Apatite inducing ability on silk fabric and its ammonium gas adsorptivity

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Abstract. Silk fabric contains silk fibroin protein which consists of an amino group. This amino group can act as a nucleation site of hydroxyapatite by inducing the Ca2+ ions from surrounding solution at an appropriate pH. To increase the initial Ca2+ ions on the surface of silk fabric, the commercial grade silk fabric was drenched in CaCl2 solution for 12 h, Na2HPO4 solution for 20 min, and CaCl2 for 20 min, respectively. Finally, the fabric was rinsed by deionized water and the drenching processes were repeated for 7 times in order to increase the inducing ability of hydroxyapatite. XRD patterns showed the phases of hydroxyapatite coexisted with monetite. The sample drenched in CaCl2 over 12 h gave more apatite peak intensity which was a result of increased Ca2+ ions over the surface and dot mapping technique with SEM showed the well distribution of both calcium (Ca) and phosphorus (P) on silk fabric. It is worth noting that hydroxyapatite induced on the surface of silk fabric can enhance the selectivity in ammonia gas adsorption. An ammonia gas adsorption resulted in better performance of silk with hydroxyapatite over raw silk fabric were displayed. These results are promising for development of Thai silk in term of superior ammonia gas adsorption characteristic.

1. Introduction
Silk fabric is a natural fabric from silkworm (B. bombyx). It has been known-well in beautifulness and unique textures. Silk fabric composed of fibroin protein which contain an amino group which is able to induce the positive ions via their amide group. Calcium ion, which is a positive charge, can be attracted to these amide group and acts as a nucleation site for hydroxyapatite (HA) formation under surrounding of phosphate anions under an appropriate pH [1].

HA is a famous material in both of biomedical and environmental fields due to its unique bioactivity, adsorptivity and stable even under the high temperature. Additionally, hydroxyapatite can be made as a good ammonium gas sensor because of its selectivity and high sensitivity to ammonia gas [2]. Moreover, it was reported that HA induced on the silk fiber via inducing mechanism showed a low crystallinity [3] which contain high surface area and suit for gas adsorption applications. From all mentioned above, this research aim at inducing HA on the silk fibers of Thai silk fabrics in order to increase the ammonia gas adsorption activity to Thai silk and fine tuning to optimize for an appropriate condition.
2. Materials and method

2.1. Materials preparation
Analytical grade of CaCl₂·2H₂O was purchased from Ajex finechem, Na₂HPO₄ from LOBO CHEMIE. Deionized water (DI) water was used as a solvent in all solutions. The commercial grade Thai silk fabric was kindly supplied from Jim Thompson Company Ltd. The commercial grade Thai silk fabric 1.5 × 1.5 cm was firstly drenched in 1.5 M CaCl₂ solution, 20 mL for 12 h in order to gather a large number of Ca²⁺ on the amide group of Thai silk fabric. Secondly, it was drenched in 1M Na₂HPO₄ solution, 20 mL (with adjusting of pH to pH 7) for 20 min in order to let hydrogen phosphate group react to Ca²⁻ bound amide group on silk fiber. Afterward, the repeating of drenching process was done for 7 times as described in following: drenching in 1M CaCl₂ solution, 20 mL for 20 min and drenching again in 1M Na₂HPO₄, 20 mL for 20 min. The reaction was completed in both of room temperature (25°C) and 100°C to convert the undesired calcium orthophosphates to the desired HA. Finally, the processed fabric was air dried at room temperature for 8 h. The deposited powder on the fabric was collected for phase analysis by XRD characterization.

2.2. Characterization
Phase analyses of the samples prepared from 2.1 were characterized by X-ray diffractometer (XRD D8-Advance, Bruker AXS model D8, German) with Cu Kα (λ = 1.5406 Å) and microstructures were investigated by scanning electron microscope (SEM, JEOL JSM-6480LV).

2.3. Ammonium gas adsorption experiment
An adsorption test was carried out with ammonia detector (GasBadge pro, industrial scientific). An ammonia detector and processed fabric were put into the chamber with filter paper (Figure 1). The concentrated NH₄OH solution, 5 μL was dropped on the filter paper and then the chamber was sealed. The experiment was monitored within 3 h for measuring of the amount of reducing ammonia.

![Testing sample](image)

![Ammonia detector](image)

![Filter paper](image)

Figure 1. Ammonium gas adsorption experiment setup.

3. Results and discussion

3.1. Phase analysis
The XRD pattern showed the phase of hydroxyapatite coexisted with monetite on the surface of Thai silk fabric, monetite was the result of decreased pH from OH⁻ loss in brushite converting reaction as shown in Figure 2. The sample at 100°C gave more monetite intensity due to faster reaction resulted in rapidly decreasing of pH. This results also pointed out that drenching in CaCl₂ for 12 h in Ca²⁺ pregathering step gave higher intensity on both calcium phosphate because more Ca²⁺ ion was attracted on the silk fiber surface.
3.2. Microstructure Investigation

SEM micrographs in Figure 3 showed the hydroxyapatite tiny particles were induced on the surface of Thai silk fabric and dot mapping analysis showed the well distribution of Ca and P over the fabric suggested that the nucleation sites were distributed over the fabric as well.

Figure 3. SEM micrographs showed the hydroxyapatite induced on the silk fabric surface and dot mapping distribution of Ca (left) and P (right).
3.3. Ammonium gas adsorption

According to Figure 4, the HA-induced silk fabric showed the better performance for ammonia gas adsorption than the raw silk fabric which came from the results of increased surface area from HA on the surface. Although, the ammonia adsorption per gram of raw silk is 270.66 mmol/g which was more than HA-induced silk fabric (179.01 mmol/g) however, the HA-induced silk fabric could diminish the ammonia gas faster than the raw silk fabric. It is implied that ammonia adsorption site on HA-induced silk fabric was plenty enough compared to the raw silk fabric, and hydroxyapatite powder (peeled-off from the deposits of HA on HA-induced silk fabric).

![Graph showing ammonium gas adsorption results.](image)

**Figure 4.** Ammonium gas adsorption results.

4. Conclusion

Hydroxyapatite could be induced onto Thai silk fabric and enhanced its ammonium gas adsorptivity due to the improved surface area. An inducing mechanism of hydroxyapatite on silk relied on amino group of fibroin protein which induced calcium ion to act as nucleation sites [4]. According to inducing mechanism, it is possible that hydroxyapatite on the surface is strongly attached to the Thai silk fabric and might be possible for cleaning by laundry process. By this technique it is promising to develop Thai silk with superior ammonium gas adsorption characteristic.

5. References

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