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Preparation and characterization of excellent antibacterial TiO_2/*N*-halamines nanoparticles

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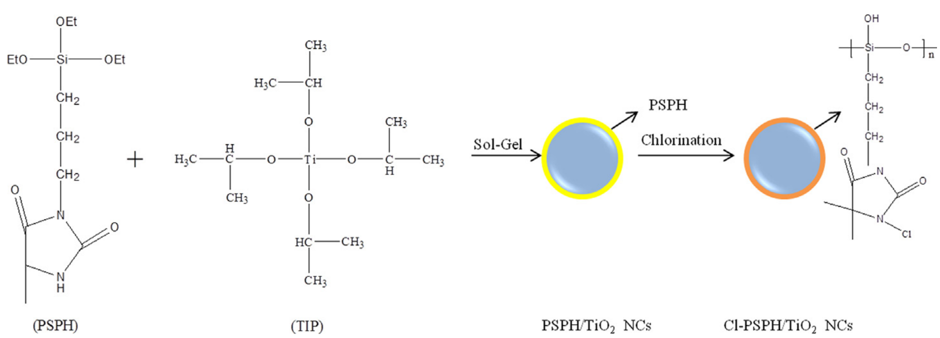
HIGHLIGHTS

- The Cl-PSPH/TiO_2 nanocomposites (NCs) possessed outstanding antimicrobial activity.
- PSPH/TiO_2 NCs were prepared by a sol-gel process at a low temperature.
- Cl-PSPH/TiO_2 NCs showed good cytocompatibility.
- Cl-PSPH/TiO_2 NCs were very stable during storage.
- The UV light stability of Cl-PSPH/TiO_2 NCs was significantly enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, *N*-halamine siloxanes poly[5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin] (PSPH) was synthesized, and PSPH/TiO_2 nanocomposites (NCs) were prepared by a sol-gel process at a low temperature (about 100 °C). Chlorinated PSPH/TiO_2 NCs (Cl-PSPH/TiO_2 NCs) were prepared by a chlorination reaction of PSPH/TiO_2 NCs in diluted sodium hypochlorite solutions. The structural characteristics of these as-prepared PSPH/TiO_2 NCs were determined by fourier transform infra-red (FTIR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), ^{13}C and ^{29}Si solid-state nuclear magnetic resonance (^{13}C NMR, ^{29}Si NMR). The characterization of these as-prepared organic-inorganic hybrid materials by FTIR, XPS and ^{29}Si NMR showed that Ti—O—Si bonds between nano-TiO_2 and PSPH were formed. The Cl-PSPH/TiO_2 NCs showed great antibacterial properties against *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895) as well. The N—Cl bond of Cl-PSPH/TiO_2 NCs showed outstanding stability under UV light irradiation. The results of in vitro cell viability test showed that the PSPH/TiO_2 NCs have excellent cytocompatibility to mammalian cells.

1. Introduction

Over the last several decades, organic-inorganic nanocomposites have attracted great attention of scientists in research due to their combined physical and chemical properties over the corresponding pure organic or inorganic materials. Moreover,

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the performance of such nanocomposites, such as mechanical, biological, electronic, biocidal, and optical properties, can be tuned to meet the requirements of a wide range of applications [1–4]. Titanium dioxide (TiO_2) is an attractive inorganic component for organic-inorganic nanocomposites due to their great advantages of non-toxicity, chemical stability, low cost, super-hydrophilicity, high photocatalytic capability and biocompatibility. Based on these unique properties, TiO_2 has been extensively used in antibacterial coatings [5,6], photocatalytic degradation of organic pollutions [7,8], self-cleaning surface [9] to dye-sensitized solar cells [10,11]. Therefore, many various multifunctional nanocomposite materials have been prepared by the surface functionalization of nano-TiO_2 with different substrates [12,13].

The usual methods to prepare organic-inorganic nanocomposites are sol-gel [14,15], in-suit polymerization [16], and chemical vapor deposition [17,18]. Among these, the sol-gel method is an interesting way taking into account the simplicity of the process, inexpensiveness, easy adaptation to industry scale and mass production. In addition, the chemical composition and the thermal treatment can control the composition and microstructures of the resulted materials, respectively [15,19,20]. In the sol-gel technology, one of the most commonly applied systems is a two-component system TiO_2:siloxanes [14,21,22]. For example, Lü et al. [22] have synthesized optical films of TiO_2-triethoxysilanecapped polythiourethane (TCPTU) with high refractive indices via a sol-gel method. However, to obtain the crystal structure of nanocomposites, the temperature used during the calcining processes is too high, which can lead to the carbonization of organic siloxanes. Some researchers [23–25] have reported nanocrystals are formed on substrates from the prepared gel coatings with hydrothermal treatment. For example, Uddin et al. [24] have shown that anatase nanocrystals are formed from titanium isopropoxide (TIP) solutions by hot water treatment ($T \le 100\,^{\circ}C$). Besides the above mentioned specific optical property, TiO_2 particles have been added with other novel functions, such as an antibacterial property, via suface modification. Chitosan/TiO_2 composite emulsion was prepared and used in modification of gauze. The modified gauze showed excellent antibacterial ability, which could suffer up to 8 times reuse [26]. However, there are few researches about antibacterial modification of TiO_2 through chemical linking.

Among organic antibacterial agents, *N*-halamine compounds [27–35] show superior antibacterial properties against a broad spectrum of microorganism within a short contact time. However, *N*-halamine siloxanes are limited in the practical application due to the poor UV stability of N—Cl bonds of *N*-halamine siloxanes and covalent bonds between *N*-halamine siloxanes and cellulose [36–38]. In our previous work, we have reported that commercial nano-TiO_2 can dramatically improve the UV stability of *N*-halamine diols and *N*-halamine siloxanes coated on cotton [39,40]. In this work antibacterial TiO_2/*N*-halamine siloxanes nanocomposites (NCs) were synthesized via a sol-gel process, and the prepared route of Cl-PSPH/TiO_2 NCs is shown in Fig. 1. Poly[5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin (PSPH) and titanium isopropoxide (TIP) were co-condensated with the forming of Si-O-Ti chemical bonds via a sol-gel process and then treated with hot water to form PSPH/TiO_2 NCs. Successful preparation of PSPH/TiO_2 NCs was determined by FTIR, TEM, XPS, XRD, ^{13}C and ^{29}Si NMR. In addition, the storage stability, in vitro cell viability, UV light stability and antibacterial efficacies against *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895) were tested.

2. Experimental section

2.1. Materials

5,5-Dimethylhydantoin was obtained from Hebei Yaguang Fine Chemical Co., Ltd. γ-Chloropropyltriethoxysilane and titanium isopropoxide (TIP) were both supplied by J&K Scientific Ltd, Shanghai, China. Other chemical reagents in this research were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further purification.

2.2. Preparation of PSPH/TiO_2 NCs

0.02 mol of TIP and 0.01 mol of triethyl amine were added into 50 cm^3 of 2-propanol (IPA) under vigorous stirring. The above solution was stirred for 2–3 min under nitrogen atmosphere. Then a second solution was prepared separately as follows: 0.72 cm^3 of water, 1.0 cm^3 of hydrochloric acid and 50 cm^3 of IPA were mixed uniformly. The two solution were mixed together and held for 30 min under nitrogen atmosphere. A transparent TiO_2 sol was obtained.

N-Halamine siloxane PSPH was synthesized according to the process reported by Worley et al. [41]. The chemical structure is shown in Fig. 2.

3%–5% PSPH and equimolar distilled water were added into the TiO_2 sol. Then the above solution was stirred vigorously until the PSPH was dissolved absolutely into the sol, and dried at 95 °C for 1 h. Finally, the produced powder was treated in boiling water for 1 h to

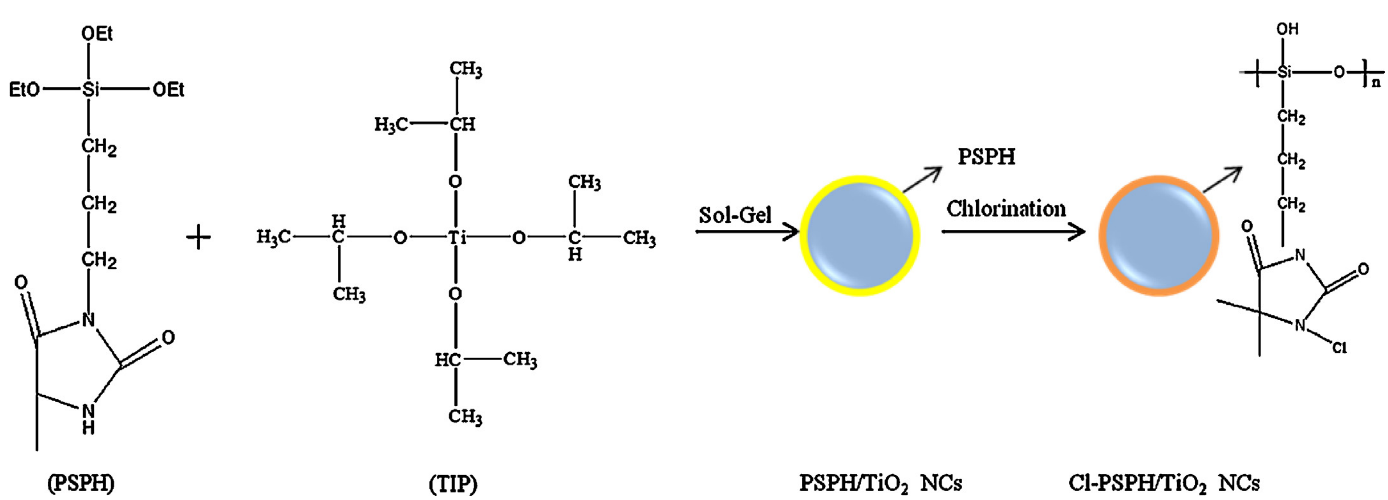

Fig. 1. The preparation scheme for PSPH/TiO_2 NCs.