB, the Fe$_2$O$_3$@meso-SiO$_2$ composite is much more active than the bare flowerlike Fe$_2$O$_3$, which suggest that the mesoporous silica coating can enhance the catalytic activity of the hierarchical Fe$_2$O$_3$.

### References