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Feature article

Developing titania-hydroxyapatite-reduced graphene oxide nanocomposite coatings by liquid flame spray deposition for photocatalytic applications

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ABSTRACT

Nanostructured titania has been extensively investigated for photocatalytic applications. Persistent challenge yet is how to effectively promote adhesion of microorganisms on the material surface for consequent enhanced photocatalytic disinfection. Here we report fabrication and characterization of titania-based nanocomposite coatings with addition of hydroxyapatite-reduced graphene oxide (HA-rGO). The nano features of TiO_2, HA, and rGO were well retained during liquid flame spray deposition. Photocatalytic activities of the coatings were examined by degradation of methylene blue and sterilization testing of *Escherichia coli* bacteria. Addition of HA-rGO effectively increased the specific surface area of the coatings and markedly enhanced adherence of the bacteria for subsequent extinguishment. The TiO_2–10 wt.% (HA-rGO) coating showed the best photocatalytic performances and further overloading of HA-rGO resulted in enwrapping of TiO_2 particles, resulting in deteriorated degradation activity. The results give clear insight into fabrication of novel photocatalytic nanocomposites by suspension thermal spray route for enhanced performances.

1. Introduction

Bacterium-related environmental issues like presence of microorganisms in drinking water have been gaining intensive concerns globally [1]. Pathogenic microorganisms, such as *Escherichia coli* (*E. coli*), *Virbio cholerae*, *Listeria monocytogens*, *Shigella* spp., and *Pseudomonas* spp., etc., in water resources lead to severe water-borne illness [2–4]. Various physical, chemical, and biological methods are therefore developed to remove microorganisms and/or pollutants [5]. To date, chlorination has been widely used for water treatment, including disinfection process for drinking water supplies and the tertiary treatment of wastewater effluents [6]. It is effective in inactivation of bacteria and most viruses [7]. However, the processing route is becoming of increasing concern due to the formation of potentially harmful chloro-organic disinfection by-products exerting carcinogenic and mutagenic influence on mammals [7,8]. Hence, new alternative disinfection techniques are urgently needed. Compared with conventional water treatment methods, such as UV irradiation, filtration and ozonization, photocatalysis showed great potential for inactivation of pathogenic microorganisms and has attracted much attention in recent years due to its advantages like nontoxicity, excellent degradation capability and cost efficiency [9–11].

Since the discovery of photo-induced splitting of water on titania electrodes by Fujishima and Honda [12], TiO_2 has been one of the key materials for photocatalytic applications and was widely used [9–11,13]. Inspired by the early work of Matsunaga et al. reported in 1985 [14], many research groups explored TiO_2-based photocatalysts and found successful killing of different microorganisms including bacteria, viruses, algae, fungi or protozoa [2,15]. Hydroxyl radical ($^{\bullet}OH$) generated by photocatalysis is found to oxidize and/or diffuse through cell wall/membrane, subsequently causing oxidation of intracellular coenzyme [16,17]. However, in most cases, TiO_2 can only decompose substances that come into contact, and it fails to work while there is no light [17,18]. Taking into account the prerequisite of intimate contact between bacteria and the antibacterial material, the material must essentially favor attachment of bacteria [17]. There are many techniques to improve the adsorption behavior and photocatalytic activities of TiO_2 [19]. Among them, heterogeneous photocatalysis system has been well established to improve the performances [20,21].

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), which has a similar chemical composition to the mineral component in natural bones and teeth, is of great interest in bone and tissue engineering. It has excellent biocompatibility, bioactivity and high affinity to proteins and lipids [22,23]. Use of HA or HA-based composites as additives in titania-based composites was therefore attempted to promote the recruitment of microorganisms or organics for subsequent photocatalytic degradation [17]. In addition, research efforts on HA/nano-carbon composites, such as HA-graphene composites, have been reported [24–26]. Progress has been made recently in fabrication of graphene-containing inorganic composites attributed to the promising properties of graphene, including unique electronic property, high transparency, flexible structure and large theoretical specific surface area [24,27,28]. Previous studies suggested that the incorporation of graphene could enhance the mechanical properties and bioactivity of HA-based composites [24–28]. Graphene-based nanomaterials could also inhibit the growth of *E. coli* while showing minimal cytotoxicity [29]. Moreover, like other carbon nanomaterials such as CNTs and fullerene, graphene-based materials have also been explored for potential photocatalytic applications [30]. It was reported that graphene could enhance the charge transfer of electrons and decrease the recombination of electron-hole pairs, which in turn improved the photocatalytic properties of TiO_2 [30,31].

For photocatalytic applications, several practical problems arise from the use of catalysts in powder form [21,30], such as difficulties in separating them from suspension or aggregation of particles in suspension [17]. Therefore, the form of coating/film is more appropriate for photocatalysts [32], which has been extensively investigated by using various processing techniques like sol-gel, chemical vapor deposition, electro-deposition, hydrothermal and thermal spray [17,33,34]. Liquid thermal spray uses liquid, for instance solution or suspension, as the starting feedstock and shows great promises in making functional coatings from nanoparticles [35–37]. Antimicrobial glassy coatings were successfully fabricated by high velocity suspension flame spray on titanium plates without degrading the substrate or forming chemical byproducts [36]. Liquid thermal spray processing route can effectively avoid possible phase transformation of sprayed materials and accomplishes favorable microstructural features such as desired porosity and high specific surface area, facilitating functional performances [17,37–39].

In this work, HA-rGO nanocomposite slurry was prepared by adding rGO sheets into the solution for synthesizing HA by the wet-chemical approach [24]. According to our previous findings that addition of 10 wt.% HA brought about the most significantly promoted photocatalytic performances of titania-based coatings [17], TiO_2–10 wt.%(HA-rGO) nanocomposite coatings were fabricated by liquid flame spray. Enhanced adherence of *E. coli* bacteria and adsorption of methylene-blue were revealed and elucidated, showing great potential of the coatings for photocatalytic applications.

2. Materials and methods

Commercial aluminum wire (Al, Ø2 mm, Beijing General Research Institute of Mining &Metallurgy, China), TiO_2 powder (pure anatase, 5 ~ 10 nm, Aladdin, Shanghai, China), hydroxyapatite (HA, lab-made needle-like particles of ~200 nm in length and 20–40 nm in diameter) and HA-reduced graphene oxide (HA-rGO) nanocomposite slurry (lab-made HA–10 wt.%rGO) were used. The HA or HA–10 wt.%rGO slurry was synthesized by a wet-chemical approach described in detail previously [24]. 316L stainless steel plates with the dimension of 20 × 20 × 2 mm in length, width and thickness, respectively, were used as the substrates. Prior to the deposition of the titania-based coatings, an aluminum coating with ~100 μm in thickness was pre-coated on the substrate to facilitate adhesion of the nanocomposite layer. The high velocity arc spray system (TLAS-500C, China) was employed to deposit the Al coatings. *Escherichia coli* bacteria (*E. coli*, ATCC 25922) were typically selected for bacterial adherence testing. Aqueous solution (5 ppm) of methylene blue (MB, Aladdin, Shanghai, China) was used as a model pollutant.

A series of suspensions (HA-rGO, TiO_2–10 wt.%(HA-rGO) and TiO_2–30 wt.%(HA-rGO)) were prepared by suspending 5 g of each sample in 150 ml deionized water and mixing in an ultrasonic disintegrator for 10 min before the spraying. The coatings were then fabricated by liquid flame spray (DS 8000, Eutectic Castolin, Germany). A suspension injector with the diameter of 1.5 mm was positioned just next to the flame torch, and the angle between the injector and flame was 30°. The pressure of the atomizing air was 0.7 MPa and the suspension feeding rate was 40 ml/min. Pressure of oxygen and acetylene was 0.5 MPa and 0.1 MPa, respectively. The flow rate of acetylene was 0.8 m^3/h and the spray distance was 200 mm.

Phases of the samples were detected by X-ray diffraction (XRD, Bruker AXS, Germany) with a scanning rate of 0.1°/s using monochromatic Cu-Ka radiation operated at 40 kV and 40 mA. Microstructural features of the powder and coatings were examined using field emission scanning electron microscope (FESEM, FEI Quanta FEG250, the Netherlands). Specific surface area of the coatings was measured using the Brunauer, Emmett, and Teller (BET) method by adsorption of nitrogen gas on ASAP 2020 M apparatus at 77.3 K. The BET surface area was calculated over the relative pressure range of 0.05–0.20 MPa. For comparison purpose, pure HA, pure TiO_2 (TO) and TiO_2 with 10 wt.%HA (TiO_2–10 wt.%HA, TO10H) coatings were also investigated in this study.

Luria broth (LB, Aladdin, Shanghai, China) medium used in this study comprised 10 g tryptone, 10 g sodium chloride, and 5 g yeast extract in 1 l deionized water. After inoculation of a single colony of *E. coli*, the media were shaken at 150 rpm for 24 h at 30 °C. Bacteria were then harvested by centrifugation at 2000 rpm for 5 min. After removal of the supernatant, bacteria were washed with phosphate-buffered saline (PBS) and resuspended in PBS at a concentration of 5×10^6 CFU/ml. The coating samples were put into a 12-well plate and then 2 ml of the bacterial suspension was added to each well. The plate was incubated at 30 °C for 6 h in dark for bacterial adhesion. For SEM observation, the samples were first rinsed with PBS to remove non-adherent bacteria. Then the samples were fixed in 2.5% glutaraldehyde at 4 °C overnight and rinsed twice in PBS. Further dehydration and critical-point drying steps were conducted using a graded series of ethanol/water solutions as described in another paper [17]. Enumeration of attached cells was carried out by counting the cells from the SEM images. Digital images were taken randomly from at least five locations for each sample.

Photocatalytic degradation activity of the coatings was evaluated by degradation of MB aqueous solution. Each sample was put into to a Ø9 cm Petri dish with 20 ml MB solution (5 ppm) followed by UV-irradiation. The irradiation was conducted using a 15 W UV lamp (PHILIPS, TLD15W BL) with the typical wave length of 365 nm, and the distance between the UV light source and the samples was 150 mm. Variation of MB concentration as determined by the absorbance at 664 nm was analyzed using a spectrophotometer (SpectraMax 190, Molecular Devices, USA).

Photocatalytic sterilization activity of the coating samples under UV-illumination was assessed using a similar suspension method reported previously [17]. The nutrient agar culture medium (Huankai Microbial Sci. Tech. Co. Ltd., China) used in this study comprised 33 g nutrient agar cultured in 1 l deionized water, and was autoclaved at 120 °C for 15 min. Then 15 ml of the nutrient agar media were poured into each Ø9 cm Petri dish. After UV-irradiation