

Enhanced antibactericidal function of W^{4+} -doped titania-coated nickel ferrite composite nanoparticles: A biomaterial system

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Abstract

The study demonstrates a distinct enhancement of antimicrobial activity of W^{4+} -doped titania that is coated on nickel ferrite nanoparticles in comparison to undoped titania. The composite nanoparticles were synthesized by uniquely combining reverse micelle and chemical hydrolysis synthesis methods [Rana S, Rawat J, Misra RDK, Acta Biomater 2005;1:691]. The superior antimicrobial activity of W^{4+} -doped titania is related to the inhibition of electron–hole recombination and decrease in the band gap energy of titania. The function of the ferrite is to facilitate the removal of nanoparticles from the sprayed surface using a small magnetic field. The coating of ferrite nanoparticles with titania retains superparamagnetic character and magnetic strength of composite nanoparticles signifying non-deterioration of magnetic properties and promoting their use as removable antimicrobial photocatalyst nanoparticles.

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1. Introduction

Photocatalytic semiconductor oxides are being increasingly synthesized as nanoparticles or as nanostructured materials for degradation of organic and inorganic microorganisms because of their large surface area [1–9]. In this regard, titania is considered a preferred and potential semiconductor photocatalytic material for applications requiring antimicrobial and sterilizing characteristics [10–15]. Unfortunately, pure titania as a semiconductor photocatalyst is characterized by low quantum efficiency because of high band gap energy (~ 3.2 eV) and high rate of e^- and h^+ recombination. Increasing the quantum efficiency requires a lower e^-/h^+ recombination rate and the minimization of the band gap energy. Besides the large band gap characteristic of titania, the absorption spectrum is in the ultraviolet light range such that it corresponds to about 5–8% of solar light. The utilization of the photocatalytic

character of titania for antimicrobial activity involving visible light requires that the absorption spectrum is extended to the visible light range. An effective method to enhance the photocatalytic activity of titania is to narrow the band gap by doping titania with a lanthanide metal cation.

The experience of doping with metal cations to promote the photocatalytic activity with dopant is varied because of their different roles in trapping electrons and/or holes on the surface. Experiments with ferric ions (Fe^{3+}) indicated an increase in the photoreduction efficiency of nitrogen [13] and methyl viologen [14] and a decrease in electron/hole pair recombination in titania. However, photoreactivity was insignificant with regard to photodegradation of phenol and 4-nitrophenol when titania was doped with Fe^{3+} (ferric ions) [15]. Enhanced photoreactivity for water cleavage [16] and nitrogen reduction [15] with Cr^{3+} -doped titania was observed, while some researchers concluded that Cr^{3+} was detrimental to photocatalytic activity [17]. Titania doped with vanadium exhibited significantly reduced photoreactivity [18], but Gratzel and Howe [19] predicted the inhibition of electron/hole pair recombination based on

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electron paramagnetic resonance (EPR) data. The lanthanide ion-doped titania exhibited a stronger photoresponse and superior reactivity for the photocatalytic degradation of rhodamine B in comparison with undoped titania nanoparticles [20]. Thus, the results of the doping effects of metal ions on the reactivity of titania have been generally inconsistent primarily because of the significant variation in the fabrication methods used for the synthesis of the undoped and doped titania and the approach adopted to make a relative comparison between the photoreactivity of the undoped and doped photocatalyst. The previous fabrication methods involved sol–gel or solid state reaction, which led to the formation of amorphous or mixed crystalline–amorphous titania.

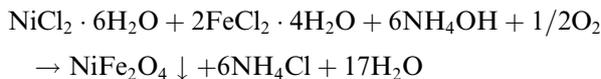
Another important disadvantage of pure titania from the viewpoint of application is that titania is an electrical insulator and is therefore not practically extractable from the sprayed surface or wound after treatment. However, a practical solution to this limitation is to consider synthesizing composite particles characterized by magnetic nanoparticles that are subsequently coated with titania. The magnetic part of the composite particles facilitates their removal by using a small magnetic field and also enables the controlled and targeted delivery of particles [21,22]. The present work is aimed at illustrating the superior antimicrobial activity of tungsten (W^{4+})-doped titania composite nanoparticles by making a relative comparison between undoped and tungsten-doped titania.

2. Experimental

2.1. Synthesis of tungsten-doped titania-coated nickel ferrite nanoparticles

The synthesis of composite nanoparticles consisting of tungsten-doped titania (TiO_2) and magnetic nickel ferrite ($NiFe_2O_4$) involved combining the reverse micelle and chemical hydrolysis processes. The first step in the fabrication of composite nanoparticles was the synthesis of magnetic nickel ferrite using the reverse micelle method, described previously by us [23,24]. In this procedure, two microemulsion systems were prepared. The first system consisted of an oil-phase microemulsion containing *iso*-octane and surfactant diiso-octyl sulphocinate (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). In a typical experiment, 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, which 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 and sonicated for 10 min. In the microemulsion I, NH_4OH was the precipitating agent. The two microemulsions were then combined and subjected to rapid mechanical stirring for 75 min. During this step, the metal hydroxides are precipitated within

the water pools of reverse micelles and oxidized to nickel ferrite. The precipitation of nickel ferrite ($NiFe_2O_4$) is given by the chemical reaction:



The precipitated nanocrystalline nickel ferrites in the microemulsion were subsequently encapsulated/coated with pure titania or tungsten-doped titania by adding an aqueous solution of acidic titanium salt ($TiCl_4$) solution in the absence or presence of tungsten chloride salt (WCl_4) in the nickel ferrite product microemulsion.

In a typical synthesis aimed at obtaining an anatase TiO_2 phase such that the $TiO_2:NiFe_2O_4$ molar ratio is 1:1, the amount of $TiCl_4$ added was 0.08 ml. The addition of $TiCl_4$ was facilitated by siphoning off $TiCl_4$ from the container while argon was being introduced into the container to prevent direct contact of $TiCl_4$ with air. Subsequently, hydrolysis of $TiCl_4$ was carried out at pH of ~ 1 (HCl in 6 ml of water). The volume of water and acid (6 ml) was kept at a minimum in the reverse micelle microreactor. In the case of tungsten-doped titania, the molar ratio of $TiO_2:NiFe_2O_4$ was maintained at 1:1 in conjunction with 2 mol% tungsten-doped titania. This was based on preliminary experiments and the viewpoint that doping titania with a higher mol% of tungsten may be detrimental to photocatalytic performance, in terms of encouraging charge recombination process. Thus, we selected 2 mol% tungsten-doped titania. In the absence and presence of tungsten chloride salt, the chemical reactions corresponding to titania and tungsten-doped titania shell, respectively, are:



In the last step, the nickel ferrite microemulsion containing acidic titanium salt for pure titania and titania and tungsten salt solutions for tungsten-doped titania were heated at 100 °C for 60 min to precipitate either pure anatase titania or tungsten-doped anatase titania on the surface of nickel ferrite nanoparticles. The solid product was separated by centrifuging at a speed of 15,000 rpm, washed a number of times with 50% methanol and distilled water, and dried in an oven at 90 °C for 30 min. A schematic of the process is summarized in Fig. 1 for the tungsten-doped titania.

2.2. Structural and magnetic characterization

The morphology and size range of composite nanoparticles consisting of pure anatase titania or tungsten-doped titania coated on nickel ferrite nanoparticles were examined by transmission electron microscopy. Structural characterization and confirmation of different phases was carried out using X-ray diffraction with Cu $K\alpha$ radiation of wavelength $\lambda = 0.1540$ nm. The magnetic behavior was

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