Effect of Calcination Temperature on the Photocatalytic Performance of N-Doped TiO2 Hollow Mesoporous Microspheres (Postprint)

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Abstract

Using triethylamine as the nitrogen source, N-doped TiO_2 hollow mesoporous microspheres (N-THS) with well-defined spherical morphology were prepared via layer-by-layer self-assembly and high-temperature calcination. The effects of calcination temperature on their structure and photocatalytic performance were investigated by means of XPS, XRD, UV-Vis DRS, and other characterization techniques. The results demonstrate that N incorporates into the TiO_2 lattice, substituting for partial O elements and altering the chemical states of Ti and O within the lattice. TiO_2 calcined at 400–600 °C exhibits an anatase phase structure; upon increasing the calcination temperature to 700 °C, a phase transition to rutile occurs, and the crystallite size of TiO_2 increases with rising calcination temperature. N-THS shows pronounced absorption capability in the visible light region, with a significant red-shift of the absorption band, and exhibits good degradation efficiency toward MO solutions. Moreover, as the calcination temperature decreases, the visible-light absorption is enhanced correspondingly and the degradation efficiency improves; the degradation rate of N-THS calcined at 400 °C reaches 93.5 % after 80 min of light irradiation.

Full Text

Preamble

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Title

Effect of Calcination Temperature on Photocatalytic Property of N-doped Titania Hollow Microspheres

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Abstract

N-doped titania hollow mesoporous microspheres (N-THS) with well-defined spherical morphology were prepared via layer-by-layer self-assembly and calcination using triethylamine as the nitrogen source. The effects of calcination temperature on the structure and photocatalytic properties of N-THS were investigated using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and UV-visible diffuse reflectance spectroscopy (UV-Vis DRS). The results demonstrate that nitrogen incorporates into the TiO2 lattice by substituting for oxygen, thereby altering the chemical states of titanium and oxygen. Samples calcined between 400-600°C exhibit pure anatase phase structure, while rutile phase emerges at 700°C. The TiO2 crystallite size increases monotonically with calcination temperature. N-THS display strong visible-light absorption with a marked red-shift in the absorption edge. All samples show excellent degradation efficiency for methyl orange solution, which improves as calcination temperature decreases. Specifically, N-THS calcined at 400°C achieves a degradation rate of 93.5% after 80 minutes of irradiation.

KEY WORDS inorganic non-metallic materials, TiO2 hollow microsphere, N-doped, visible-light photocatalysis, calcination temperature

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Introduction

TiO2 is widely recognized in photocatalysis for its excellent photocatalytic performance, chemical stability, and non-toxicity. However, pure TiO2 can only absorb ultraviolet light, which accounts for merely ~4% of solar energy, resulting in low photocatalytic efficiency [1]. Doping TiO2 with certain metal or nonmetal elements can enhance its photocatalytic activity [2-4]. Current research on TiO2 doping primarily focuses on nanopowders, with relatively few studies investigating doping modifications of TiO2 hollow microspheres [5]. TiO2 hollow microspheres are typically prepared by high-temperature calcination to remove template cores, and the calcination temperature significantly influences the morphology, crystal structure, and photocatalytic efficiency of N-doped TiO2 hollow microspheres. Building upon previous work [6,7], this study employs cationic polystyrene microspheres (PS) as templates, tetrabutyl titanate (TBOT) as the precursor, triethylamine (TEA) as the nitrogen source, and polydiallyldimethylammonium chloride (PDADMAC) as the polyelectrolyte interlayer to fabricate N-doped TiO2 hollow mesoporous microspheres (N-THS) through layer-by-layer self-assembly and high-temperature calcination. Methyl orange was used as a model pollutant to investigate the effects of calcination temperature on the structure and photocatalytic properties of N-THS.

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1 Experimental Methods

Following the procedure described in reference [6], an appropriate amount of PS/TiO2/PDADMAC composite microspheres was dispersed in 90 mL of anhydrous ethanol. After uniform dispersion, 40 mL of an ethanol solution containing TBOT and TEA (mass ratio of TEA to TBOT = 2:1) was added, followed by dropwise addition of an ammonia-ethanol solution. The reaction proceeded for 5 hours, after which the product was collected by centrifugation, washed, and freeze-dried to obtain N-doped TiO2 double-layer composite microspheres. The composite microspheres were then calcined in a muffle furnace to remove the PS template, yielding N-doped TiO2 hollow mesoporous microspheres (N-THS). The calcination protocol involved heating to 300°C at a rate of 2°C/min, holding for 2 hours, then further heating to the target temperatures of 400, 500, 600, or 700°C and holding for 3 hours. The resulting samples are designated as N-THS-400, N-THS-500, N-THS-600, and N-THS-700, respectively.

The morphology and structure of the microspheres were examined using an S-4800 scanning electron microscope (SEM) and a JEM-2100F transmission electron microscope (TEM). The crystal structure of N-THS was determined by D/max-RB X-ray diffraction (XRD). Surface composition was analyzed using a KAL Axis Ultra X-ray photoelectron spectrometer (XPS). UV-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a U-3900 UV-visible spectrophotometer.

Photocatalytic performance was evaluated through the degradation of methyl orange (MO) solution. In a typical experiment, 70 mg of N-THS was added to 70 mL of MO solution (15 mg/L). After stirring in the dark for 30 minutes to achieve adsorption equilibrium, the suspension was irradiated with a 250 W high-pressure mercury lamp while maintaining a distance of 10-15 cm between the light source and solution. Cooling water was circulated to prevent thermal effects. Samples were collected every 20 minutes during irradiation, centrifuged to remove N-THS particles, and the supernatant was analyzed using the U-3900 spectrophotometer at 464 nm to determine the residual MO concentration and calculate the degradation rate.

2 Results and Discussion

Figure 1 [Figure 1: see original paper] presents SEM and TEM images of N-THS calcined at 400°C. The micrographs clearly reveal a well-defined hollow mesoporous structure with a microsphere diameter of approximately 1.20 m and a shell thickness of about 30 nm. The simultaneous volatilization of the PS template and nitrogen dopant during high-temperature calcination induces substantial shrinkage of the TiO2 shell and creates the mesoporous architecture.

Figure 2 [Figure 2: see original paper] shows XPS spectra of TiO2 hollow mesoporous microspheres before and after N-doping. The survey spectrum (Fig. 2a) confirms the presence of Ti2p, O1s, and a weak N1s peak on the N-THS surface. The binding energies at 458.4, 464.1, and 529.6 eV correspond to Ti2p3/2, Ti2p1/2, and O1s characteristic peaks, respectively. Compared with pure TiO2 hollow microspheres (THS) and commercial Degussa P25 [8], the Ti2p and O1s peaks of N-THS exhibit slightly lower binding energies and minor shifts. In the high-resolution N1s spectrum (Fig. 2d), characteristic peaks appear at 399.6 and 396.9 eV. The peak at 399.6 eV likely originates from chemisorbed N–O species, while the weaker peak at 396.9 eV corresponds to β-N, attributed to Ti–N bonds. This confirms that nitrogen substitutes for oxygen in the TiO2 lattice and modifies the chemical states of Ti and O [9].

Figure 3 [Figure 3: see original paper] displays XRD patterns of N-THS calcined at various temperatures. Samples calcined at 400, 500, and 600°C show diffraction peaks that perfectly match the standard anatase TiO2 pattern. The intensity of the characteristic (101) plane diffraction peak sharpens with increasing calcination temperature, indicating improved crystallinity. At 700°C, distinct rutile phase peaks emerge, signifying the anatase-to-rutile phase transition. Using the Scherrer equation [10], the TiO2 crystallite sizes were calculated to be 10.9, 14.9, 16.1, and 22.4 nm for N-THS-400, N-THS-500, N-THS-600, and N-THS-700, respectively. This demonstrates that elevated temperatures promote rapid grain growth, leading to larger crystallite sizes.

Figure 4a [Figure 4: see original paper] compares the UV-Vis DRS spectra of N-THS calcined at different temperatures with P25. All N-THS samples exhibit pronounced visible-light absorption and a significant red-shift compared to P25. However, the absorption intensity gradually decreases as calcination temperature increases from 400 to 700°C. This phenomenon arises because higher calcination temperatures not only affect phase transformation and crystallite size but also cause volatilization of nitrogen species adsorbed on the TiO2 surface, reducing the N-doping concentration.

The enhanced visible-light absorption of N-THS can be attributed to the formation of new impurity energy levels above the TiO2 valence band due to nitrogen doping, which narrows the band gap [11]. According to the indirect band gap semiconductor formula: αh = A(h -Eg)n/2, Tauc plots of (αh)1/2 versus photon energy (h) were constructed. Extrapolation of the linear region to (αh)1/2 = 0 yields the band gap energy. As shown in Figure 4b, the band gaps of N-THS calcined at 400, 500, 600, and 700°C are approximately 2.53, 2.77, 2.83, and 2.89 eV, respectively—all lower than that of commercial P25 (2.90 eV).

Figure 5a [Figure 5: see original paper] illustrates the temporal evolution of UV-Vis spectra during photocatalytic degradation of MO solution over N-THS-400. The characteristic MO absorption peak at 464 nm decreases markedly with irradiation time, becoming nearly flat after 80 minutes. The inset photographs showing color changes of the MO solution at different intervals corroborate these results. Figure 5b reveals that N-THS calcined at 400, 500, and 600°C all exhibit excellent degradation efficiency, achieving rates of 93.5%, 86%, and 77%, respectively, after 80 minutes of irradiation. The superior photocatalytic activity of N-THS can be attributed to three factors: (1) the hollow architecture provides high specific surface area and mesoporous structure, facilitating efficient mass transport and adsorption compared to P25 powder; (2) reduced crystallite size in the hollow spheres shortens charge carrier migration distances, decreasing electron-hole recombination probability; and (3) nitrogen introduction creates impurity levels above the valence band, narrowing the band gap and red-shifting the absorption edge, thereby enabling visible-light response. Additionally, the high-pressure mercury lamp used in the photocatalytic experiments emits wavelengths >365 nm, containing substantial visible light and minor near-UV components. N-THS can utilize both spectral regions simultaneously (Figure 6 [Figure 6: see original paper]), achieving a dual photocatalytic effect that enhances overall performance [12].

The inferior degradation efficiency of N-THS calcined at 700°C (Figure 5b) stems from two factors. First, higher calcination temperatures reduce surface hydroxyl group density, diminishing $\bullet$OH radical formation via reaction with photogenerated holes [13]. Second, elevated temperatures promote crystallite growth and anatase-to-rutile transformation, both of which decrease photocatalytic activity.

3 Conclusion

Based on research of TiO2 hollow mesoporous microspheres, N-doped TiO2 hollow mesoporous microspheres with excellent spherical morphology were successfully prepared using triethylamine as the nitrogen source via layer-by-layer self-assembly and high-temperature calcination. Nitrogen incorporation into the TiO2 lattice modifies the chemical states of Ti and O. Increasing calcination temperature to 700°C induces an anatase-to-rutile phase transition, while TiO2 crystallite size grows monotonically with temperature. N-THS exhibit strong

UV absorption and, due to nitrogen doping, pronounced visible-light absorption with a marked red-shift in the absorption edge. N-THS calcined at 400, 500, and 600°C demonstrate excellent degradation efficiency for MO solution, achieving rates of 93.5%, 86%, and 77%, respectively, after 80 minutes of irradiation.

References

[6] J. N. Liu, G. W. Zhang, W. Ao, K. Yang, S. X. Peng, M. G. Christel, "Hollow mesoporous titania microsphere with low shell thickness/diameter ratio and high photocatalysis" , *Applied Surface Science*, 258(20), 8083 (2012).

[7] G. W. Zhang, Y. Ye, F. D. Zhu, K. Yang, "Fabrication of mono-dispersed hollow titania nanospheres with enhanced photocatalytic property" , *Rare Metal Materials and Engineering*, 43(6), 87 (2014).

[8] A. L. Linsebigler, G. Lu, J. T. Yates, "Photocatalysis on TiO2 surfaces: principles, mechanisms and selected results" , *Chemical Reviews*, 95(3), 735 (1995).

[9] S. H. Liu, H. R. Syu, "One-step fabrication of N-doped mesoporous TiO2 nanoparticles by self-assembly for photocatalytic water splitting under visible light" , *Applied Energy*, 100, 148 (2012).

[10] X. B. Chen, C. Burda, "Photoelectron spectroscopic investigation of nitrogen doped titania nanoparticles" , *Journal of Physical Chemistry B*, 108(40), 15446 (2004).

[11] G. C. Liu, H. Dong, S. Y. Liu, "Citric acid-catalyzed synthesis of N-doped mesoporous TiO2 and their photocatalytical properties" , *Chinese Journal of Materials Research*, 24(6), 631 (2010).

[12] H. Satoshi, M. Yuya, S. Hideki, A. Masahiko, S. Nick, "Characteristics of microwaves on second generation nitrogen-doped TiO2 nanoparticles and their effect on photoassisted processes" , *Journal of Photochemistry and Photobiology A: Chemistry*, 217, 191 (2011).

[13] C. N. Rusu, J. T. Yates, "Defect sites on TiO2(110) detection by O2 photodesorption" , *Langmuir*, 13(16), 4311 (1997).

[5] Q. Wu, W. Li, D. Wang, S. Liu, "Preparation and characterization of N-doped visible-light-responsive mesoporous TiO2 hollow spheres", *Applied Surface Science*, 299, 35 (2014).

Note: Figure translations are in progress. See original paper for figures.