Utilization of nata de coco as a matrix for preparation of thin film containing spin crossover iron (II) complexes

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Abstract. Spin crossover iron(II) complexes have potential applications as smart materials since the complexes show reversible transition between diamagnetic low-spin(LS) state and a paramagnetic high spin(HS) state under the application of temperature change, pressure or light irradiation. The complexes generally prepared as a powder compound isolated from direct reaction between aqueous iron(II) solutions with ligand in ethanol or methanol solution. For application as electronic molecular devices, the complex was prepared as a thin film using several matrixes derived from naftion, silica and other synthetic polymer. In this work, nata de coco, a natural bacterial cellulose polymer, has been utilized as a matrix for preparation spin crossover triazole iron(II) complexes. The morphology of the complex and the composition of elements on the surface of nata de coco have been explored using SEM-EDX analysis.

1. Introduction
Nata de coco is a jelly-like food product originates from the Philippines, produced by fermentation of coconut water using Acetobacter xylinum. It consists of natural cellulose fibers and commonly known as Bacterial Cellulose (BC). The BC fiber has excellent mechanical properties and high water holding capacity, high tensile strength and biodegradable; make it potentially applied in a wide range of polymer science researches. BC has also been modified using many organic polymer to improve toughness and water absorptivity and it is known popularly as a biodegradable and environment-friendly ‘green’ composite [1-3].

The cellulose fibers in nata de coco form a unique three dimensional network with nano-size cavities that suitable for in situ metal deposition like Platinum, Palladium and silver nano particles synthesized from their complex solutions. The thin film material containing nano metal particles have been evaluated as fuel cell materials [4-5]. The ability of nata de coco as a matrix for preparation nano metal particles from their aqueous complex solution, inspired us to utilize it as a matrix for preparation transition metal complexes to produce a thin film.

Spin crossover iron(II) complexes are smart materials that undergo transition between paramagnetic high spin(HS) and diamagnetic low spin(LS) states that can be tune by external perturbation such as temperature, pressure or light irradiation[6]. The transition between the two states

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is abrupt, reversible and generally accompanied by distinct color changed. This property offers promising opportunities for application in molecular sensors and electronic devices [7]. Several iron(II) complexes have been synthesized from iron(II) precursors such as iron(II) sulphate heptahydrate, iron(II) perchlorate hexahydrate and iron(II) tetrafluoroborate hexahydrate. Most of these salts are very soluble in water or ethanol. The reaction of iron(II) salts with 1,2,4 triazole (H-trz) and amino triazole(NH2-trz), the very well known ligands, produces solid complexes in powder form. To improve its functional devices properties, the complexes need to be synthesized in nanometer scale and prepared as a thin film.

Numerous matrixes have been investigated to prepare thin film materials: Nafion, a fluorinated polymer has been used to prepare Fe(H-trz)-nafion and Fe-(NH2-trz)-nafion. At room temperature, the film containing the complexes is colorless and change to lilac at liquid nitrogen temperature. Nafion is anionic resin, therefore no other anion variation can be prepared using Nafion matrix [8]. A thin film of [Fe(H-trz)2(trz)][BF4] in a silica matrix has been prepared and it has been reported that the original optical and magnetic properties of spin crossover materials are still observed in the film [9]. The utilization of nata de coco as a matrix to prepare spin crossover iron(II) complexes was considered in order to demonstrate that the natural polymer with unique molecular structure has a scientific contribution in preparation of thin film smart materials[10].

2. Experimental methods

The following chemicals: Fe(BF4)2.6H2O; 1,2,4 triazole (H-trz = C2H3N3); 4-amino, 1,2,4 triazole(NH2-trz= C2H4N4), ascorbic acid and argon gas were used without further purification. Nata de coco has been prepared using local coconut water and Acetobacter xylinum was obtained from local laboratory in ITB. The preparation of nata de coco sheet was adopted from the work by Radiman and Yuliani[11]. Nata de coco sheet was cut into squares of 3cm x 3cm, and soaked for one hour inaqueous Fe(BF4)2 solution (30 mL, 0.1M) containing ascorbic acid (0.1g) to prevent oxidation of iron (II). After that, it was rinsed with water and methanol before it was soaked in amethanol solution of H-trz (30 mL, 0.3M) for another one hour. The sheet containing H-trziron(II) tetrafluoroborate complex was rinsed using methanol and dried overnight at room temperature to form a thin film. Similar procedures have been applied for the preparation of the film containing NH2-trziron (II) tetrafluoroborate complex.

The magnetic properties were measured using Magnetic Susceptibility Balance Sherwood Scientific Ltd, operated at room temperature. Scanning Electron Microscope (SEM) JEOL JSM-6400 has been used to analyze the complex morphology. The atomic ratio has been carried out using SEM-Energy Dispersive X-ray analysis (EDX) JEOL-JSM 6510LA.

3. Results and discussion

A white sheet of nata de coco in 20 cm long, 20 cm wide and 4-5 cm thick can be simply obtained after 6 days fermentation process of the coconut water. At this moment, the amount of water inside the nata de coco is still extremely high. Therefore the polymer sheet needs to be pressed and dried at room temperature to obtain nata de coco in form of a thin film. The SEM image of the film shows that nata de coco consists of cellulose fibers with average diameter of about 50 nm with its length of several micrometers. The fibers produce three dimensional structures as shown in Figure 1 with varied sizes cavity or holes. These holes are suitable for matrix in the preparation complexes.

When nata de coco sheets soaked in aqueous iron(II) solution followed by imersion in methanol solution of H-trz ligand, no change in color is observed. However this does not mean that the complex has not been formed inside the cavity of cellulose fibers. A distinct lilac color was observed on the drying process of the nata de coco sheet to produce a thin film. SEM image of the film containing this complex shows that the complex shape is long rod with average diameter around 100 nm and with various length from 0,5 up to 1 μm, as shown in Figure 2. The counter anion (BF4−) was detected from EDX data and the ratio of Fe:F was found to be 1:4. This value is in agreement with the complex.
formula reported as Fe(H-trz)_2(trz)] BF_4[9]. From this data it is known that one H-trz molecule in the complex has been deprotonated and became anionic trz.

Figure 1. SEM image of nata de coco sheets, (inset) sheets form.

The preparation of nata de coco film containing NH_2-trziron(II) tetrafluoroborate complex produces a transparent film, which indicates that the iron(II) is in the high spin states. When the film is immersed in liquid nitrogen, its color became lilac, as shown in Figure 3. The color changing of the complex from colorless to lilac demonstrates the reversible transition from high spin iron(II) to lowspin iron(II) in the complex film.

Figure 2. SEM image nata de coco film containing Fe(H-trz)_2(trz)]BF_4, (inset) thin film.
The preparation of the complex from direct reaction of aqueous solution of iron(II) salt and H-trzligand without using nata de coco as a matrix, the solid product was obtained as a powder compound. The magnetic moment of this complex is 1 BM, which indicates that the iron(II) in the complex is in the low spin states. The SEM image of this complex showed that in the solid powder form, the long-rod shapes are overlapped each other to form irregular clusters as shown in Figure 4a.

When the H-trz ligand was replaced with NH₂-trz, the white powder of complex was obtained, indicating that the iron(II) in the complex was in the high spin states. Magnetic properties of this compound was found to be 5 BM resulting from 4 unpaired electrons of iron(II). The molecular shapes of the complex are long rods with large slices between the rods as shown in the SEM image of the complex in Figure 4b. These larger shapes might be due to the amino substituen in triazole ligands.

4. Conclusion
Based on our current works, it is found that nata de coco is a good matrix for the preparation of iron(II) spin crossover complexes. The hydrophylic properties of nata de coco make it easy to diffuse
aqueous iron(II) solution inside cellulose fibers and anchored it via hydrogen bonding. The most crucial part of the preparation complex inside nata de coco is in the dehydrating process of nata de coco to form a thin film. When the drying is too fast the thin film will shrink and the film surface will not be smooth, because the water content in nata de coco is extremely high. The slow drying process will improve the film quality in terms of surface film. However the other unwanted chemical reaction like oxidation reaction of iron(II) might occur and reduce the quality of thin film.

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