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Acta Biomaterialia 2 (2006) 421–432
Acta BIOMATERIALIA
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Antimicrobial function of Nd^{3+}-doped anatase titania-coated nickel ferrite composite nanoparticles: A biomaterial system

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Received 12 December 2005; received in revised form 9 March 2006; accepted 16 March 2006

Abstract

The present study describes and makes a relative comparison of the antimicrobial function of undoped and neodymium-doped titania coated-nickel ferrite composite nanoparticles processed by uniquely combining the reverse micelle and chemical hydrolysis approaches. This methodology facilitates the formation of undoped and doped photocatalytic titania shells and a magnetic ferrite core. The ferrite core is needed to help in the removal of particles from the sprayed surface using a small magnetic field. Doping of the titania shell with neodymium significantly enhances the photocatalytic and anti-microbial function of the core–shell composite nanoparticles without influencing the magnetic characteristics of the nickel ferrite core. The increased performance is believed to be related to the inhibition of electron–hole recombination and a decrease in the band gap energy of titania. The retention of magnetic strength ensures controlled movement of the composite nanoparticles by the magnetic field, facilitating their application as removable anti-microbial photocatalyst nanoparticles. The consistent behavior of the composite nanoparticles points to the viability of the synthesis process adopted.

Keywords: Antimicrobial function; Photocatalysis titania; Doping; Composite nanoparticles

1. Introduction

Photocatalysis using nanostructured semiconductor oxides is attracting increasing interest for the decomposition of organic and inorganic microorganisms present in air and water [1–9]. Among the different semiconductor photocatalytic processes, titania (TiO_2)-mediated photooxidations have emerged as potential candidates for antimicrobial, self-cleaning and self-sterilizing activities [10–15]. However, one of the primary limitations of using pure TiO_2 semiconductor photocatalysis is the low quantum efficiency of TiO_2 due to its high band gap energy (~3.2 eV) and high e^- and h^+ recombination rate. Enhancing its efficiency requires a reduction of this recombination rate and a lowering of the band gap energy. Titania is a large band gap semiconductor and its absorption spectrum is in the range of ultraviolet light, which is only 5–8% of solar light. It is important to extend the absorption spectrum to the visible light range if the photocatalytic character of titania is to be used for antimicrobial activity involving visible light. Narrowing the band gap is an effective way to enhance the photocatalytic performance of titania, and this can be done by doping with a lanthanide metal cation dopant. This narrowing can also be facilitated if the electronic coupling effect between the dopant and semiconductor is sufficiently strong to alter the band structure.

In recent years, a number of dopants have been tried in order to enhance the photocatalytic performance of titania. The experience with dopants has been varied because of their different roles in trapping electrons and/or holes on

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1742-7061/$ - see front matter
doi:10.1016/j.actbio.2006.03.005

the surface. Fe^{3+} was observed to increase the efficiency of photoreduction of N_2 [13] and methyl viologen [14] and to inhibit electron/hole pair recombination in TiO_2. However, in the case of the photodegradation of phenol and 4-nitrophenol, doping TiO_2 with Fe^{3+} resulted in insignificant photoreactivity [15]. Enhanced photoreactivity for water cleavage [16] and N_2 reduction [15] have been reported for Cr^{3+}-doped TiO_2, while other researchers have shown that Cr^{3+} was detrimental to photocatalytic activity [17]. TiO_2 doped with Mo and V exhibited significantly reduced photoreactivity [18], while Gratzel and Howe [19] observed inhibition of electron/hole pair recombination with these dopants, based on electron paramagnetic resonance (EPR) data. Lanthanide-ion doped-TiO_2 exhibited higher photoresponse and superior reactivity in the photocatalytic degradation of rhodamine B in comparison to undoped TiO_2 nanoparticles [20]. In general, the doping effects of metal ions on the reactivity of TiO_2 have been inconsistent primarily because of the large variation in experimental conditions for the synthesis of the undoped and doped titania and the methods used to compare the photoreactivity of undoped and doped counterparts. It may also be noted that in the earlier work, sol–gel or solid state reaction methods were used which resulted in amorphous coatings of titania.

One important disadvantage of pure titania is that titania is an electrical insulator and is difficult to extract from the sprayed surface or wound after treatment. However, we can facilitate this removal if composite particles consisting of a magnetic core and a photocatalytic shell are fabricated. In previous papers [21,22], we reported the synthesis of composite nanoparticles consisting of a photocatalytic titania shell and a nickel ferrite magnetic ($NiFe_2O_4$) core. The synthesis process involved a combination of the reverse micelle technique and a chemical precipitation process. The role of magnetic core was to facilitate removal of composite particles by using a small magnetic field and also to enable controlled and targeted delivery of particles. The objective of the present work was to illustrate and describe the antimicrobial activity of photocatalytic neodymium-doped titania composite nanoparticles in relation to undoped titania which are characterized by a photocatalytic shell and a magnetic core of ferrite. It is also demonstrated that introduction of Nd^{3+} dopant into the TiO_2 photocatalytic shell does not negatively impact the magnetic behavior of the nickel ferrite core, permitting their removal from the sprayed surface using a small magnetic field.

2. Experimental

2.1. Synthesis of Nd^{3+}-doped TiO_2-coated $NiFe_2O_4$ nanoparticles

The synthesis of composite nanoparticles consisting of photocatalytic TiO_2 shells and magnetic $NiFe_2O_4$ cores consisted of two primary processes, namely the reverse micelle process and chemical hydrolysis. The detailed procedure for the fabrication of TiO_2 coated $NiFe_2O_4$ nanoparticles is described elsewhere [21,22]. Here the experimental part concerning the fabrication of Nd^{3+}-doped TiO_2-coated $NiFe_2O_4$ nanoparticles is outlined. First, nanoparticles of nickel ferrites were prepared by the reverse micelle method [23,24]. The procedure involved the preparation of two microemulsion systems. The first system consisted of an oil-phase microemulsion containing 108 ml of iso-octane and 24 g of surfactant diiso-octylsulphoccinate (AOT) and the second was an aqueous phase emulsion consisting of iso-octane and surfactant AOT with the reactant salts, hydrated iron chloride and hydrated nickel chloride. Microemulsion system I consisted of 2 ml of 30% NH_4OH + 2.4 ml of water + 66 ml of 0.50 M AOT–iso-octane and was sonicated for 10 min. Microemulsion system II containing 0.275 g of $FeCl_2 \cdot 4H_2O$ and 0.164 g $NiCl_2 \cdot 6H_2O$ dissolved in 8 ml of water + 66 ml of AOT–iso-octane was sonicated for 10 min. In the microemulsion I, NH_4OH was the precipitating agent. On subjecting the two microemulsions to rapid mechanical stirring for 75 min, the metal hydroxides were precipitated within the water pools of the reverse micelles and oxidized to ferrite. The precipitation of $NiFe_2O_4$ occurred according to the following reaction:

$$NiCl_2 \cdot 6H_2O + 2FeCl_2 \cdot 4H_2O + 6NH_4OH + \frac{1}{2}O_2 \rightarrow NiFe_2O_4 \downarrow + 6NH_4Cl + 17H_2O$$

Thus, these nanocrystalline nickel ferrites in the microemulsion constituted the core of the composite nanoparticles. Subsequently, the second part of the process was initiated by introducing an aqueous solution of acidic titanium salt solution in the absence or presence of Nd^{3+}-salt into the nickel ferrite product microemulsion to process undoped and doped composite nanoparticles. In the presence of Nd^{3+}, the chemical reaction can be given by:

$$Nd^{3+}\text{–}TiCl_4 + H_2O \rightarrow Nd^{3+}\text{–}TiOCl_2 + 2HCl$$

The amount of $TiCl_4$ (0.08 ml $TiCl_4$) and $NdCl_3$ (1.3 mg) added to the nickel ferrite system was in accordance with the molar ratio of 1:1 in the TiO_2:$NiFe_2O_4$ system and 1 wt.% Nd^{3+} doped into the TiO_2 photocatalytic shell. This was followed by heating the nickel ferrite microemulsion containing acidic titanium salt and neodymium salt solutions at 100 °C to precipitate Nd^{3+}-doped titania on the surface of the nickel ferrite nanoparticles. The solid product was separated by a centrifuging at a speed of 15,000 rpm, washed a number of times with 50% methanol and acetone mixture and distilled water, and dried in an oven at 90 °C for 30 min. A schematic of the process is summarized in Fig. 1.

2.2. Structural and magnetic characterization

The composite nanoparticles (TiO_2–$NiFe_2O_4$) were characterized by transmission electron microscopy and X-ray diffraction techniques. X-ray diffraction studies were carried out using Cu Kα radiation of wavelength $\lambda = 0.1540$ nm.

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