Synthesis and characterization of Fe-doped TiO₂ hollow nanospheres prepared by carbon sphere as hard template

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Abstract: Fe-doped TiO₂ hollow nanospheres (THs-Fe) with various Fe-dopant concentrations (0.25, 0.50, 0.75 and 1.00 mol%) were prepared using carbon spheres as templates. After calcination, the obtained hollow structure TiO₂ were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS) and ultraviolet-visible spectroscopy (UV-Vis). The analysis results revealed that the crystallite size and crystallinity of the samples decreased with increasing Fe content. Morphology and particle size were investigated by electron microscopic techniques and the results showed that dopant concentrations had a significant influence on average particle size. The average diameter of hollow spheres decreased from 146.92 to 61.57 nm when Fe-content increased from 0.25 to 1.00 mol%. The UV-Vis absorption spectra exhibited that the absorption edge of THs-Fe was shifted toward the visible light region with increased Fe content. The energy gap (Eg) was decreased from 2.85 to 1.84 eV when the dopant content increased from 0.25 to 1.00 mol%.

1. Introduction
Titanium dioxide (TiO₂) is a functional material which is widely used in a verities of applications, such as photocatalyst, solar cell, gas sensor, pigment, UV-protection and self-cleaning surface coating due to its high catalytic, chemical and biological inertness, strong oxidizing power, high reflective index, low cost, long-term stability and nontoxicity [1-3]. It is well known that such characteristics are all caused by crystalline structure, morphology and crystalline size of the material. However, the application of TiO₂ has been limited by several factors in practice. The most restrictive one is TiO₂ can only use ultraviolet as the excitation source, due to its wide band gap (3.2 eV for anatase), in order to improve the photocatalytic performance and the electron transparent properties [4-6]. Several methods are reported in the literature to address this issue. Among this, doping with metal and nonmetal elements could reduce the width of the energy gap and extend the absorption spectrum of TiO₂ into the visible region. This result is attributed to that the dopant opens up possibility of changing electronic structure of TiO₂ and altering their optical properties [4,7]. Among the various dopant, Fe is considered to be a suitable candidate as dopant because the radius of Fe³⁺ (0.69 Å) is similar to that of Ti⁴⁺ (0.75 Å). As a result, Fe³⁺ can be conveniently integrated into TiO₂ matrix [8]. Thus, the width of the energy gap of TiO₂ could be reduced and leads to an increase in absorbing visible light efficiency [6].

In this present work, Fe doped TiO₂ hollow nanospheres were successfully synthesized by a sol-gel route using carbon spheres (CS) as a template. The effect of various Fe-dopant concentrations of 0.25, 0.50, 0.75 and 1.00 mol% on microstructure, morphology and optical properties were studied.
2. Experimental

2.1. Preparation of carbon spheres
In a typical experiment, 24.5 g D-Glucose anhydrous and 245 mL deionized water was mixed for 30 min. The solution was then transferred into Teflon-line stainless steel autoclave and maintained the heat-treated hydrothermal reaction at 180 °C for 4 h. After cool down the solution, the brownish-black product was collected by centrifugation and washing by several cycles of water and absolute ethanol. The product was dried in a vacuum oven at 80 °C for 3 h. The obtained powder was then subjected to FESEM and the result showed that mean diameter of the carbon spheres is 505.41±75.04 nm.

2.2. Preparation of Fe doped TiO$_2$ hollow nanospheres (THs-Fe)
Firstly, Fe(NO$_3$)$_3$.9H$_2$O was dissolved into the mixture of 48 mL absolute ethanol with 0.5 mL deionized water. Then, 300 mg of CSs was added into the above solution. Secondly, the Ti(OBu)$_4$ diluted with 30 mL absolute ethanol was added into the brownish solution under vigorous stirring at 80 °C for 6 h. Finally, the products were subjected to 3 cycles of washing by ethanol and subsequently dried in a vacuum oven at 80 °C for 3 h. To remove the CS core and simultaneously convert the amorphous to crystalline, the resultant powder was calcined at 450 °C in air atmosphere using a heating rate of 16 °C.min$^{-1}$ for 1 h. In this work, the Fe content was varied to be 0.25, 0.50, 0.75, and 1.00 mol% and the resultants were denoted by THs@0.25Fe, THs@0.50Fe, THs@0.75Fe, and THs@1.00Fe, respectively.

3. Results and discussion
Figure 1 shows the XRD pattern of the Fe-doped TiO$_2$ hollow nanospheres with different Fe contents. It can be seen that all the samples exhibit the characteristic peaks of anatase TiO$_2$ (JCPDS card No.21-1272). The intensity of diffraction peaks is found to be decreased with increasing Fe-content. This indicates the decrease in crystallinity of TiO$_2$. This result is attributed to several defects in the anatase crystallites produced by the substitution of part of Ti$^{4+}$ site by Fe$^{3+}$, which may inhibit crystallite growth [9]. The crystallite size was calculated by the Scherrer’s formula, $D = k \lambda / \beta \cos \theta$, where $D$ is crystal size, $k$ is a constant (k=0.899), $\lambda$ is the wavelength of the X-ray irradiation, $\beta$ is full-width-at-half-maximum of the (101) plane and $\theta$ is the Bragg’s angle [10]. The mean crystallite size of THs@Fe is summarized in table 1.

![Figure 1. XRD patterns of different Fe doped TiO$_2$ hollow nanospheres.](image-url)
absorption edge observed in THs@0.75Fe and THs@1.00Fe samples correspond to the Fe induced intermediate states and may be due to Fe adsorbed on TiO₂ or incorporated into the TiO₂ matrix. The E₆ value of all the samples was evaluated by extrapolating plots of (αhv)¹/² versus (hv) photon energy, where α is the absorption coefficient, as shown in the inset of figure 2. The absorption edge and E₆ of THs-Fe are depicted in table 1.

**Figure 2.** Absorption spectra of as-prepared THs@Fe. The inset shows the plots of (αhv)¹/² versus (hv) photon energy.

The morphology of THs@0.25Fe, THs@0.50Fe, THs@0.75Fe and THs@1.00Fe samples were investigated by FESEM and the results are shown in figures 3(a), 3(e), 3(i) and 3(m), respectively. The micrographs show that an average diameter of hollow spheres decreases with increasing Fe-content. To investigate the effect of dopant on microstructure, the hollow spheres were further characterized by TEM technique. The bright-field TEM images of THs@0.25Fe, THs@0.50Fe, THs@0.75Fe and THs@1.00Fe are shown in figures 3(b), 3(f), 3(j) and 3(n), respectively. It can be seen that the hollow structure is very evident, since the strong contrast between the dark edges and bright centers. The average diameter and shell thickness of THs-Fe are summarized in table 1. The clear lattice fringes in the HRTEM images in figures 3(c), 3(g), 3(k) and 3(o) show the identification of the crystallographic spacing (d_{hkl}) of anatase TiO₂ structure, the lattice fringes of 3.52, 2.38 Å are corresponding to the (101) and (004) planes, respectively. The SAED patterns (figures. 3(d), 3(h), 3(l) and 4(p)) show several Debye-Scherrer rings, corresponding to the reflection of TiO₂ nanocrystal. These results well agree with the XRD analysis. To confirm the existence of Fe, the samples were analyzed by EDS and the results are revealed in table 1. It can be seen that the concentration of Fe element increased with increasing Fe-dopant.

**Table 1.** Summary of sphere diameter, shell thickness, absorption edge, band gap energy and element content of the THs@Fe samples.

| Samples       | diameter (nm) | Shell thickness (nm) | Absorption edge (nm) | Band gap energy (eV) | Element content (at.%) |
|---------------|---------------|----------------------|----------------------|----------------------|------------------------|
|               |               |                      |                      |                      | Ti         | O          | Fe          |
| THs           | 327.03±22.12  | 28.36±6.63           | 403.03               | 3.11                 | 0±0±0      | 0±0±0     | 0±0±0       |
| THs@0.25Fe    | 146.92±23.97  | 12.79±1.71           | 409.86               | 3.08                 | 61.95 ±1    | 37.67 ±1  | 0.37 ±1     |
| THs@0.50Fe    | 145.93±19.00  | 8.12±2.14            | 490.21               | 2.46                 | 54.89 ±1   | 42.40 ±1  | 2.70 ±1     |
| THs@0.75Fe    | 90.13±40.02   | 6.21±1.87            | 682.84               | 1.73                 | 49.68 ±1   | 39.42 ±1  | 10.88 ±1    |
| THs@1.00Fe    | 61.57±10.34   | 3.60±0.79            | 698.03               | 1.68                 | 41.16 ±1   | 43.52 ±1  | 15.31 ±1    |
4. Conclusion
The hollow THs-Fe nanospheres were successfully synthesized using carbon spheres as a hard template. The analysis results revealed that the crystallite size and crystallinity of the samples decreased with increasing Fe content. The average diameter of hollow spheres decreased with increasing the dopant content. The UV-Vis absorption spectra exhibited that the absorption edge of THs-Fe was shifted toward the visible light region with increased Fe content.

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