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# Direct liquid phase deposition fabrication of waxberry-like magnetic $Fe_3O_4$@$TiO_2$ core-shell microspheres

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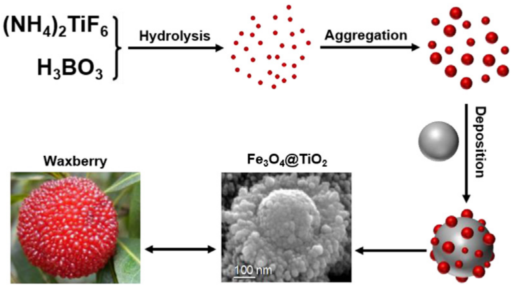
## HIGHLIGHTS

- Waxberry-like core-shell Fe3O4@-TiO2 microspheres were fabricated by facile LPD route.
- They have considerable saturation magnetization and small coercivity.
- They can be used as recyclable photocatalyst for removal of dyestuff in aqueous solution.
- The growth mechanism of the core-shell structure was proposed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Magnetic $Fe_3O_4$@$TiO_2$ core-shell microspheres are ideally applied in several specific fields due to their unique properties. A facile liquid phase deposition route for the fabrication of $Fe_3O_4$@$TiO_2$ core-shell microspheres was developed. The core-shell structure was obtained by direct deposition of $TiO_2$ on the surface of $Fe_3O_4$ microspheres. The prepared products were characterized by using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). The waxberry-like microspheres were nearly spherical with diameters of about 500 nm and average shell thickness of 80 nm. The shell layer was composed of smaller primary $TiO_2$ nanoparticles with sizes from 10 to 20 nm. A possible growth mechanism of the core-shell structure was proposed. The photo-catalytic decomposition of methylene blue and the recycling of prepared core-shell microspheres were also investigated.

## 1. Introduction

$Fe_3O_4$ is a kind of important functional material, which has interesting physical properties such as considerable magnetic behavior and strong spin polarization [1–3]. $TiO_2$ possesses several attractive features like highly chemical stability, photoactivity, nontoxicity, antimicrobial activity, and excellent affinity to organic compounds [4–8]. The hierarchical structure by combining micro/nano $TiO_2$ particles and magnetic carrier is a promising method to extend their application in several specific fields [9–13]. For example, $Fe_3O_4$@$TiO_2$ core-shell materials have been prepared for

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the electromagnetic or microwave absorption. They exhibited higher anisotropy energy and better wave absorption capacity than their bare $Fe_3O_4$ competitor [10,11]. $Fe_3O_4$@$TiO_2$ particles have also been used in the proteome analysis. Phosphopeptides could be effectively identified and enriched by MALDI-TOF mass spectroscopy due to the magnetic properties of $Fe_3O_4$ and the affinity of $TiO_2$ towards phosphopeptides [12–14]. As a photoactivatable material, $TiO_2$ will generate oxidative radicals under UV irradiation, which makes it become photosensitizer for cancer cells. The prerequisite to this purpose is that photoactive particles and anti-cancer drug are simultaneously delivered. It has been proved that maganetic $Fe_3O_4$@$TiO_2$ is an ideal candidate that can act as both the photoactive particle and drug transporter [9,15].

In addition, $TiO_2$ is one of the most extensively used catalysts in photocatalytic degradation of dye and organic contaminant in wastewater [16–18]. However, the separation and recycling of very small $TiO_2$ particles suspended in solution remains a challenge. Especially in large-scale use, it takes up a substantial part of the total cost. In order to effectively separate $TiO_2$ from the treated solution, the photocatalysts with magnetic core and $TiO_2$ shell have been designed and investigated [19–21]. In many cases, magnetic photocatalysts showed generally lower activities than pure $TiO_2$. One of the reasons is that the calcination treatment during the preparation of magnetic photocatalysts conducted at higher temperature caused the $Fe^{3+}$ ions to diffuse into the $TiO_2$ lattice which led to the trapping of electrons and holes [16,17,21]. The development of a simple synthesis route without calcination is the potential trick to overcome this defect.

Up to now, $Fe_3O_4$@$TiO_2$ core-shell structures have been fabricated through sol-gel, co-precipitation, hydrothermal, and template routes [11,12,22]. However, those processes required three or even more steps. A multi-step route to prepare well-defined $Fe_3O_4$@$TiO_2$ core-shell structure was successfully developed by Li et al. [12]. This method began with the solvothermal formation of $Fe_3O_4$, and then a hydrothermal process to obtain $Fe_3O_4$@C, further the adsorption of tetrabutyl titanate on $Fe_3O_4$@C, and finally an additional calcination to remove the carbon. Alternatively, Zhu proposed another method for the $Fe_3O_4$@$TiO_2$ core-shell nanotubes. $\gamma$-$Fe_2O_3$ were obtained as the first step [11]. $\gamma$-$Fe_2O_3$@$TiO_2$ were then synthesized by a wet-chemical method. In the third step, the obtained $\gamma$-$Fe_2O_3$@ $TiO_2$ was then reduced at 623 K for 5 h under $H_2$ to finally get the $Fe_3O_4$@$TiO_2$ core-shell nanotubes. Xuan et al. reported that hollow spherical $Fe_3O_4$@$TiO_2$ photocatalysts were prepared through a poly(styrene-acrylic acid) (PSA) template method, which contained three steps as well, i.e., the synthesis of PSA@$Fe_3O_4$ composite spheres, the synthesis of PSA@ $Fe_3O_4$/$Ti(OH)_x$ core-shell spheres, and the last step of getting $Fe_3O_4$@$TiO_2$ by hydrothermal removal of PSA [22].

Liquid phase deposition (LPD) is a novel process for preparing oxides thin films from aqueous solutions at room temperature [23–25]. It has been also applied to fabricate $TiO_2$ with core-shell structure, such as $TiO_2$-$SiO_2$, Au-$TiO_2$, and $MnCO_3$-$TiO_2$ [26–28]. In a typical process, metal oxide deposited onto the immersed template through the chemical equilibrium reaction between metal fluoro complex ions and metal oxide. The expected reactions in the preparation of $TiO_2$ by LPD processed as follows:

$$TiF_6^{2-} + 2H_2O \rightleftarrows TiO_2\downarrow + 6F^- + 4H^+ \quad (1)$$

$$BO_3^{3-} + 4F^- + 6H^+ \rightleftarrows BF_4^- + 3H_2O \quad (2)$$

As the hydrolysis of $(NH_4)_2TiF_6$, $TiO_2$ would be formed and deposited on the surface of $Fe_3O_4$ template (or suspended in the solution) (Equation (1)). Generally, this reaction slowly occurred at room temperature. As adding $H_3BO_3$ to the solution to consume the $F^-$ and $H^+$ ions (Equation (2)), the reaction in Equation (1) was accelerated by shifting to the right-hand side. However, there have been few work that successfully prepared $Fe_3O_4$@$TiO_2$ core-shell microspheres by liquid phase deposition.

In this work, a facile direct LPD synthesis route to fabricate waxberry-like magnetic $Fe_3O_4$@$TiO_2$ core-shell spheres was developed. The shell layer with 80–100 nm in thickness contained smaller primary $TiO_2$ nanoparticles in size from 10 to 20 nm that were successfully loaded on the surface of $Fe_3O_4$ microspheres at room temperature. A possible growth mechanism of the $Fe_3O_4$@$TiO_2$core-shell structure was also proposed. In addition, the photocatalytic activity and the recycle efficiency of the magnetic core-shell microspheres were evaluated by decolorization of MB in aqueous solution.

## 2. Materials and methods

### 2.1. Synthesis of $Fe_3O_4$ microspheres

All chemicals used here were analytical-grade and without further purification. Magnetic $Fe_3O_4$ core microspheres were prepared by the solvothermal reaction as described in our previous work [29]. In a typical experiment, 2.5 mmol of $FeCl_3 \cdot 6H_2O$ was dissolved in 30 mL of ethylene glycol to form a clear solution. 25 mmol $CO(NH_2)_2$ was then added into the solution. After vigorous stirring for 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 473 K for 12 h. The black solid products were obtained after washing with absolute ethanol and being dried at 333 K overnight.

### 2.2. Synthesis of $Fe_3O_4$@$TiO_2$ core-shell microspheres

$Fe_3O_4$@$TiO_2$ was synthesized by liquid phase deposition route at room temperature. $Fe_3O_4$ core microspheres, $(NH_4)_2TiF_6$, and $H_3BO_3$, were used as the template, Ti Source, and the fluoride ions consumer, respectively. $(NH_4)_2TiF_6$ and $H_3BO_3$ were dissolved separately in distilled water to form the master solutions at a concentration of 0.5 mol $L^{-1}$. Typically, 50 mL of $(NH_4)_2TiF_6$ and 100 mL of above $H_3BO_3$ solutions were mixed in a beaker flask. As stirring, 500 mg of $Fe_3O_4$ microspheres were then added into the mixture. $TiO_2$ was formed and deposited on the surface of $Fe_3O_4$ microspheres during the hydrolysis of $(NH_4)_2TiF_6$. In order to investigate the influence of reaction time on the preparation of $Fe_3O_4$@$TiO_2$, the reaction system was kept at 298 K for 4, 12, 18, and 26 h, respectively.

### 2.3. Characterization

Scanning electron microscopy (SEM) images were obtained using a Hitachi S-3400 field emission electron microscope at an accelerating voltage of 20 kV. X-ray powder diffraction patterns (XRD) were collected on a Philips X'pert PRO diffractometer using Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm), with an accelerating voltage of 40 kV and tube current of 40 mA. Fourier Transform Infrared (FTIR) spectra were measured on a Bruker Tensor 27 spectrometer with KBr pellets. The resolutions were 4 $cm^{-1}$ and 16 scans for each measurement. The magnetic properties of the samples were investigated by using a vibrating sample magnetometer (VSM, 7407, LakeShore) with applied magnetic fields up to 18 kOe at 300 K.

### 2.4. Evaluation of photocatalytic activity

Photocatalytic decomposition of MB was evaluated in a 250 mL quartz reactor. A 300 W Xenon-lamp was used to simulate the