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Apatite-Coated Ag/AgBr/TiO_2 Visible-Light Photocatalyst for Destruction of Bacteria

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Recently, TiO_2 has been introduced as one of the most promising photocatalysts in the degradation of different pollutants[1−3] and the destruction of bacteria.[4−7] The main drawbacks of the low quantum yields and the lack of visible-light utilization hinders its practical application. To overcome these problems, numerous studies have been recently performed to enhance the photocatalytic efficiency and visible-light utilization of TiO_2 which include impurity doping, metallization,[8−12] and sensitization.[13,14] Chun Hu et al.[13] demonstrate that AgBr on P-25 TiO_2 support is the main photoactive species for destruction of the bacteria under visible light. Their evidence indicates that AgBr is the visible-light active component of the catalyst and that Ag^0 species on the surface of the catalyst is probably contributing to enhancing the electron−hole separation and interfacial charge transfer. On the other hand, Nonami et al.[15] showed that a multifunctional composite material titanium dioxide covered with apatite can adsorb bacteria without exposure to the light. They also reported that whenever TiO_2 is coated with apatite, the photocatalytic activity decreased.

In this Communication, we prepared Ag/AgBr/TiO_2 covered apatite with deposition of hydroxyapatite as adsorption bioceramic and AgBr as photosensitive materials. One gram of P-25 TiO_2 and 0.05 g hydroxyapatite was added to 100 mL of distilled water, and the suspension was stirred magnetically. Then 1.2 g of cetyl methyl ammonium bromide (CTAB) was added to the suspension, and while the mixture was stirred magnetically, 0.21 g of $AgNO_3$ in 2.3 mL of NH_4OH (25 wt % NH_3) was quickly added to it. The resulting suspensions were stirred at room temperature for 18 h. Then the product was filtered, washed with distilled water, and dried at 80−110 °C. Finally, the prepared photocatalyst was calcined in air at 500 °C for 3 h. Other catalysts such as Ag /TiO_2 (the Ag concentration in the sample was 5% mol),[16] apatite-covered TiO_2 in SBF solution,[17] and Ag/AgBr/TiO_2[13] were also prepared to make a comparison of the efficiency and activity of the catalyst with them. Figure 1 shows the XRD patterns of the catalysts. The calcined photocatalyst displayed crystalline reflection peaks that are characteristic to the anatase and rutile TiO_2 and also Ag, AgBr, and hydroxyapatite (HAP).

The energy dispersive X-ray (EDX) spectrometry clearly shows the presence of Ti, Ag, Ca, and P elements on the surface of catalyst. Figure 2 shows scanning electron microscopy (SEM) of apatite-covered Ag/AgBr/TiO_2. The SEM pattern indicated that the TiO_2 surface is coated by apatite particles, and the average size of TiO_2 is about 100 nm.

Photocatalytic activity experiments on Ag/TiO_2, Ag/AgBr/TiO_2, and apatite-covered Ag/AgBr/TiO_2 for degradation of *E. coli* (ATCC 8739) were carried out by preparing 1×10^7 colony-forming units (CFU/mL) bacteria cell concentration. The photocatalytic reaction was started by irradiation of the mixture under visible light.

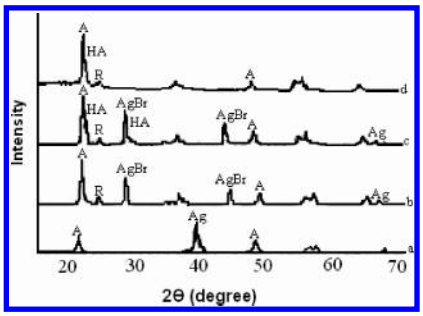

Figure 1. XRD pattern of (a) Ag/TiO_2, (b) Ag/AgBr/TiO_2, (c) apatite-covered Ag/AgBr/TiO_2, (d) apatite-covered TiO_2 (A, anatase; R, rutile; HA, hydroxy apatite).

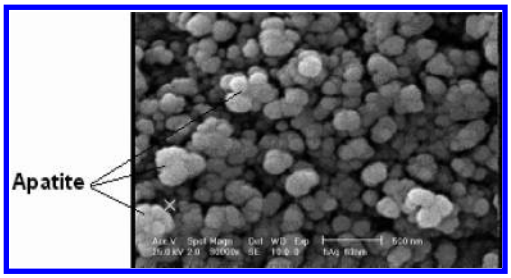

Figure 2. Scanning electron microscopy (SEM) of apatite-covered Ag/AgBr/TiO_2 (the scale bars in the figure represent 500 nm).

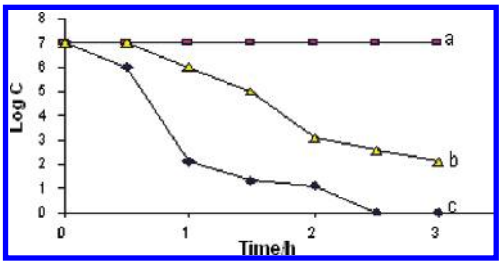

Figure 3. The efficiency of the *E. coli* inactivation (1×10^7, 30 mL) in aqueous dispersions including 12 mg of catalysts (a) Ag/TiO_2, (b) Ag/AgBr/TiO_2, and (c) apatite-covered Ag/AgBr/TiO_2 under visible light.

A 250-W mercury lamp (MBF−Osram) placed over a petri dish was used as a light source. The reaction mixture was stirred with a magnetic stirrer to prevent the precipitation of the photocatalyst, and in certain time intervals, 2 mL of the reaction mixture was diluted with 0.9% saline. Then 1 mL of diluted solution was incubated at 37 °C for 24 h on sybeen caseion digest agar, and the colonies were counted. Figure 3 shows photocatalytic degradation of *E. coli* over Ag/TiO_2, Ag/AgBr/TiO_2, and apatite-covered Ag/AgBr/TiO_2 photocatalysts. Unlike Ag/TiO_2, Ag/AgBr/TiO_2 photocatalyst exhibited a high activity for *E. coli* degradation under visible light. The new synthesized photocatalyst showed higher photoactivity compare to Ag/AgBr/TiO_2 photocatalyst.

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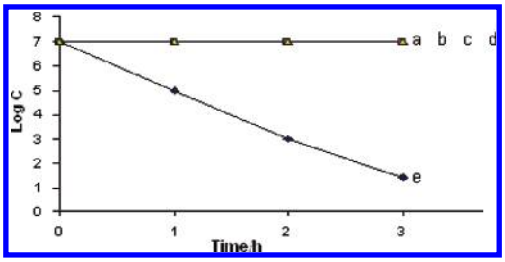


Figure 4. Temporal course of the *E. coli* inactivation (1×10^7, 30 mL) in aqueous dispersions containing 24 mg of catalysts (a) Ag/TiO_2, (b) $Ag/AgBr/TiO_2$, (c) apatite-covered TiO_2, (d) TiO_2/P-25, and (e) apatite-covered $Ag/AgBr/TiO_2$ under dark condition.

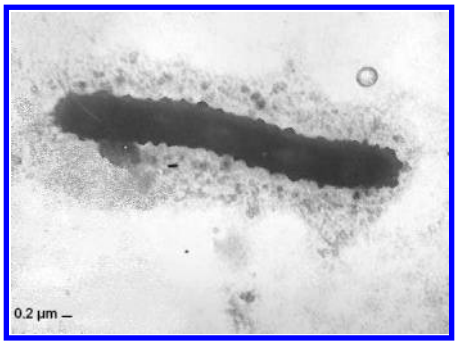
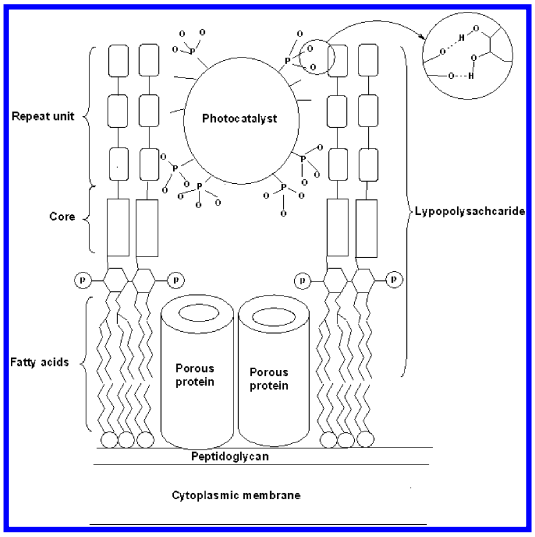


Figure 5. TEM image of apatite-coated $Ag/AgBr/TiO_2$ nanoparticles adhere to the outer cell of *E. coli* in dark media.

Scheme 1. The Outer-Cell Wall



To measure the catalytic activity under dark media, 24 mg of each photocatalyst was added to bacterial suspension, and the experimental was carried out under similar conditions.

The result demonstrates that only apatite-covered $Ag/AgBr/TiO_2$ can inhibit the growth of bacteria (Figure 4).

The inactivation of *E. coli* was evaluated in the dark in the presence of apatite-coated $Ag/AgBr/TiO_2$ photocatalyst. As a result of transmission electron microscopy (TEM) investigation, that outer membrane of the cell was not damaged (Figure 5), which is due to the catalyst nanoparticles adhering to the outer membrane of the cell. Hence the bacteria cannot nourish from aqueous media.

During the preparation steps of the sample for TEM including double washing with buffer phosphate and addition of solvents, adsorbed particles of catalyst were stable. Thus, it seems that hydrogen bonding between phosphate groups of apatite and polysaccharide strings of membrane is formed whenever the apatite-coated $Ag/AgBr/TiO_2$ particles adsorb to cell wall (Scheme 1); a strong evidence for this interaction is that the EDX spectroscopy result indicates that the surface of catalyst is covered by a phosphate group near to 50%.

The inactivation of *E. coli* is mainly due to destruction of the cell wall by various reactive species (e.g., OH radical, $HO_2^{\bullet}$, and H_2O_2).[18,13] However, this photocatalyst has the ability to adhere to the outer cell of *E. coli* so it enhances the photocatalytic activity under visible light.

In conclusion, the prepared $Ag/AgBr/TiO_2$-covered apatite has a high ability to adsorb bacteria in the dark and also has a significantly high photocatalytic activity under visible light.

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