Fabrication of chitosan and calcium carbonate bio-crystals for humidity sensor prepared from annealed shrimp shells and eggshells

P Chaiyo, S Muekhunthod, J Nutariya, O Thumthan, S Sumran and S Pukird*

Department of Physics, Faculty of Science, Ubon Ratchathani University 34190, Thailand

E-mail corresponding author: psuparkor27@yahoo.com

Abstract. We reported the catalyst-free humidity sensor prepared from shrimp shells and eggshells. The annealed shrimp shells and eggshells were ground to powder and mixed together at various ratios. The samples were characterized and investigated by X-ray diffraction technique (XRD), Scanning electron microscope (SEM) and humidity sensing measurements. As a result, XRD patterns of shrimp shells and eggshells show chitosan and $CaCO_3$ structures, respectively. Their SEM images indicate massive agglomeration. Moreover, the humidity sensor demonstrates the highest sensitivity of shrimp shells and eggshells at the ratio of 1:1 for 4.81 at 85%RH. The resistance and relative humidity relationship indicates non-linear inverse behavior. However, the resistance of the samples decreases at higher relative humidity.

1. Introduction

Humidity sensors are widely used in many fields such as industry, air conditioning, agriculture, medicine, laboratory, and others. Humidity value is measured as relative humidity (RH). The relative humidity can be calculated as ratio of amount of water vapor in air to amount of water vapor needed to make the air saturated at the same temperature. Many materials can be fabricated to be humidity sensors for instance, metal oxides, polymers, films, ceramics, organic, and inorganic materials [1-5].

Shrimp shell chemical composition consists of chitin, calcium carbonate and protein [6]. Chitosan can be derived from chitin, which are carbohydrate polymer and linear polysaccharide. In addition, chitosan was used in many applications such as medicine, pharmacy, food, batteries, and many more [7-10].

Eggshells are composed of 95% of calcium carbonate, 0.3% of phosphorus, 0.3% of magnesium, less than 2% of organic matter and traces of sodium, iron, copper, and potassium. Therefore, eggshells are called natural calcium carbonate. Eggshells are fabricated for uses in various applications for instance biodiesel, photocatalytic, wastewaters and humidity storage [11-13, 16].

In this work, we synthesized chitosan and calcium carbonate bio-crystals from annealed shrimp shells and eggshells, respectively. The shrimp shells were mixed with eggshells with various ratio conditions. The humidity sensors were fabricated from chitosan and calcium carbonate bio-crystals. Moreover, the humidity properties were measured under air atmosphere at room temperature with many relative humidity values, which measured relative humidity from 20%RH – 95%RH.

2. Method

The shrimp shells and eggshells were cleaned by water and dried up. After that, they were annealed at temperatures of 100 ºC for 2 h. Then, they were ground to obtain fine powder. The morphology and crystal structures of the samples were characterized by scanning electron microscopy (SEM) and X-ray diffractometer (XRD) techniques. Next, the sample powder was compressed into pellet. Finally, the resistance of the samples was measured at difference values of relative humidity.

3. Results and discussions

The crystal structures of samples were characterized by XRD technique. The results show chitosan and $CaCO_3$ structures. For the shrimp shells, a strong peak appears at 2theta of 20º. This peak corresponds to crystal structures of chitosan [14]. For the eggshells, there are peaks at 23.13º, 29.50º, 36.09º, 39.49º, 43.26º, 47.59º, 48.69º, and 57.53º and indicate rhombohedral crystal system according to JCPDS pattern (85-1108). The peaks designate $CaCO_3$ crystal structures [15]. Moreover, the samples of shrimp shells doped eggshells consist of chitosan and $CaCO_3$ phase apparently.

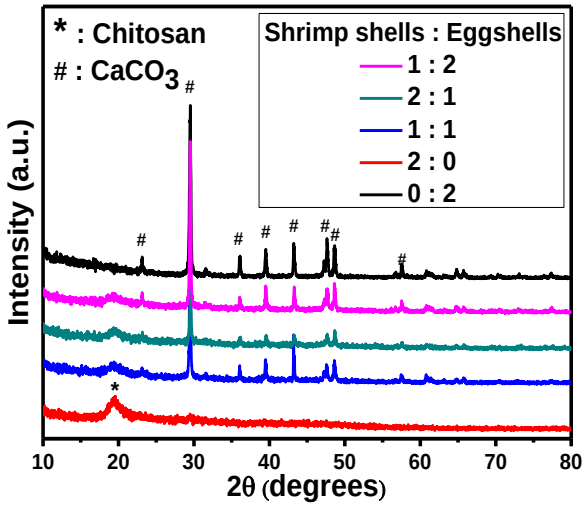

Figure 1. XRD patterns of shrimp shells and eggshells.

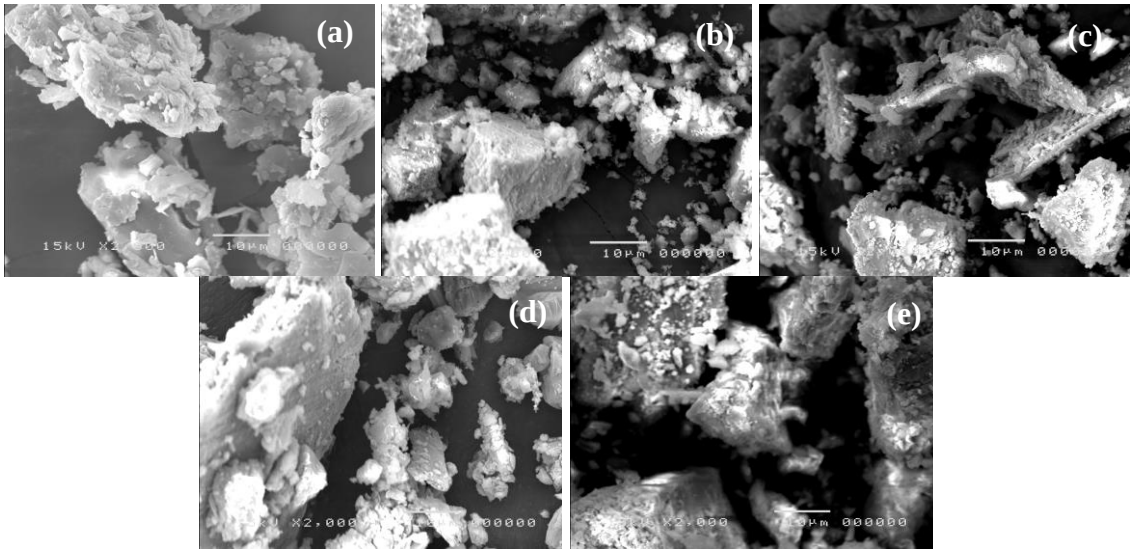

Figure 2. SEM images of shrimp shells and eggshells, the ratios of shrimp shells to eggshells are (a) 2:0, (b) 0:2, (c) 1:1, (d) 2:1, and (e) 1:2.

The morphology of the samples was characterized by SEM technique. Figure 2 shows SEM images of shrimp shells and eggshells with different ratio conditions. The morphology of shrimp shells and eggshells exhibits massive agglomeration of bio-crystals. However, the morphology of egg shell only appears as agglomeration of particles, which is finer than that of shrimp shell.

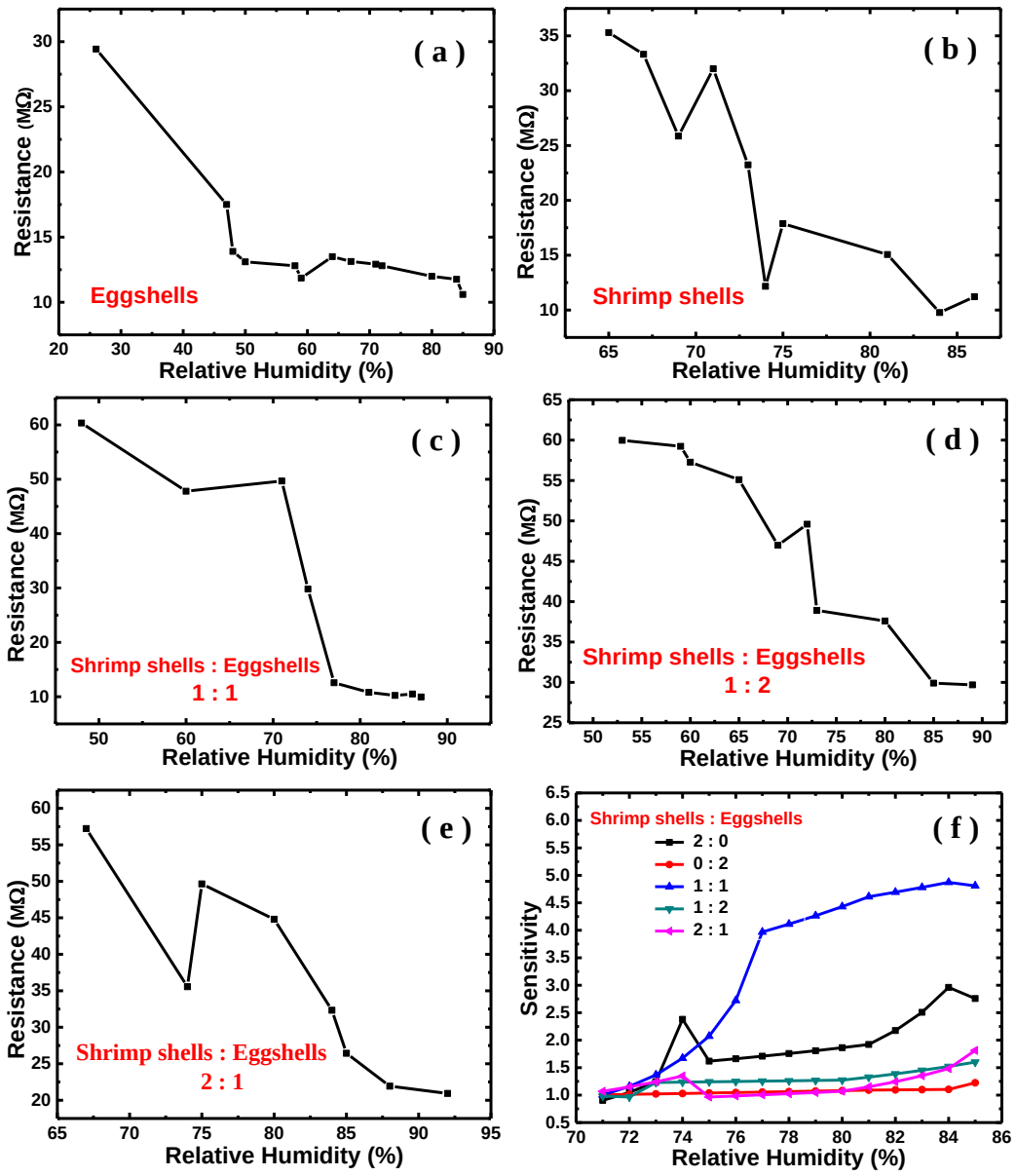

Figure 3. (a-e) Humidity sensitivity of shrimp shells and eggshells with different ratio conditions and (f) humidity response measurements of the mixtures.

The humidity responses were measured under air atmosphere. Figure 3 (a) to (e) show relationships between resistance and relative humidity of the samples. All graphs indicate non-linear relationship. The resistance and relative humidity is non-linear inverse relationship. The results indicate that the shrimp shells and eggshells mixtures can absorb water vapor in the air [16].

In addition, the sensitivity can be calculated by the following equation,

$$S = \frac{R_a}{R_{RH}} \quad (1)$$

Where S is sensitivity, R_a is resistance in the air at relative humidity of 70%, and R_{RH} is resistance in the air at difference values of relative humidity. The relative humidity of the samples was selected from 70% to 85% because this value was saturation value of water vapor absorption of the samples. Figure 3(f) demonstrates the highest sensitivity of the sample at the ratio 1:1 of shrimp shells to eggshells. The value for sensitivity was 4.81 at relative humidity of 85%. The sensitivity values of shrimp shells, shrimp shells to eggshells at 1:2 and 2:1 ratios are 2.76, 1.60 and 1.81, respectively. The sensitivity of eggshells shows the lowest value of 1.22 at 85%RH when compared to other samples. However, all sensitivity results indicate non-linear relationship. But, the sensitivity of the samples increases at higher relative humidity. Besides, the sensitivity can be improved by doping shrimp shells and eggshells at various ratios.

4. Conclusion

Chitosan and calcium carbonate can be prepared by annealed shrimp shells and eggshells. The XRD results indicate chitosan and calcium carbonate crystal structures of shrimp shells and eggshells, respectively. For the SEM images, the morphology of shrimp shells and eggshells shows massive agglomeration of bio-crystals. The agglomeration of particles can be found in eggshells. The relationship of resistance and relative humidity shows non-linear inverse behaviour. In addition, the humidity properties measurements indicate good response to the mixture of shrimp shells and eggshells at the ratio of 1:1.

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