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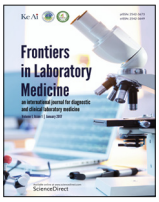

Highly crystalline sphere and rod-shaped TiO_2 nanoparticles: A facile route to bio-polymer grafting

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ABSTRACT

The goal of this report is to provide a versatile one step method based on UV irradiation in order to graft a bioactive polymer bearing sulfonate groups called poly(sodium styrene sulfonate) (polyNaSS) onto titanium nanoparticles (TiO_2 NPs) through covalent bond. The synthetic approach consists in two steps: (1) fabrication of TiO_2 nanocrystals with different shape and size by solvothermal method previous hydrolysis of titanium(IV)isopropoxide (TTIP) in the presence of benzyl alcohol (BzOH) and acetic acid (AcOH) at 180 °C, (2) TiO_2 NPs were immersed in a solution of monomer bearing sulfonate group and were placed under UV irradiation to induce the formation of radical to initiate the polymerization of the monomer. To demonstrate the success of the procedure, modified nano-surfaces were characterized by different techniques including colorimetric method by complexation, ATR–FTIR and SEM (EDS). This approach is promising to develop bio-active polymer–TiO_2 nanoparticles as carriers and further successful application in the field of regenerative-nanomedicine.

Contents

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Introduction

TiO_2 nanoparticles (TiO_2 NPs) have become a modern and widely used material in nanotechnologies due to their unique and tunable size-dependent electrical, magnetic, optical and chemical properties, which largely differ from those of bulk titanium oxide.[1,2] TiO_2 NPs have been applied to the preparation of biomaterials and biosensors because of their biocompatibility, stability and strong adsorptive ability on various electrode materials.[3–5] Some authors have utilized TiO_2 NPs to conjugate proteins in order to realize biosensors for chemical compound detection.[6,7] Other authors have conjugated aminoacids and protoporphyrin molecules by solvothermal method showing a good activity and structural properties of Hybrid TiO_2 NPs.[8,9] A major challenge in biomaterials is the design of material surfaces which provide optimal same time and promote durability of the implant.[10,1] It is evident that the titanium biomaterial's activity depends fully on its biocompatibility[11] and surface properties.[12] Studies on TiO_2 nanocrystals have mostly been focused on controlling structural and morphological properties without taking advantage of their surface chemical functionalities that may be of primary importance in various applications with biologic interest.[5,13] These applications originate from the unique physical and chemical properties of TiO_2 which depend not only on crystal phase and particle size, but also on particle shape.[14,15] Moreover, changing the shape of the nanoparticles allows for more flexibility and provides more modulation of electronic states than simply changing the size of the particles.[16] Controlling over the shape of TiO_2 NPs is therefore of key importance in the fabrication of new advanced materials with desired properties. Based on the considerations above, a surfactant-free synthesis of highly crystalline TiO_2–anatase nanospheres and nanorods was designed and reported. Size and shape of the growing seeds will be controlled by the coordinating action of the acetic acid that complexes them with the carboxylic ligand in the surface.[19] In recent years various molecules and polymers were grafted onto TiO_2 NPs in order to study the photocatalytic effect.[17,18] The photocatalysis reaction is well known to active oxygen species, by oxidative or reductive reductions under UV conditions.[19] These active oxygen species lead to a degradation reaction by attacking polymer chains and accelerating chain cleavage.[20]

Nakayama et al. have investigated the photodegradation properties of nanocomposite films composed by TiO_2 NPs chemically modified by propionic acid and n-hexylamine dispersed into PLA matrice.[21] The resulting of agglomeration TiO_2 NPs as drawback, reduces the efficiency of photodegradation by the decrease of interfacial areas between TiO_2 and polymer chain.[21] The LBPS team has shown that polymers bearing anionic groups such as carboxylate, sulfonate or phosphate can improve biological response (osteoblast cell adhesion and differentiation.[22–26] Recently, in order to improve the long-term osteo-integration of titanium, bioactive polymers bearing ionic groups such as sulfonate were covalently grafted by the "Grafting from" technique onto titanium surfaces.[25,27–29] First, titanium implants were oxidized to form titanium peroxides at the surface and then titanium samples were immersed in an aqueous solution of monomer (sodium styrene sulfonate (NaSS)) and placed under UV irradiations. Under UV, titanium peroxides form radicals to initiate the polymerization of monomer.[7,10,17,28] The use of UV irradiation permits to develop an easy process with fast reaction time and a low cost.[30] Here, we report the functionalization of titanium nanoparticles with bioactive polymers by using UV technology. To show the presence of polymers bearing sulfonate groups onto the nanoparticles, we have used different characterizations such as Fourier-transform infrared spectra recorded in attenuated total reflection mode (ATR–FTIR), scanning electron microscopy with Oxford energy dispersive spectroscopy (SEM–EDS). And to determine the rate of grafting of the polymers onto the nanoparticles, we have used a dye (Toluidine blue). This study grew up the need to better understand the interaction and behavior of TiO_2 NPs with biopolymer in order to open a new class of Hybrid Nanomaterials for regenerative nanomedicine applications.

Results and discussion

Here we report the synthesis and characterization of four types of TiO_2 NPs with different shape (sphere (**NP1**–**NP2**) and rods (**NP3**–**NP4**)) and size in order to evaluate the grafting of polyNaSS onto the nanoparticle surface.

Synthesis and characterization of TiO_2NPs

The non-aqueous-solvothermal method, used in this study for the synthesis of TiO_2 NPs was largely described previously, and is based on the Niederberger's "benzyl alcohol route" with some modifications.[31] The potentiality of this method was to tune nanoparticle shapes by varying the concentration molar ratios of reagents, i.e., TTIP/BzOH and AA/BzOH,[15] which is expected to control the rate of water in the reaction system. Fig. 1 shows representative TEM images of the synthesized TiO_2 NPs at different BzOH/TTIP and AA/BzOH molar concentration ratios, revealing the formation of nano-objects with different shape and size. In according with the previous study, varying the molar ratio of reagents (BzOH/TTIP and AA/BzOH) we modulated the shape and size of TiO2 NPs, obtaining Nanosphere (**NP1** and **NP2**) with a size of 7 and 10 nm respectively and nano-rods (**NP3** and **NP4**) with a size of 15 and 22 nm (Fig. 1-panel A). These results are in agreement with previous findings showing that the addition of acetic acid allowed the size and shape of TiO_2 NPs to be controlled under milder conditions (180 °C, reaction time ~18 h).[15]

The crystallographic properties of these NPs were confirmed by XRD analysis (Fig. 1-panel B) in which similar XRD patterns for nano-spheres (red-line) and nano-rods (black-line) exhibited well-defined peaks corresponding to pure anatase and confirming a high crystallinity of the samples. The peaks shown in the patterns corresponded to diffraction from the (101), (004), (103), (200), (105), (211) planes of anatase and no other phases were detected. The characteristic line broadening of diffraction peaks is due to the nano-sized nature of the anatase crystals. In addition, the (004) diffraction peak of nano-rods appears stronger and sharper compared to that of nano-spheres, reflecting the evolution along the [001] direction *c* axis of the anatase lattice, as described elsewhere.[17]

The mechanism of growth seems to involve two main steps as described previously[32]: (i) hydrolysis of titanium precursors to produce unstable hydroxylalkoxides, and (ii) subsequent condensation reactions by means of oxolation to form Ti–O–Ti.[33] This process is the direct esterification reaction between BzOH and AA with the elimination of benzyl acetate,[34] which is also able to confine the crystal growth. These findings confirms the relevancy of the procedure used to elongate sphere-shaped TiO_2 NPs according to a well-defined crystallographic direction, leading to the formation of highly crystalline rod-shaped particles with identical structure of nano-spheres. The studied system is thus suitable to investigate exclusively the influence of NP shape on the grafting of biomolecules and/or polymer for nanomedicine applications.

Grafting of polyNaSS onto TiO_2 NPs: mechanism and chemical physical evaluation

In previous studies, the grafting of poly (sodium styrene sulfonate) (polyNaSS) onto titanium surfaces by radical polymerization