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Apatite-coated titanium dioxide photocatalyst for air purification

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Abstract

A multifunctional composite material, titanium dioxide covered with apatite, has been developed for application in air purification and as an antimicrobial, antifungal, and antifouling coating. This composite can absorb and decompose bacteria and various other materials. TiO_2 powder was soaked in a simulated physiological solution containing phosphate ions for periods of about 1 h at 37 °C. The composite material has the following characteristics: (1) the apatite adsorbs contaminants even without exposure to light; (2) material adsorbed by the apatite is decomposed by the titanium dioxide photocatalyst on exposure to light; (3) the apatite is used as an inert spacer, allowing blending of the material with resins, organic coatings, and other organic materials; (4) though the photocatalyst requires some time to fully decompose organic materials, capture of contaminants by the apatite ensures complete decomposition.

Keywords: Titanium dioxide; Photocatalysis; Composite; Apatite; Low temperature ceramic processing

1. Introduction

When exposed to light, a titanium dioxide photocatalyst generates an extremely strong oxidizing power that oxidizes harmful substances, such as microbes, molds, odors, or soils that come into contact, and eliminates them by decomposition into carbon dioxide, water and other small molecules [1–4]. Titanium dioxide works as a catalyst and does not undergo any change, so that it can theoretically be used indefinitely. However, the uses of titanium dioxide are limited, because, when blended into organic materials such as organic paint, textile, plastics, and paper, it tends to photochemically decompose these materials. There are other problems as well. For example, due to its lack of action to attract substances, it can only decompose substances that happened to have come into contact, and this decomposing action fails to work when there is no impinging light.

In contrast, apatite is chemically inert. It has been used for chromatographic columns by taking advantage of its ability to selectively adsorb protein, for respirators by capitalizing on its ability to adsorb pollen, and for hand creams by commercializing its ability to adsorb bacteria. However, since apatite is only capable of adsorption and is incapable of decomposition, saturation will be reached over time, and the adsorption action weakens as well [5].

We have developed a multifunctional ceramic composite material by covering the surfaces of a titanium dioxide photocatalyst with apatite, where the apatite adsorbs bacteria and organic substances, and the titanium dioxide decomposes them.

A variety of apatite-covering methods, such as sintering and aqueous solution growth, are conceivable. However, since our objective here is to develop an environmental purification (decontamination) material, we want to select a fabrication method which is as environmentally friendly and as low in cost as possible. The wet process using an aqueous solution requires more than a week to produce apatite, leading to increased cost. Since sintering at high temperatures is normally required to obtain crystals of apatite, the process is also energy intensive.

We therefore focused our attention on a type of biomimetic material processing, which came into use in recent years as an artificial bone synthesis method. This method represents an environmentally harmonizing material process that emulates some functions of a living organism. More specifically, this new ceramic synthesis process attempts to synthesize ceramics at room temperature and atmospheric pressure by mimicking in vivo mineralization. In vivo inorganic component synthesis processes are characterized by extremely small loads on the environment

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and can, therefore, be regarded as ideally environmentally harmonizing materials processes. In addition to being low in energy consumption, the process is free from harmful emissions. Even when its products are discharged into the environment, they tend not to pose any problems.

In artificial bone research, a method to synthesize apatite is being pursued by which apatite is deposited on the surfaces of glass, silica and similar materials from a supersaturated “pseudo-body solution” containing inorganic ions in approximately the same concentrations as their counterparts present in human body fluid. The precipitation of apatite crystals will take 1–2 weeks or longer. For biological materials such as artificial bone, long fabrication time and high cost may not become an impediment because they are generally expensive. However, an environmental material must be low-cost and fast to produce. When emphasis is placed on productivity, it is desired to complete the synthesis in a much shorter time, preferably within several hours.

It is assumed that in the pseudo-body fluid, clusters of calcium phosphate ($Ca_9(PO_4)_6$) are generated. These clusters are found as basic units in crystal structures of all calcium phosphate compounds that are considered to have a bearing on bone production. We believe that all biological calcium phosphate compounds may be produced through the aggregation of these clusters. As has already been discussed [6], octacalciumphosphate $Ca_8H_2(PO_4)_6$ (OCP) is under physiological conditions more easily formed than apatite. There is therefore the possibility to accomplish the synthesis in a shorter time by making a detour by way of OCP rather than producing a precipitate of apatite directly. We adjusted the chemical composition in such a manner that OCP would precipitate, and immersed titanium dioxide in a pseudo-body solution held at 37 °C, in order to let apatite be produced on the surface of the titanium dioxide under physiological conditions.

2. Experimental procedures

A pseudo-body solution (hereafter named PBS) with a phosphate ion concentration which is 9.5 times that of the human blood plasma was prepared by dissolving reagent NaCl, KCl, KH_2PO_4, Na_2HPO_4, $CaCl_2$, $MgCl_2 \cdot 6H_2O$ in distilled water. The composition is given in Table 1. The solution was buffered at pH 7.30–7.65.

TiO_2 thin film [7] or powder was immersed in PBS. After being soaked in PBS for 1 h, they were removed from the solution, washed with distilled water and dried at 37 °C.

The surface structure of the specimens before and after soaking in PBS was analyzed using thin-film X-ray diffraction (RAD-RVB, Rigaku Co., Tokyo, Japan) and SEM observation. The absorbent and photocatalytic properties of the TiO_2 and apatite-coated TiO_2 were characterized by the absorption and decomposition of acetaldehyde. Acetaldehyde, a harmful chemical material, was used to characterize the photocatalytic activity of the specimen. The UV radiation ($1.0\,mW\,cm^{-2}$) from a black light source (10 W) passed into a reactor ($1300\,cm^3$) and irradiated the specimen in an acetaldehyde atmosphere (500 ppm) at room temperature for 2 h.

3. Results and discussion

As shown in Fig. 1, extremely small crystals of OCP formed on the surface of the thin film of titanium dioxide within an hour, and began to cover the entire surface. At longer contact time, the OCP crystals broke up and changed into apatite. This apatite contained only calcium and phosphorus, whereas magnesium and sodium, which were also present in the pseudo-body solution, were not detected. Judging from the measured calcium-to-phosphorus molar ratio of approximately 1.5 as posed to the stoichiometric molar ratio of 1.76, the crystals were a calcium-deficient apatite. Apatite found in bone and the enamel of teeth that are in the early stages of eruption is reported to be calcium-deficient. Microscopic observation of the cross-section of the specimen as shown in Fig. 2, revealed that an apatite film with a thickness of approximately 0.7 μm has formed on the approximately 0.3 μm thick titanium dioxide layer. The relative density of apatite within this film was approximately 40%. The crystals have a plate-like shape, measuring approximately 0.1–0.5 μm in length and 2–10 nm in thickness. Most of them have grown in the vertical direction on the titanium dioxide film. As a result, an ideal structure has developed, in which the greater part of the surface area of the titanium dioxide film remains exposed while, at the same time, being covered by a layer of apatite. In terms of crystallography, euhedral crystals of apatite are hexagonal columns in shape. However, as mentioned in our previous report [5], the crystals observed here were considered to be plate crystals that have grown in the direction of the *c* axis.

Our investigations about the mechanism of apatite formation in living organisms have shown that, in many cases, the crystallization passes through a precursor stage. The ultimately formed apatite retained the geometry of its precursors and is, thus, plate-like in shape. As those precursors, we can think of OCP, tricalcium phosphate (TCP), amorphous calcium phosphate (ACP) and similar calcium phosphate compounds. Of these calcium phosphate compounds,

Table 1
Concentration of pseudo body solution

Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	${HCO_3}^-$	${HPO_4}^{2-}$	${SO_4}^{2-}$
145.0	4.2	0.5	0.9	141.0	0	9.5	0

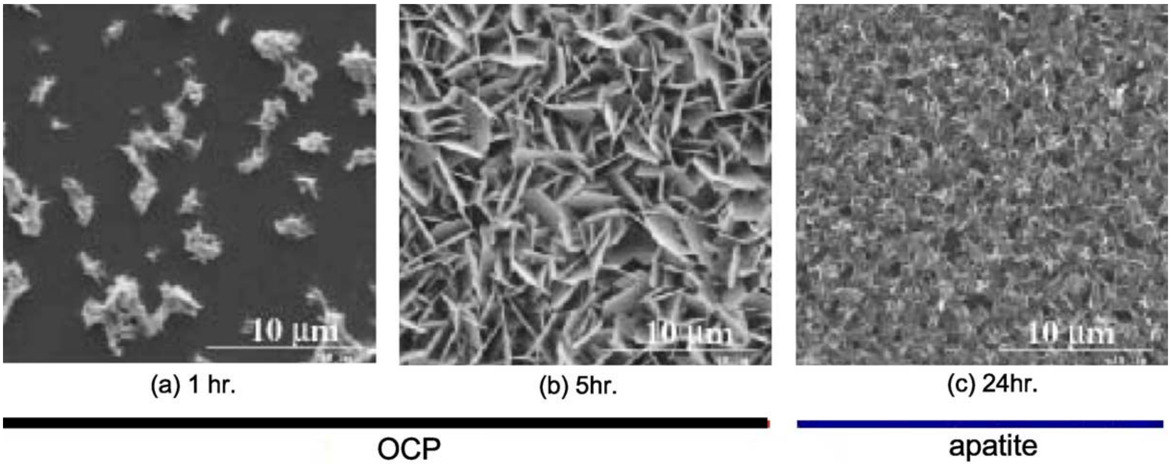


Fig. 1. Appearance of calcium phosphate particles formed on thin films of titanium dioxide.

only OCP and TCP form euhedral crystals with plate-like shape. Euhedral crystals of OCP are plates extending in the direction of the *c* axis, while those of TCP are hexagonal columns that are vertical with respect to the *c* axis. Since the crystals of the apatite obtained are plates grown in the direction of the *c* axis, they are close to those of OCP. We therefore assume that the plate-shaped apatite formed from OCP as its precursor.

Since the formation of apatite calls for high alkalinity and high temperature, the environment in a living organism is not suited for the formation of apatite. On the other hand, OCP has its optimum formation condition under physiological conditions, or at approximately 40 °C and between pH 5.9 and 7.0. At temperatures or pH readings higher than these formation conditions, the hydrolysis of OCP to apatite occurs.

OCP contains the structural motif of apatite within its crystal structure. The portion that takes on apatite's crystal structure forms a layered formation. Water-containing layers exist in between the layers. Brown et al. reported [8] that if these water-bearing layers are removed, OCP turns into apatite. There exists a crystallographic orientation relationship between OCP and the formed apatite, and this reaction is referred to as a topotactic relationship. Thus, the formation of apatite in the living organism presumably takes place by way of OCP as a precursor.

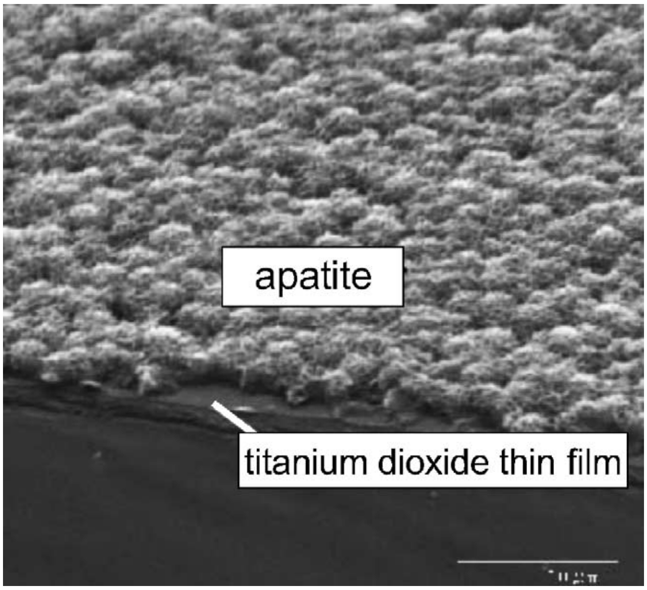


Fig. 2. Apatite films formed on titanium dioxide layer.

By varying the composition of the pseudo-body solution and the immersion conditions (such as temperature and time), it is possible to vary the apatite's geometry, size, density, thickness and the time required for precipitation. The process via OCP allows to develop the apatite structure in approximately 1–10 h, making it possible to obtain crystals of apatite in a far shorter time than would be required for the direct growth.

When transparent materials such as glass are coated with apatite, their transparency is somewhat impaired. However, the loss of transparency due to the coating of titanium dioxide and apatite is small.

Unlike other antibacterial agents such as silver, the titanium dioxide photocatalyst cannot demonstrate its antibacterial action when no light is hitting it. On the other hand, the composite material containing apatite, is able to adsorb and eliminate bacteria such as *Escherichia coli* even under dark conditions. During antibacterial testing, apatite adsorbed large numbers of bacteria as shown in Fig. 3 in an experiment conduced under light-shielded conditions.

We prepared a specimen by forming film of titanium dioxide on ceramic fibers, and then coating these fibers with apatite as shown in Fig. 4. By using this specimen, we decomposed acetaldehyde. As a result, the acetaldehyde concentration decreased by more than 100 ppm in the presence of the apatite-coated material even under light-shielded conditions as shown in Fig. 5, suggesting that apatite has the ability to adsorb aldehydes. Virtually no adsorption occurred with titanium dioxide-only specimens just as is the case with blank testing using no specimens. With both types of specimens, the concentration begins to decrease

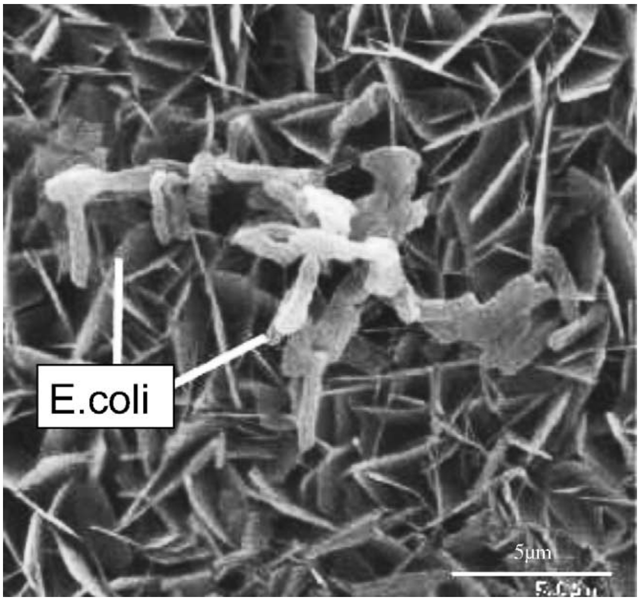


Fig. 3. *Escherichia coli* adsorbed on apatite.

once light irradiation is started because of the photocatalytic activity.

As discussed above, the apatite of the apatite-composed material adsorbs bacteria and aldehydes even when no light is irradiated. Therefore, the apatite phase is capable to adsorb such substances at night or in places where no light is available, and the titanium dioxide decomposes those substances when light becomes available, thus avoiding the drawback of conventional photocatalysts that are inactive without light.

Next, we have applied a coating to the powder as shown in Fig. 6. As is the case of thin films, the powder was simply soaked in the pseudo-body solution. However, in order to uniformly coat the particles, they were soaked in the solution while being slowly stirred at 37 °C for an hour to prevent settling down of the powder. As a result, titanium dioxide particles coated with apatite were obtained. The weight ratio of apatite to titanium dioxide was quantitatively determined from the results of powder X-ray diffraction analysis and was approximately 6% by weight.

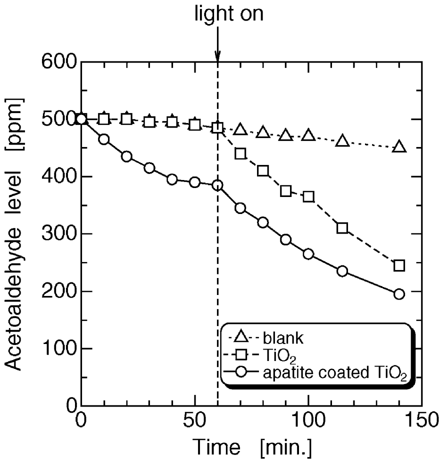


Fig. 5. Changes in acetaldehyde levels with experimental duration.

Fig. 7 shows the results of experiments conducted to remove NO (nitrogen oxides) using sintered tiles coated with apatite-covered titanium dioxide. A specimen cut to 10 cm per side is placed inside a hermetically sealed container with an internal volume of 2.0 l. This container is then filled with a simulated contaminated gas containing NO whose concentration has been adjusted to 25 ppm. This is the concentration in automotive exhaust emission. With the help of a detecting tube, measurements are periodically made to determine the NO concentrations in the container. With titanium dioxide alone, the concentration of the NO decreased if the catalyst was irradiated. However, under dark conditions, there was virtually no adsorbing action just as was the case with blank testing.

On the other hand, a specimen coated with apatite-coated titanium dioxide adsorbed the NO even without light irradiation. When light was irradiated, decontamination continued and the concentration of the contamination gas decreased to approximately 10 ppm after 1 h, from the original NO concentration of 25 ppm. This demonstrated the adsorbing action of the apatite. What is more, it has been shown that the decomposition power of the apatite-coated titanium dioxide under light-irradiated conditions is virtually no different

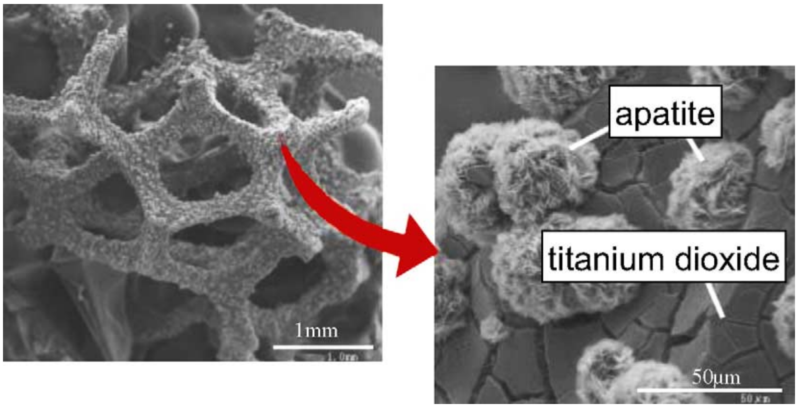
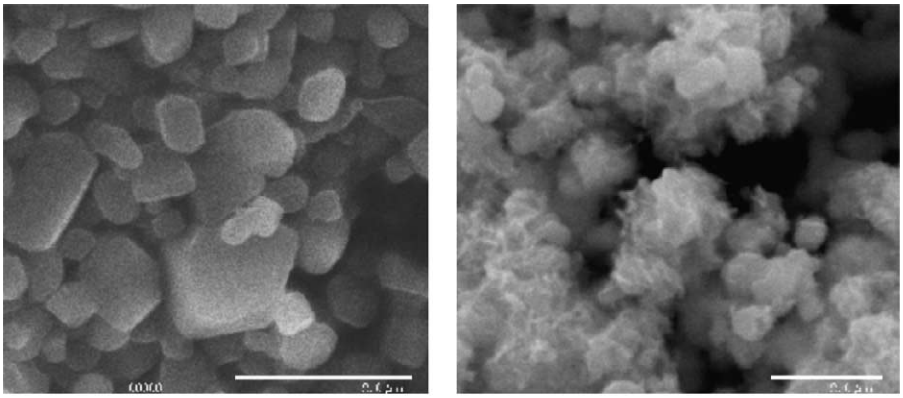


Fig. 4. Titanium dioxide and apatite deposited on porous ceramics fibers.



(a) Titanium dioxide powder

(b) Apatite coated TiO_2 powder

Fig. 6. Apatite-coated titanium dioxide powder.

from that of the titanium dioxide photocatalyst itself. It has also been found that the apatite coating caused virtually no degradation of the photocatalytic activity. We have shown that titanium dioxide coated with apatite is capable of adsorbing NO at night or in places where no light is available.

To study the compatibility of the composite powder, we blended it into an acrylic resin. One sample of acrylic resin was prepared with the composite powder, and another with titanium dioxide powder, both to a loading of 5%. We polished the surfaces of both these specimen, and exposed them to UV light from a fluorescent lamp for 15 days. Photocatalytic activity has no selectivity. Therefore, in the specimen blended with the bare titanium dioxide powder, organic matter, such as the resin, that is in contact with the TiO_2 becomes decomposed, adversely affecting properties such as strength, color, and surface properties.

In a bending testing, the specimen containing 5% of the bare titanium dioxide powder exhibited a statistically significant decrease in bending strength and elasticity coefficient. However, no significant differences existed between the specimen incorporating the composite powder and a specimen with no powder blended.

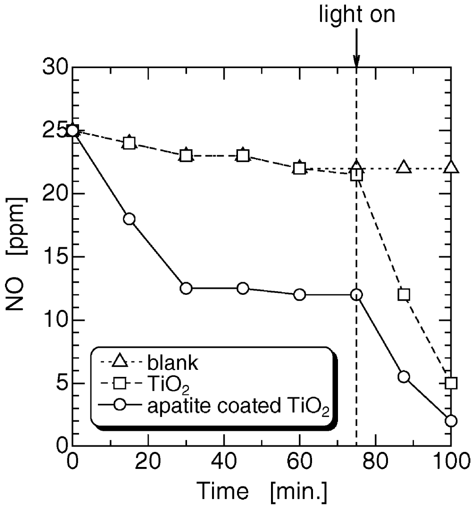


Fig. 7. Changes in NO levels with experimental durations.

Micrographs of the surface (Fig. 8) reveal that the specimen mixed with titanium dioxide developed a large number of pores. These pores cause loss of mechanical strength and discoloration over extended periods of use. On the other hand, the specimen mixed with the composite powder exhibited no pores. This proves that because of being coated with apatite, the titanium dioxide did not come into direct contact with the resin, and no decomposition of the resin took place. Unlike conventional titanium dioxide particles, the composite powder can therefore be blended into resins and paper.

Using this powder, the variety of uses for titanium dioxide increases. For example, blending now becomes possible into organic paints/coatings, fibers, wood, and plastics. Since the surfaces are covered by apatite, and this apatite serves as a spacer to prevent titanium dioxide from coming into direct contact with media, the possibility of decomposing these media is eliminated. In the case of a composite material using nanometer-sized fine powder of titanium dioxide, it can be incorporated into textile or blended into paper. Cosmetics using titanium dioxide have already been commercialized to protect the skin from ultraviolet rays. However, there has been some concern about the effects of its photocatalytic activity on the skin. Since apatite is highly compatible with skin, apatite-coated titanium dioxide is expected to be used in cosmetics and the like (without safety concerns).

Prototype coatings have been produced by using the apatite-coated titanium dioxide particles, which could be applied not only to concrete structures and ceramics/earthenware, just like ordinary coats/paints, but also to metal, wood, textile and paper. When they were applied to exterior walls and rooftops, they provided a self-cleaning capability. In the interior of homes, these materials can be applied to the joints between tiles in bathrooms and kitchens to prevent mold growth, they can be used to prevent odors in toilets and from garbage, and they can be employed to adsorb and decompose volatile organic compounds (VOCs)

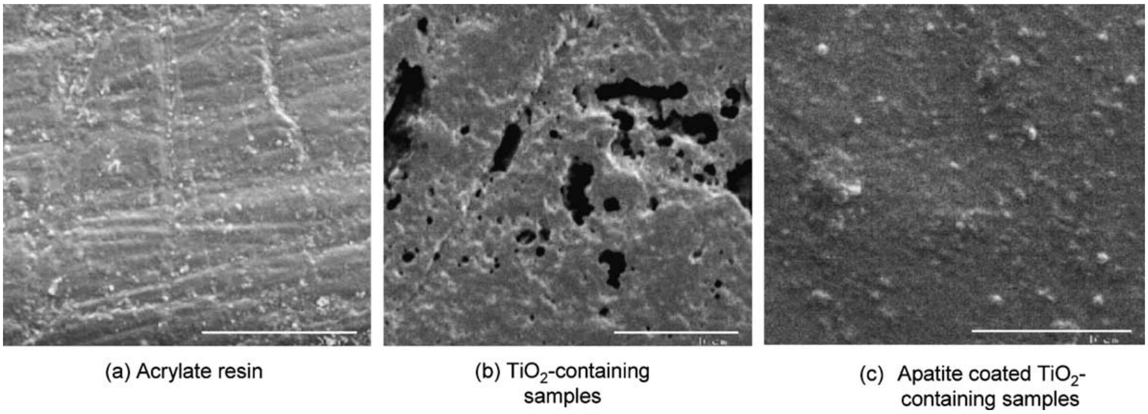


Fig. 8. Acylate resin surfaces coated with TiO_2 or apatite-coated TiO_2.

that cause ‘sick house syndrome’, such as formaldehyde. Furthermore, when applied to tiles in hospital operating rooms, the apatite-coated titanium dioxide particles act as round-the-clock antibacterial material which is capable of adsorbing germs night and day.

The proposed process to coat titanium dioxide particles with apatite uses an environmentally friendly material fabrication process emulating a living organism. In addition to the photocatalytic property of titanium dioxide, we could impart the adsorbing function of apatite. It has been shown that this material possesses the capabilities to adsorb and decompose acetaldehyde and NO. When the composite material was mixed into an acrylic resin, no decomposition of the resin and no degradation in strength were observed.

4. Conclusion

A TiO_2 photocatalyst was soaked in PBS containing an excess of phosphate ions. After soaking for 1 h, an apatite phase was formed on the TiO_2 surfaces. This composite is able to absorb and decompose bacteria and various other materials. We expect this material to have applications as an antibacterial and environmental purification material.

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