Microwave-assisted hydrothermal crystallization: an ultrafast route to MSP@mTiO$_2$ composite microspheres with a uniform mesoporous shell$^\dagger$

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An ultrafast, green and efficient microwave-assisted hydrothermal crystallization method was developed to convert the amorphous titania shell of MSP@TiO$_2$ to uniform mesoporous anatase structure for highly selective and effective enrichment of phosphopeptides.

Magnetic mesoporous nanocomposites with well-defined structure, designed composition and tailored properties have received immense scientific and technological interest because of their unique magnetic responsiveness and large specific surface area.$^1$ As an emerging member, magnetic mesoporous titania microspheres, which are constructed with a magnetic core and a mesoporous crystalline titania shell, have had great success in a wide range of applications, such as catalysis,$^2$ photocatalysis,$^3$ and selective enrichment of phosphopeptides.$^4$

To synthesize magnetic mesoporous titania, the commonly employed strategy is to coat an amorphous titania shell onto a magnetic core followed by converting the amorphous shell into crystalline one. Calcination is the traditional and simplest approach to realize the transformation process.$^5$ However, the obtained product possesses low specific surface area and relatively poor dispersibility in solvents. Hydrothermal crystallization could be an alternative method to achieve both good crystallinity and high specific surface area.$^6$ Nevertheless, this process is time-consuming ($>$16 h) and energy inefficient. Therefore developing a novel rapid and green technique to overcome these deficiencies is of great importance.

In recent years, the introduction of microwave irradiation to chemical reactions has attracted numerous attention because of its successful application in organic synthesis,$^5$ polymer chemistry,$^6$ material science,$^7$ and biochemical processes.$^8$ Taking advantage of the rapid volumetric heating, dramatically reduced reaction time, increased product yields and enhanced product purity could be usually achieved in comparison to conventional reaction systems. Based on these merits, microwave-assisted synthetic strategies have also been extensively employed to fabricate various nanomaterials including polymeric microspheres,$^9$ metallic nanoparticles,$^{10}$ quantum dots,$^{11}$ metal oxides,$^{12}$ composite microspheres,$^{13}$ etc. However, the use of microwave energy to realize the ultrafast, green and effective crystallization transformation has rarely been reported.

With all these in mind, we herein report a significant advancement in the hydrothermal crystallization by using the rapid and energy-saving microwave heating. By applying this method, the crystallization transformation process for preparing magnetic mesoporous titania could be ultra-quickly finished within 10 minutes. As illustrated in Scheme 1, magnetic supraparticles (MSPs) stabilized by sodium citrate were firstly synthesized by solvothermal reaction. Sol–gel process was then carried out to encapsulate the MSPs with a compact and amorphous titania shell. Finally, the MSP@TiO$_2$ microspheres were dispersed in the high microwave-absorbing solvent containing ethanol and deionized water with a volume ratio of 2 : 1. The dispersion was then transferred into a microwave reaction vessel and the sealed vessel was heated by a single-mode microwave irradiation of 2.45 GHz. In sharp comparison to conventional hydrothermal treatment took place in an autoclave, the microwave-assisted reaction was dramatically sped up and completed within just 10 minutes.

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Scheme 1 Schematic illustration of the synthetic procedures for preparation of MSP@mTiO$_2$ by using microwave-assisted hydrothermal crystallization.
Representative TEM images were applied to identify the structure transformation. As shown in Fig. 1a, about 240 nm sized magnetic supraparticles with nearly spherical morphology were found to be composed of many discrete small nanocrystals. After encapsulation with the amorphous titania shell, well-defined core/shell structure could be distinctively observed and the thickness of the titania shell was around 90 nm (Fig. 1b). It could be clearly found that the amorphous titania layer was continuous and compact in terms of its structure. As presented in Fig. 1c, the compact titania shell of MSP@TiO2 was replaced by a discrete and porous structure after 10 min's microwave-assisted hydrothermal process at 180 °C. The high-resolution TEM (HRTEM) image (Fig. 1d) and selected-area electron diffraction (SAED) pattern (Fig. 1d inset) further revealed that the TiO2 shell of MSP@mTiO2 is polycrystalline.

The phase evolution of the TiO2 in the shell was closely monitored as a function of the reaction time to confirm the crystalline transition processes. It can be seen that tiny crystals were just formed at the outermost surface of the shell when the temperature reached 180 °C (Fig. 2a and S1†). As the reaction continued, the crystallization was gradually extended into the external layer to yield a considerable amount of nanocrystals (Fig. 2b–d). The SAED pattern provided additional powerful evidence for these transition processes. When the reaction time was less than 3 min (Fig. 2e and f), the SAED pattern indicated that the TiO2 shell is still amorphous. With the reaction time increased to 6 min (Fig. 2g), a preliminary polycrystalline shell structure was formed. As the reaction time further prolonged to 10 min, the crystallinity of the shell was strengthened (Fig. 2h). We also tried to further increase the reaction time, but the morphology and the crystallinity seemed to remain the same.

The crystallization transition process was continued to be vigorously investigated by powder X-ray diffraction (PXRD, Fig. 3a). Prior to the crystallization treatment of the TiO2 shell, both MSPs and MSP@TiO2 showed a simple PXRD pattern (Fig. S2†), which is well ascribed to the typical cubic structure of Fe3O4 (JCPDS 19-629). No emergence of characteristic TiO2 crystal peak agreed well with the essence of the amorphous TiO2 shell. At the very beginning of the crystallization process, the detected signal still only contains the characteristic peaks of Fe3O4 (Fig. 3a-i). When the reaction time reached 3 min, a relatively weak peak of TiO2 was observed at the 2θ value of 25.1° (Fig. 3a-ii), corresponding to the reflections of (101) crystalline plane. With the reaction time increased to 6 min, multiple diffraction peaks were detected. As the reaction time was further prolonged to 10 min, enhanced signals of these peaks were observed, which indicated that the increase of the reaction time promoted the evolution of the TiO2 nanocrystals. When the reaction time was further prolonged to 20 min or even more, the detected patterns were nearly same as that corresponding to the reaction time of 10 min. The average grain size in the shell was calculated by Scherrer’s formula. The strongest peak at 25.1° in the PXRD pattern was used, the average nanocrystal size in the TiO2 shell of the product prepared with reaction time of 10 min was about 6.6 nm. All in all, the PXRD results agreed well with the SAED characterizations and all of them clearly demonstrated that the crystallization transition process was completed within only 10 min.

The well-structured MSP@mTiO2 microspheres synthesized with reaction time of 10 min were subjected to further study their porosity and magnetic properties. The specific surface area was characterized using nitrogen adsorption–desorption measurement. A typical type IV gas sorption isotherm (Fig. 3b) was indicative of the mesoporous character of the TiO2 shell. According to the calculations made using the BET mode, the MSP@mTiO2 resulted in a specific surface area of as high as 1219 m²/g.
that the three kinds of microspheres have no obvious remanence or coercivity at 300 K, indicating that they all possess a superparamagnetic feature. By comparing the Ms values before and after coating the TiO2 layers, the TiO2 content was estimated to be as high as 70 wt% and 68 wt% for MSP@TiO2 and MSP@mTiO2 respectively. The high TiO2 content together with the high specific surface area endow the MSP@mTiO2 with potential good performance in their applications.

To verify the effectiveness of the microwave-assisted hydrothermal crystallization, we examined the capability of the obtained MSP@mTiO2 in selective enrichment of phosphopeptides. Crystalline TiO2 has been proved to have excellent selectivity toward phosphopeptides. Meanwhile, mesoporous TiO2 is particularly attractive because it has much bigger specific surface area than its solid counterpart, which brings a higher enrichment capacity. Moreover, the change of the feeding ratio between MSPs and TBOT will lead to a different thickness of the mTiO2 shell. More mTiO2 content will result in larger specific surface area and more binding sites for the phosphopeptides. As a result, the enrichment capacity will increase as the mTiO2 shell thickness increases. To test the specificity of MSP@mTiO2 in phosphopeptides enrichment, tryptic digest of standard phosphoprotein β-casein was mixed with standard non-phosphoprotein BSA at a molar ratio of as high as 1 : 500. As shown in Fig. 4a, no signal of phosphopeptide was detected and the spectrum was dominated by high abundance of nonphosphopeptides. However, after being enriched by MSP@mTiO2, all the three phosphopeptides along with their doubly charged phosphorylated peptides and dephosphorylated counterparts formed during the MALDI ionization process could be easily detected with a very clean background in the spectrum (Fig. 4b). The enrichment capacity was further investigated and estimated to be about 180 mg g⁻¹ (Fig. 4c). Overall, the exceptional specificity and high capacity toward phosphopeptides provide robust evidence for the existence of crystalline and mesoporous titania shell.

In summary, we have explored a brand-new crystallization approach to get access to the crystalline and mesoporous titania shell by microwave-assisted hydrothermal treating the amorphous counterpart. The TEM, SAED, XRD together with the BET results all clearly demonstrated that the reaction time could be greatly reduced to only 10 min by using microwave volumetric heating and good microwave-absorbing solvents. This approach was applied in the fabrication of MSP@mTiO2 composite microspheres and comparing to conventional hydrothermal crystallization, the product prepared with the aid of microwave irradiation has a higher specific area and smaller average pore diameter. Besides, the as-obtained product possesses remarkable specificity and extraordinary capacity in selective enrichment of phosphopeptides.

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Notes and references


