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Facile one-pot synthesis of Eu, N-codoped mesoporous titania microspheres with yolk-shell structure and high visible-light induced photocatalytic performance

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ABSTRACT

A new type of Eu, N-codoped mesoporous TiO_2 microspheres with yolk–shell structure (TiO_2@void@TiO_2) was successfully synthesized by a facile one-pot hydrothermal method at low temperature (180 °C). The physical and chemical properties of as-synthesized samples, such as morphology, crystal phase, surface elements composition, porous structure, specific surface area and optical response, were characterized in detail. The resultant samples were porous microspheres with a diameter of about 1–3 μm, and were composed of a large number of smaller nanoparticles. An interior circular cavity in each microsphere was formed between core and shell to construct a special yolk–shell structure, and a large number of pores were produced in shell and yolk by CO_2 gas bubbles resulting from hydrothermal decomposition of the urea molecules, which tremendously increased the specific surface area and the pore volume of as-obtained samples. The absorption edges of Eu, N-codoped TiO_2 were extended to longer wavelength, which led to notable absorption in the visible-light region. The photocatalytic performances of all samples were evaluated by photocatalytic decoloration of rhodamine B and methyl orange under visible light irradiation ($\lambda > 420$ nm). Eu, N-codoped TiO_2 with 0.1 at.% Eu dopant showed the highest photocatalytic activity, the efficiency of which was 5 times higher than that of Degussa P25. The enhanced photocatalytic performance could be attributed to the synergic effects of many factors, such as high specific surface area, large pore volume and strong absorption to visible light, which were created by the Eu, N-codoping and the unique yolk–shell structure. Based on the above results, the mechanism of enhanced photocatalysis on Eu, N-codoped TiO_2 under visible light was proposed.

1. Introduction

As a promising material for environmental cleanup [1], hydrogen generation [2] and solar energy conversion [3], titania (TiO_2) has attracted extensive interest due to its excellent properties, such as environmental friendliness, chemical stability and low cost [4,5]. However, the photocatalytic performance of TiO_2 is limited by several factors, such as restrictive light absorption (only responsive to ultraviolet light with wavelength below 387 nm due to its wide band-gap), fast charge–carrier recombination and low interfacial charge-transfer rate of photogenerated carriers [6], which severely restrict its practical applications.

Ion doping and morphology control are considered as two of very promising strategies to improve the photocatalytic performance of titania. Anion doping, such as N, C and S, has been confirmed to be an effective method for extending the absorption edge of titania to visible light region [7–9]. While rare earth ions doping, for instance, Eu^{3+}, La^{3+}, can play the role of inhibiting the recombination of photogenerated electrons and holes [10,11]. Therefore, codoping with non-metal ions and rare earth ions may be a good attempt to further improve the photocatalytic activity of titania through the synergistic effects of the two dopants.

On the other hand, it is well known that the photocatalytic performance of titania can be improved by controlling its morphology and structure. To date, titania with different morphologies, such as rod, tube, wire, sheet, and sphere, have been successfully prepared. It is worth mentioning that titania with very complicated structures, such as core–shell [12], shell-in-shell [13], multi-shells [14], flower-like [15], have been synthesized by a variety of approaches in recent years, and it has been revealed these delicate structures can endow them with unique and intriguing properties.

Remarkably, a special class of core–shell structure with a distinctive core@void@shell configuration, which is called yolk–shell

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