INVESTIGATION OF FACTORS AFFECTING THE SYNTHESIS OF TiO2/HAP COMPOSITE MATERIALS VIA SOL-GEL METHOD

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Abstract

Advanced materials have been of interest in recent years because of their outstanding properties that bring many useful applications to humans, they can be highly compatible with alternative materials. In particular, coating materials on HAp base increase the biocompatibility of HAp. In this study, we synthesize TiO2/HAp composite materials using the sol - gel method. Samples were made under different synthesis conditions in terms of HAp/TTIP ratios: (1:1); (1:1.5); (1:2); (1:2.5); (1:3). Factors affecting the synthesis process, such as the incubation time and pH of the solution, were also investigated. The optimal conditions for the synthesis process are the ratio HAp/TTIP: 1 gram HAp with 2 ml TTIP; stirring time: 16 hours; pH of the gel solution: pH = 0.5, as determined from the analysis of the X-ray diffraction spectrum and SEM surface morphology. The research results are the basis for research on biomedical materials.

Keywords: properties, SEM, sol – gel method, TiO2/HAp, X-ray

1. Introduction

Calcium Hydroxylapatite (HAp) is a calcium-containing compound, whose main component is calcium and is characterized by the ratio of calcium to phosphorus (Ca/P = 1.67) (Stefini, 2013). Both synthetic and natural HAp are extremely biocompatible substances (Barakat, 2009). In nanoform, HAp is a form of calcium phosphate that is easily absorbed by the body due to the Ca/P ratio being the same as that in human bones and teeth. Compared to other sources of calcium supplements, HAp nanopowder is maximally absorbed by the body and causes few adverse effects due to the accumulation of calcium and phosphorus in the body. HAp can be in the form of nanopowder, film, or porous ceramic. In porous form, HAp has many applications in biomedical technology; it is used to make bone grafts, make dentures, etc. because it is highly biocompatible, well tolerated, and does not cause allergies. In particular, porous ceramic HAp can be used as a matrix material when combined with other materials to create composite materials with the advantages of ceramic HAp and the advantages of other composite materials. Titanium dioxide (TiO_2) is a typical composite material. They are applied in many different fields, such as food, cosmetics, space, and biomedicine, due to their good biocompatibility (antibacterial, non-toxic, and non-allergenic to the body) (Juha-Pekka Nikkanen, 2007; Kolodiazhnyi, 2009; Aiza Jaafar and Zainol, 2023). The synthesis of biological nanocomposites combined with calcium phosphate and titanium dioxide will form a bioceramic with a large surface area and many interconnected micropores that help tissues easily penetrate and develop (Ensanya Ali Abou Neel, 2007; Kolodiazhnyi, 2009). TiO_2/HAp composites combining inorganic bone materials HAp and TiO_2 exhibit the outstanding properties of each original component of HAp and TiO_2. On the other hand, HAp combined with TiO_2 creates a composite form that can easily be molded into different patterns for bone grafts during surgery, resulting in better bone regeneration (Johnson, 2011; Anavadya, 2024). There are many methods to synthesize TiO_2/HAp nanocomposites, such as chemical synthesis, the microwave hydrothermal method (Sujatha Pushpakanth, 2008), and the pyrolysis method. For each method, depending on the synthesis conditions, products with different properties of particle size and particle size distribution are obtained. In this study, the factors affecting the synthesis of TiO_2/HAp composite materials by the sol-gel method were investigated. The results of the optimal conditions in the synthesis process are the basis for studies on the biomedical applications of TiO_2/HAp materials.

2. Method

The synthesis process of TiO_2/HAp composites is shown in Figure 1. Micrometer-sized HAp powder is dissolved in ethanol, then mixed with iso titanium (IV) isopropoxide by a magnetic stirrer (at 1000 rpm) to form a “sol”. This method will help the solutions mix well together.

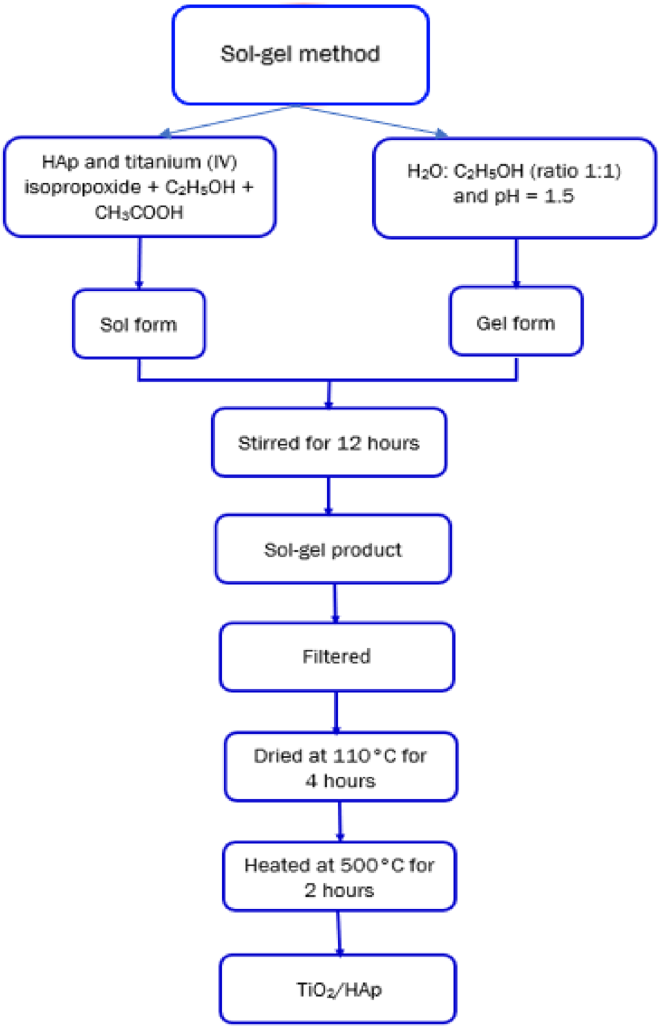

Figure 1. Schematic of synthetic process of composite TiO_2/HAp

The solution is adjusted with H_2O: ethanol (ratio 1:1) and pH = 1.5 with 2M HCl to form a “gel”. Mix the gel solution and sol solution and incubate for 12 hours with a magnetic stirrer at 1000 rpm. After 12 hours, the sol-gel will become a glue. Then filter and dry at 110°C for 4 hours, so that titanium (IV) isopropoxide reacts with alcohol to form an adhesive on the HAp surface. Next, the sample will be heated at 500°C for 2 hours to remove the remaining organic compounds.

The structure of the material was determined by modern physical-chemical methods such as: XRD, SEM combined with comparison with reference documents.

3. Results and discussion

3.1 TiO_2/HAp samples with different HAp/TTIP ratios

Observing the experimental samples TiO_2/HAp with different HAp/TTIP ratios: (1:1); (1:1.5); (1:2); (1:2.5); (1:3), it is easy to see that these samples are all white (Figure 2). This proves that at the drying temperature of 110°C and at the calcination temperature of 500°C, the organic compounds were decomposed, and TTIP was transformed into TiO_2 on the HAp surface.

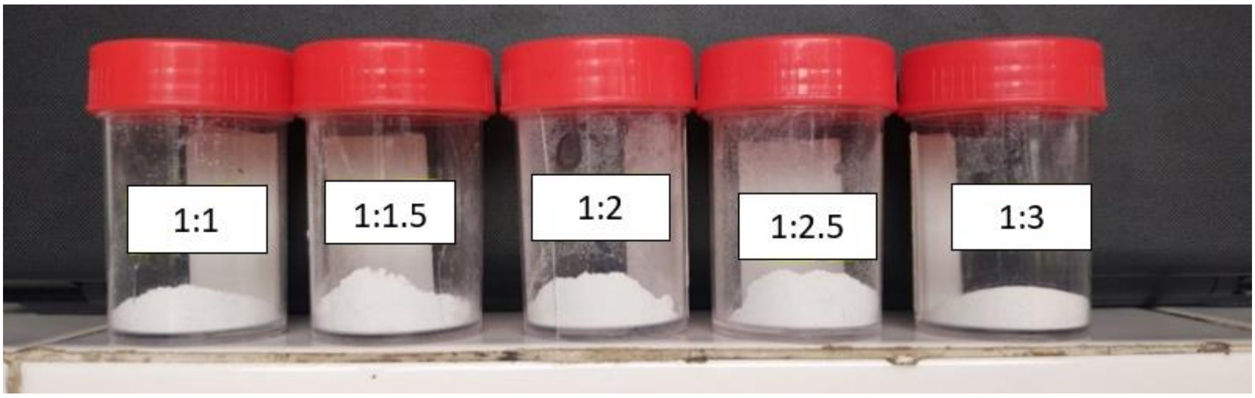

Figure 2: Samples with different HAp/TTIP ratios (1:1; 1:1.5; 1:2; 1:2.5; 1:3)

The characteristics of TiO_2/HAp samples were investigated by the X-ray diffraction (XRD) spectrum shown in Figure 3 for TiO_2/HAp material samples at different HAp/TTIP ratios: (1:1); (1:1.5); (1:2); (1:2.5); (1:3) after stirring at 1000 rpm, drying at 110°C for 4 hours and calcining at 500°C for 2 hours. Samples 3, 4 and 5 showed the appearance of diffraction peaks at $2\theta = 25.7^0;\ 2\theta = 37.7^0;\ 2\theta = 48^0$ corresponding to the (101), (004), (200) planes existing in the crystal structure, the characteristic peaks of TiO_2 crystals. In addition, diffraction peaks were also observed at $2\theta = 26^0;\ 32^0;\ 40^0;\ 46.5^0;\ 49.5^0;\ 53.2^0$ correspond to the faces (002), (211), (310), (222), (213) and (004) which are the characteristic diffraction peaks of HAp crystals.

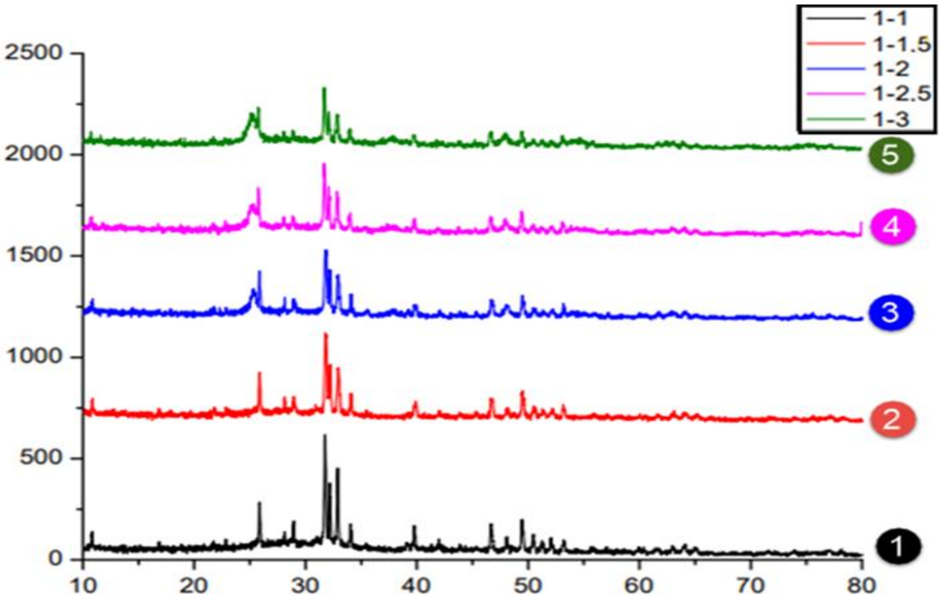

Figure 3. XRD of samples with different HAp/TTIP ratios (1:1; 1:1.5; 1:2; 1:2.5; 1:3)

This result is similar to the research results of Anavadya (2024). At the HAp/TTIP ratios of (1:1) and (1:1.5), the characteristic peaks of TiO_2 did not appear, proving that TiO_2 did not exist on the HAp surface. From the ratio of 1:2 and above, the characteristic peaks of TiO_2 were clearly shown on the XRD diffraction pattern of the obtained material. The reason is that when the TTIP ratio increases, the amount of TiO_2 covering HAp increases, so the characteristic peaks of TiO_2 appear more clearly.

At a ratio of 1:2, the peak $2\theta = 25.7^0$ corresponding to the (101) face has the highest intensity, the peak is sharper and has a narrower width compared to the remaining patterns and other characteristic peaks of TiO_2 are also clearly shown. It is shown that at this ratio, TiO_2 covers the largest HAp.

3.2. The effect of pH and incubation time

3.2.1 Effect of pH

Observing the XRD patterns in Figure 4 of the TiO_2/HAp material samples at different pH conditions, characteristic diffraction peaks of TiO_2 appear at $2\theta = 25.7^0;\ 37.7^0;\ 48^0$ corresponding to the (101), (004), (200) faces and characteristic diffraction peaks of HAp crystals at $2\theta = 26^0;\ 32^0;\ 40^0;\ 46.5^0;\ 49.5^0;\ 53.2^0$ corresponding to the (002), (211), (310), (222), (213) and (004) faces, similar to the analytical properties of the characteristic peaks of TiO_2/HAp by the author A. El ouinani (A. El ouinani, 2017). This proves that, at all pH conditions investigated, a TiO_2 coating appeared on HAp. For the sample examined at pH = 0.5 (line 2 in Figure 4), the peak at $2\theta = 25.7^0$ corresponding to the (101) plane is the characteristic X-ray diffraction peak of TiO_2 with the strongest intensity and has a significant change compared to other samples. In addition, other characteristic peaks of TiO_2 are also most clearly expressed (sharp peaks and narrow peak widths). This shows that at pH = 0.5, the amount of TTIP converted to TiO_2 and coated on HAp is the highest.

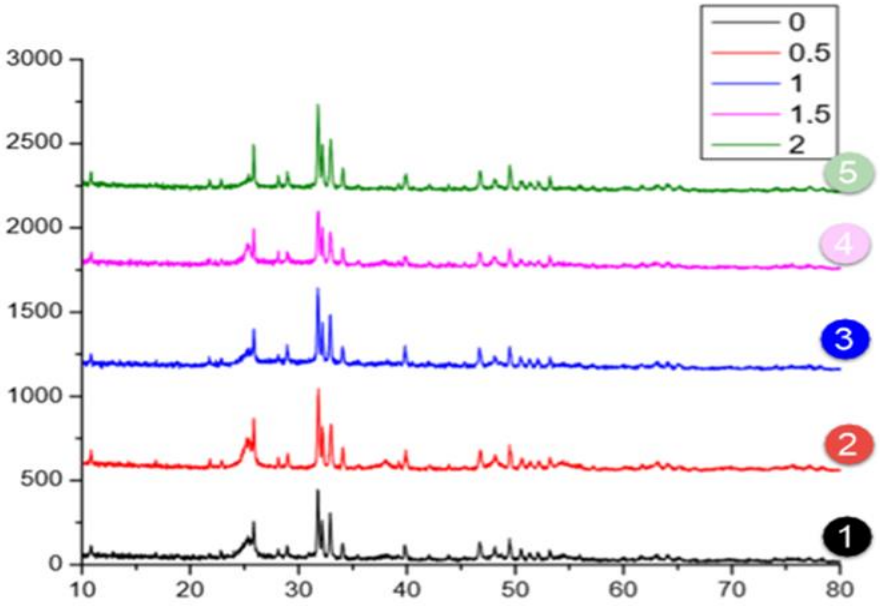

Figure 4. XRD of samples with different pH conditions: without adjustment pH; pH = 0.5; pH = 1; pH = 1.5; pH = 2

3.2.2 Effect of incubation time

The XRD patterns of TiO_2/HAp samples at different annealing times are shown in Figure 5. This pattern shows the characteristic peaks of TiO_2 at $2\theta = 25.7^0;\ 37.7^0;\ 48^0$ corresponding to the (101), (004) and (200) planes at annealing times of 16 hours and 24 hours (lines 2 and 3) and the characteristic peaks of HAp at $2\theta = 26^0;\ 32^0;\ 40^0;\ 46.5^0;\ 49.5^0;\ 53.2^0$ corresponding to the (002), (211), (310), (222), (213) and (004) planes. With annealing times of 8 hours, 36 hours and 48 hours, the XRD patterns do not show the characteristic peaks of TiO_2, indicating that the TiO_2/HAp material has not appeared yet. For the sample with an incubation time of 16 hours, the peak at $2\theta = 25.7^0$ corresponding to the (101) surface is the characteristic X-ray diffraction peak of TiO_2 and has the strongest intensity and is significantly different from other samples; in addition, other characteristic peaks of TiO_2 are also clearly shown. The reason why other samples do not have TiO_2 on the HAp substrate is that when stirring the samples for a short time (8 hours), TiO_2 does not have enough time to coat the HAp because when stirling for an extended period of time, TTIP evaporates, preventing TiO_2 from coating the HAp in time.

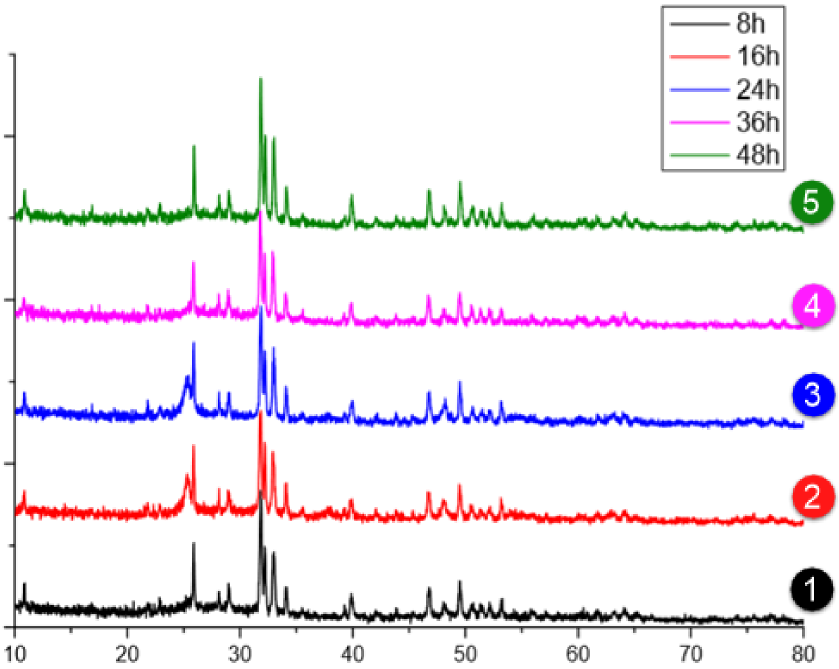

Figure 5. TiO_2/HAp samples with different stirring times: 8 hours; 16 hours; 24 hours; 36 hours; 48 hours

In summary, the ratio of HAp/TTIP affects the formation of TiO_2 on the HAp surface, other factors such as the pH of the environment, incubation time combined with magnetic stirring also significantly affect the material synthesis process. Based on the presented survey results, the optimal conditions for synthesizing TiO_2/HAp materials are the ratio of HAp/TTIP: 1 gram of HAp with 2 ml of TTIP; stirring time: 16 hours; pH of the gel solution: pH = 0.5.

3.3. Surface morphology of the optimized sample

Under ideal research conditions, the TiO_2/HAp sample was examined using scanning electron microscopy (SEM): the HAp/TTIP ratio was 1:2; the gel solution's pH had an impact of 0.5; and the incubation period of 16 hours had an impact. Figure 6 illustrates these findings. It is evident that a coating of TiO_2 material covers the substrate material's surface.

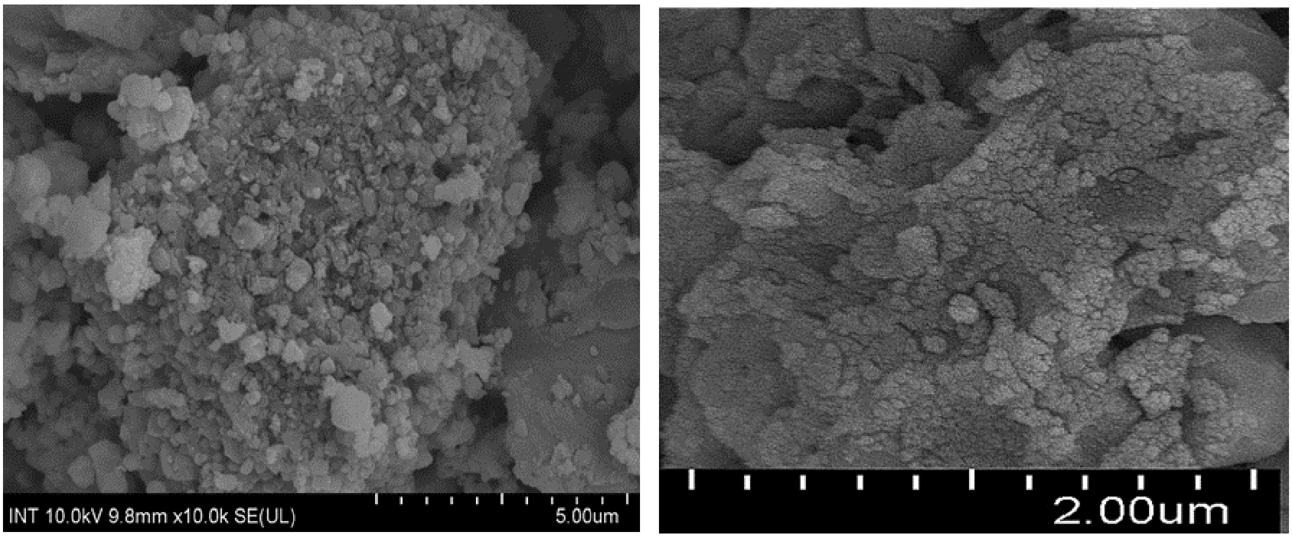

Figure 6. SEM of the sample under optimal conditions: HAp/TTIP ratio of 1:2; gel solution pH = 0.5; aging time of 16 hours.

4. Conclusion

TiO_2/HAp composite materials were successfully synthesized by the sol-gel method with different synthesis conditions such as HAp/TTIP ratio, solution pH and incubation time. Physicochemical characterization surveys were conducted by the X-ray diffraction method, scanning electron microscopy (SEM). The results showed that the process of TiO_2 coating on HAp depends on the material synthesis conditions. From the analysis, the author found the optimal conditions for synthesizing TiO_2/HAp composite materials as follows: HAp/TTIP ratio: 1 gram HAp with 2 ml TTIP; stirring time: 16 hours and pH of gel solution is pH = 0.5. This result is the basis for research on the properties and applications of TiO_2/HAp composite materials in the field of biomedical materials.

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