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ScienceDirect
JOURNAL OF RARE EARTHS
JOURNAL OF RARE EARTHS, Vol. 32, No. 8, Aug. 2014, P. 727
www.re-journal.com/en/

Synthesis, characteristics, and antibacterial activity of a rare-earth samarium/silver/titanium dioxide inorganic nanomaterials

WU Jiang (吴 江)[1], ZHANG Guoliang (张国梁)[1], LIU Jie (刘 杰)[2], GAO Hongbing (高蕻冰)[3], SONG Chunxiang (宋春香)[3], DU Haoran (杜浩然)[3], ZHANG Li (张 丽)[3], GONG Zhongping (巩忠萍)[3], LÜ Yuguang (吕玉光)[3,*]

(1. School of Stomatology, Jiamusi University, Jiamusi 154002, China; 2. Department of Prosthodontics, The Affiliated Hospital of Medical College, Qingdao University, Qingdao 266003, China; 3. College of Pharmacy, Jiamusi University, Jiamusi 154002, China)

Received 30 December 2013; revised 1 April 2014

Abstract: An inorganic nanomaterials combination of Sm, Ag, and TiO_2 was synthesized using supercritical fluid drying (SCFD) combined with sol-gel techniques. The structure, photocatalysis and bacteriostatic activity of the materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XRPS), photocatalytic performance, and antibacterial activity experiments. The XRD results showed that the average particle diameter of $Sm/Ag/TiO_2$ was 14.62 nm and Ag and Sm ions were dispersed on the surface of TiO_2 in a highly dispersed, amorphous form. The TEM image showed that the size of the particle was 12 nm using the scherer formula. The XPS result showed that the element Sm was doped and Ag was loaded inorganic nanomaterials successfully. $Sm/Ag/TiO_2$ exhibited optimal photocatalytic properties at 600 ºC, the photocatalytic optimal proportion of $Sm/Ag/TiO_2$ was 2:2:100. When the molar ratio was 2:2:100, the bacteriostatic circle diameter was 16 mm for Staphylococcus aureus, the minimum bacteriostatic concentration was 200 μg/mL for white beads coccus, and the minimum bactericidal concentration was 2×10^4 μg/mL for white beads coccus. The SEM results showed that the antibacterial material attached to the candida albicans cell surface, cells appeared fold deformation. Therefore the inorganic nanomaterials $Sm/Ag/TiO_2$ had high temperature resistance, good photocatalytic and antibacterial characteristics in visible light.

Keywords: inorganic nanomaterials; samarium/silver/titanium dioxide; photocatalytic; antibacterial activities; rare earths

The oral microecosystem is often closely related to oral health and disease regardless of whether the microecosystem is balanced. In the clinical treatment of various oral diseases, the oral material must exhibit certain characteristics, including long-action, heat-resistance, non-toxicity, and color stability. Antibacterial agents must adapt to the oral environment to maintain the dynamic balance of the oral microbial ecology system and a long curative effect in clinical treatment.

At present, inorganic antimicrobial nanoagents are widely used in various fields[1,2]. Antibacterial agents are represented by either Ag or Ti series. However, the silver antibacterial agents have a broad antibacterial spectrum[3–5] and a high sterilization rate, and it is not easy for the microbes to develop resistance. However, these materials are expensive and unstable[6,7]. The effect of Ti-series antibacterial agents is limited by light conditions and the electron-hole pairs[8]; Dolgov et al.[9] proposed composite based on TiO_2 host doped with Sm^{3+} ions and co-doped with silver nanoparticles was proposed as a new fluorescent material. Combined plasmonic and sensitizing influences of silver on the Sm^{3+} ions were considered as reasons for enhanced Sm^{3+} fluorescence. However, rare-earth elements with 4f electron configurations are able to produce more unique electronic and nuclear structures, which can extend the life of the light-born electron hole. These rare-earth elements are less expensive, have higher color stability, and are less toxic than Ag^+. In addition, these elements provide excellent antibacterial, anticoagulant, anti-inflammatory, anti-cancer, and anti-tumor biological capabilities[10–13].

An inorganic nanomaterials $Sm/Ag/TiO_2$ is synthesized using supercritical fluid drying (SCFD) combined with sol-gel technology. The main objective of this experiment is to study the characterization, photocatalytic and antibacterial activities of the inorganic nanomaterials $Sm/Ag/TiO_2$.

1 Experimental

1.1 Preparation of the inorganic nanomaterials Sm/Ag/TiO_2

At room temperature, 10 mL of tetra butyl titanate was

Foundation item: Project supported by National Natural Science Foundation of China (21346006), National College Students' Innovation and Entrepreneurship Training Major Project (201310222013), the Department of Scientific Research Projects in Heilongjiang Province (B201015), and Scientific Research Project in Heilongjiang Province's Department of Education (12541821, 12541783, 12543078)

* **Corresponding author:** LÜ Yuguang (**E-mail:** lvyuguang2010@163.com; **Tel.:** +86-454-8610808)

DOI: 10.1016/S1002-0721(14)60133-2

used as a precursor, anhydrous ethanol was used as a solvent, and glacial acetic acid was used as an inhibitor of nitric acid, which was used as a catalyst to adjust the sol pH value from 2 to 4 to create a uniform, stable, and transparent TiO_2 sol-gel. The molar ratio of $Ti(OC_4H_9)_4$, C_2H_5OH, and H_2O was l:12:9. The synthesis of TiO_2 nanopowder required magnetic stirring at medium speed. Then, the inorganic Sm/Ag/TiO_2 nanomaterials was synthesized by mixing the powders of Ag, the rare-earth Sm, and TiO_2 in a muffle furnace (SX2 12-2.5) and then heating the mixture to different temperatures. Finally, the supercritical fluid extraction technique was used.

1.2 Characteristics analysis

The inorganic nanomaterials Sm/Ag/TiO_2 was analyzed by XRD (HR-6000) with a Cu target X-ray tube at 40 kV, 30 ma and scanning range of 10º–80º. The particulate morphology of Sm/Ag/TiO_2 was observed on TEM (HITACHI-800). The spectra of Sm/TiO_2 and Ag/Sm/TiO_2 was analyzed by X-ray photoelectron spectroscopy (ESCALAB250).

1.3 Photocatalytic performance

In this experiment, evenly configured methyl orange solution was mixed with the catalyst, the UV lamp was turned on, and photo-catalytic degradation was performed after the UV light became stable. At the same time, a magnetic mixer was used to oxidize the solution. Samples were collected at specific times; the photocatalyst was centrifuged until it became clear. Then, the absorbance of the methyl orange solution was measured using a spectrophotometer (UV-2501, Shimadazu).

The decolorization rate is provided by Eq. (1):

$$\eta = [(A_0 - A_t) / A_0] \times 100\% \quad (1)$$

where η is the decolorization rate, A_0 is the light intensity before initial absorbance of the solution, A_t is the intensity of the solution after light absorbance, and t represents time.

1.4 Antibacterial activity experiments

In this experiment of bacteria suspension configuration, the staphylococcus aureus (No. ATCC29213) and white beads coccus (No. ATCC90028) were cultured in BHI broth and sandcastle agar culture medium (Wuxi Saiwei Trading Co., Ltd.), respectively. Second passages were used after sub-culturing. A single colony was selected from both the BHI broth and sand castle mediums; a hemacytometer was used to prepare 1×10^5 CFU/mL of cell suspensions of both microbial types, which were then incubated in a 37 ºC incubator (in Tianjin) with exposure to oxygen for 24 h before being placed aside.

In this bacteriostatic ring experiment, sterile cotton swabs were acquired from staphylococcus aureus suspensions and evenly spread in three layers on a plate surface with agar. Then, the plates were covered and placed at room temperature for 3 min before 5-mm-diameter holes were created on the medium surface. The holes were not less than 24 mm apart, and every hole was not less than 15 mm from the flat edge. Then, 0.2 mL of different antibacterial concentrations was added in the holes and cultivated at 37 ºC for 24 h in visible light. The inhibition rate was calculated by measuring the diameter of the inhibition circle around each hole.

In this liquid dilution experiment, the antibacterial agents, which were mixtures of different concentrations of suspension liquids with normal saline, were heated for 2 h at 120 ºC. Then, the candida albicans suspension was mixed with the antibacterial agent suspension. The solution in which the antibacterial agent was not used served as the positive control, and the solution in which the microbe was not used served as the negative control. After incubation with oxygen exposure for 24 h under 37 ºC in visible light, 0.02 mL of the mixture liquid was dropped on agar medium. After 24 h, the minimum inhibitory concentration (MIC), i.e., the lowest concentration of an antimicrobial that is required to inhibit growth of a microorganism after overnight incubation, and the minimum bactericidal concentration (MBC), i.e., the minimum concentration of antibiotic required to kill a microbe, were recorded. The experiment was repeated three times, and the results were averaged.

For the SEM analysis, 3 mL of 1×10^5 CFU/mL candida albicans solution were cultured into 3 mL of sandcastle medium, and then, 0.12 g of Sm/Ag/TiO_2 antibacterial powder was added on 10 mm^2 glass slides and mixed with the bacterium solution. Then, the slides were incubated at 37 ºC for 48 h in visible light; the slides were then removed, washed with PBS three times, fixed with glutaraldehyde, dehydrated in ethanol, dried, and sprayed. Finally, the samples were observed using SEM.

2 Results and discussion

2.1 XRD analysis

The grain growth and transitional phases of Ag/TiO_2 and Sm/Ag/TiO_2 were compared. Using XRD analysis (Fig. 1), the crystalline phases were observed to be in an anatase TiO_2 powder, and TiO_2 anatase characteristic peaks were present at 2θ=25.2º, 34.58º, 37.81º, and 52.36º. According to the Scherrer equation, the average particle diameter of Ag/TiO_2 was 14.01 nm; however, the average particle diameter of Sm/Ag/TiO_2 was 14.62 nm. Because the Sm/Ag/TiO_2 characteristic peaks were observed in the Sm^{3+} ions, Sm^{3+} ions were highly fragmented in the powder, and the material was a nanomaterial. According to XRD analysis of different proportions of Sm/Ag/TiO_2 at 500 ºC for 100 min, the optimal molar ratio of Sm/Ag/TiO_2 is 2:2:100 (Fig. 2). Ag and Sm ions