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Self-assembly multi-layer of diazonium resin and its coupling reaction with J-acid and H-acid

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Abstract

Self-assembled alternating fabrication film using the diazonium resin and coupling compound was prepared as a multi-layer deposition on the glass slide. Besides, the diazo coupling reaction proceeded at the same time to form nano-scale azo dye layer. The corresponding results of multi-layer and diazo coupling reaction were characterized by UV–vis absorbance measurements. The growth of multi-layer formed by the sequential adsorption and coupling reaction of the diazonium resin and coupling compound was determined.

Keywords: Diazonium resin; Layer-by-layer; Self-assembly; Coupling reaction; Multi-layer; J-acid; H-acid

1. Introduction

The preparation technique of self-assembled multi-layer films may provide new feasibilities to achieve the manufacture of ultrathin films for nano-technology application. Also, it is quite effective skill to obtain the ideal model surface whose properties are controllable. Commonly, multi-levels of polyelectrolyte layers are prepared by alternate electrostatic layer-by-layer adsorption or electrostatic self-assembly of polyions. This alternate adsorption of charged polyions is readily achieved to the oppositely charged surfaces. The electrostatic attraction between oppositely charged molecules seems to be a good driving force for multi-layer build-up. There has been great attention to understand the mechanism and principle of the self-assembly multi-layer films [1–5].

In this work, the diazonium resin compounds [2,6,7] using the polycondensation of 4-diazodiphenylamine sulfate with paraformaldehyde were prepared to manufacture multi-layer fabrication films on the glass plate. In addition to layer-by-layer adsorption, azo dye coupling reaction between diazonium resin and coupling compound was expected and its resulting multi-layer of the azo dye was obtained.

In general, the azo dyes are by far the most important class, accounting for over 50% of all commercial dyes [8,9]. Almost without exception, azo chromophores are prepared by diazotization of a primary aromatic amine followed by coupling reaction of the resultant diazonium salt with an electron-rich nucleophile. As a weak electrophile, a diazonium salt can react with highly electron-rich species such as hydroxyl and amino compounds. This coupling reaction is known as phenol and amine coupling, respectively. Consequently, hydroxyl compounds such as phenols and naphthols are coupled in an alkaline condition, whereas amine compounds are coupled in a slightly acidic medium.

In this context, the work herein comprises an examination and a characterization of the alternate multi-layer adsorption and coupling reaction of the azo dyes in terms of their absorption properties. The general preparation scheme of diazonium resin and diazo coupling reaction is shown in Fig. 1.

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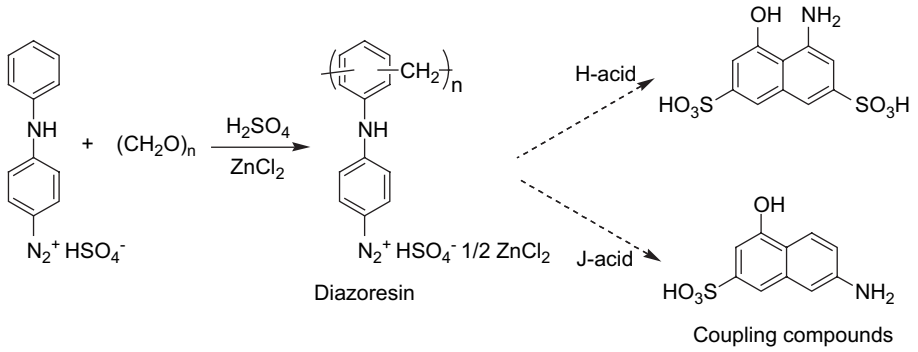

Fig. 1. Preparation of the diazonium resin and coupling compounds.

2. Experimental

2.1. Preparation of the diazonium resin

Five grams (0.017 mol) of 4-diazodiphenylamine sulfate was added to 50 ml flask and 8 ml of concentrated H_2SO_4 was added dropwise with stirring. The flask was cooled using an ice-water bath. Then 0.6 g (0.02 mol) of paraformaldehyde was added in batches at a temperature of 0–5 °C and the reaction was continued for 3 h, keeping at this temperature. The reaction was poured carefully into 30 ml of the ice water. Five grams of zinc chloride was added to precipitate the diazonium resin as a 1/2 $ZnCl_2$ complex. After filtration and drying in vacuum, a yellow-green powder was obtained. The preparation of diazonium resin was carried out and kept in the dark.

2.2. Coupling reaction with J-acid and H-acid

The coupling reaction of diazonium resins and coupling compounds such as J-acid and H-acid was conducted. Firstly, the diazonium resin layer having positive charge was presented on the negatively charged glass slide ($20 \times 10 \times 1$ mm), which occurred by ionic attraction force. The surface of the glass slide was pretreated to provide a net negative charged surface by placing it in 2% KOH aqueous solution under sonication for 30 min. A negatively charged glass plate was then immersed into diazonium resin aqueous solution (0.05 g/200 ml) for 20 min. After rinsing in Milli-Q-water, diazonium resin placed on the glass was dried with gentle stream of nitrogen. Secondly, layered diazonium resin transferred into J-acid and H-acid aqueous coupling solution (0.04 g/200 ml). In this solution, 0.5 g of NaOH was added to provide alkaline condition for phenol type coupling reaction. The commonly used J-acid and H-acid, which called as coupling compound in azo chromophore synthesis, were arbitrarily chosen. In this step, after introducing a self-assembled layer caused by electrostatic force, sequential diazo coupling reaction proceeded with placed diazonium resin layer in alkaline condition. This preparation process was repeated until the desired number of the multi-layer was achieved.

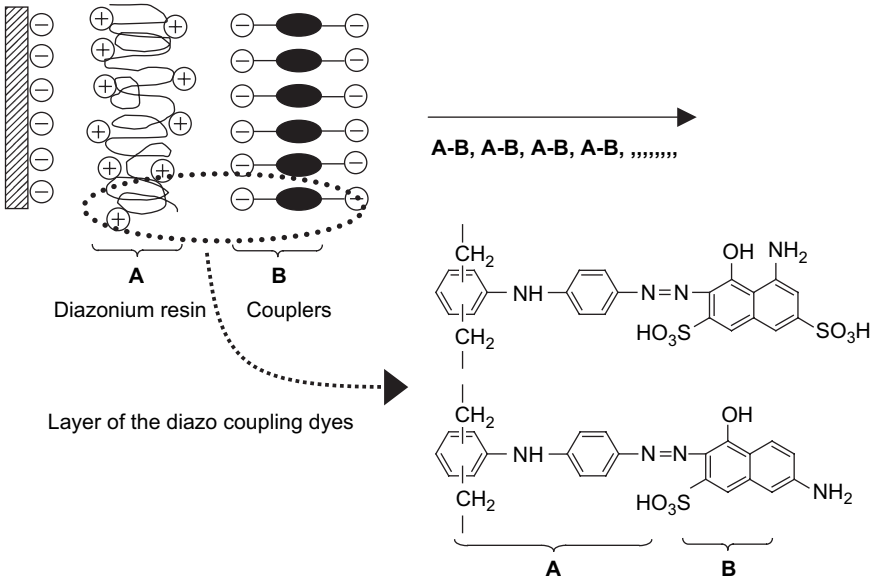

Fig. 2. Scheme of the self-assembled fabrication dye films.

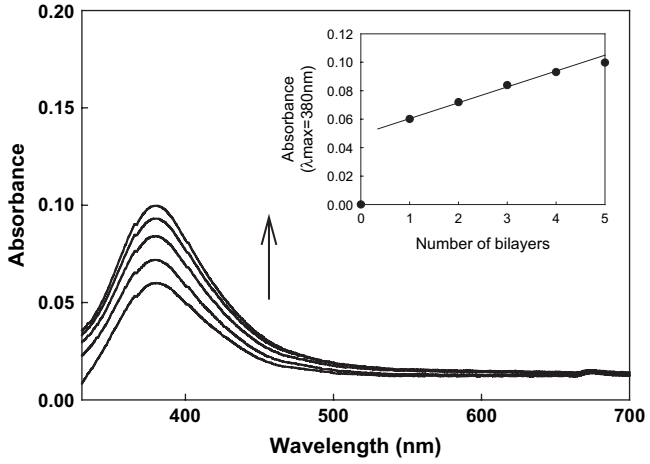

Fig. 3. UV–vis absorption spectra of the diazonium resin/coupling compound layers without diazo coupling reaction.

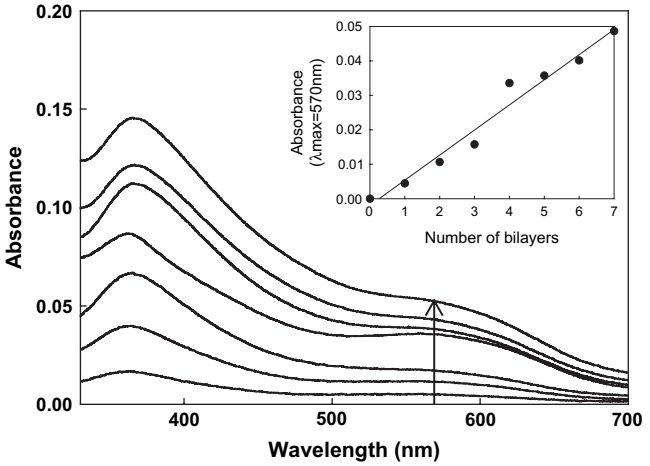

Fig. 5. UV–vis absorption spectra of the diazonium resin/H-acid layers with diazo coupling reaction.

3. Results and discussion

In Fig. 2, a schematic representation of the self-assembled and diazo coupled films fabricated with alternating layers of the diazonium resin and coupling compound is given. Fig. 2 shows that in step A, a substrate with a negatively charged surface was immersed into the solution of the positively charged diazonium resin. A self-assembled diazonium resin layer firstly occurred at this step. In step B, the glass plate having positively charged diazonium resin was dipped into the solution containing negatively charged J-acid and H-acid coupling compounds.

The self-assembled layers caused by electrostatic force were formed on the surface. This behavior could be considered as common process to produce layer-by-layer fabrication films. However, in this study, the self-assembled layer underwent diazo coupling reaction at the same time to form a layer of the azo dyes. This approach seems to be quite an interesting technique and can also be extended to dye chemistry for lots of meaningful work.

The gradual growth of the dye layers formed by the successive adsorption and coupling reaction of diazonium resin and coupling compound was examined by UV–vis spectroscopy. The adsorption spectra of the self-assembled multi-layer having diazonium resin and coupler are shown in Figs. 3–5. In the case of Fig. 3, it shows only self-assembled fabrication film with alternating layers of two components without diazo coupling reaction. It clearly displays absorption growth of the layers at 380 nm, which corresponds to the absorption of the diazonium resin part. However, Figs. 4 and 5 show that new absorption shoulder peaks caused by diazo coupling reaction with J-acid and H-acid appeared around 520 and 570 nm, respectively.

From the results in Figs. 4 and 5, it can be proposed that the fabrication and diazo coupling reaction were successfully achieved because of the electrostatic attraction between positive charges on the diazonium resin and negative charges on the J-/H-acid and its corresponding phenol type coupling reaction.

Further results obtained using the diazo coupling reaction in the aqueous solution medium support the findings showed in Figs. 4 and 5 insofar as the azo dyes were synthesized by coupling reaction between diazonium part and coupling part in alkaline condition and the new absorption peaks were clearly

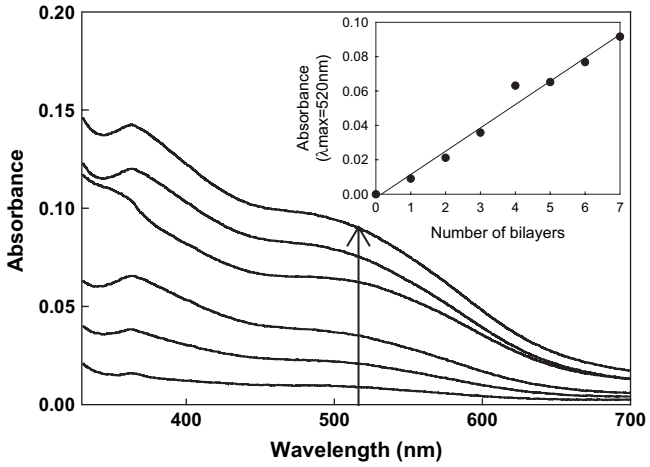

Fig. 4. UV–vis absorption spectra of the diazonium resin/J-acid layers with diazo coupling reaction.

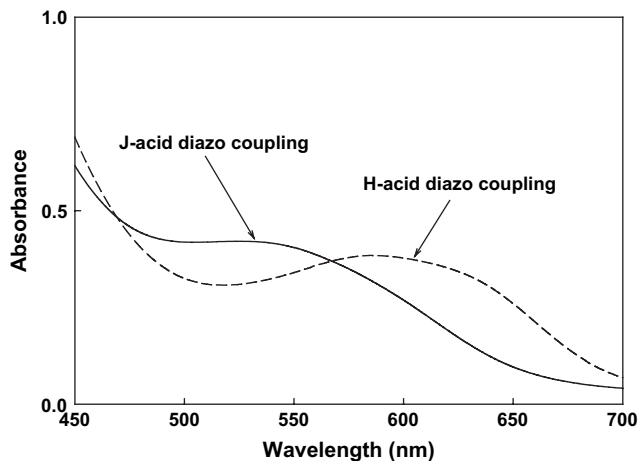

Fig. 6. UV–vis absorption spectra of the diazonium resin/J-, H-acid diazo coupling reaction in the solution.

observed (Fig. 6). The obtained peaks from the formed azo dyes were around 520 and 570 nm, respectively. These absorptions are clearly identical to the results from the diazo dye multi-layers on the glass slide.

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