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Fabrication of long-lasting multilayers of diacetylene@silica nanoparticles patterned on solids for sensory figures

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ABSTRACT

Diacetylene (DA) vesicles were immobilized on a substrate using silica nanoparticles shell by the layerby-layer method to develop a sensory figure multilayer. Silica nanoparticles were densely formed on the surface of the DA vesicle by surface modification and electrostatic interactions; these nanoparticles function as shell on the surface of the vesicles, enhancing the surface activity and structural stability of the vesicles. The DA-silica core-shell nanoparticles can be easily immobilized on rigid, flexible, and porous substrates. In addition, alphabet patterning was achieved by photopolymerization of the substrate on a photomask for the development of visible and fluorescent sensors. Using this polydiacetylene (PDA)based patterning sensory figure, chemical stimuli were recognized within 5 s, signaled by a blue-tored color change and photoluminescence. In addition, it was confirmed that the manufactured PDAbased patterning sensory figure works normally even after 3 months, and long-lasting is possible. Based on this work, the patterning technology applicable to various substrates can be applied to the development of PDA-based sensing materials for industrial field sensors.

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Introduction

Conjugated polymers have been widely investigated for use in electronics, optics, sensors, medicine, and biology because of their optical and electrical properties resulting from the delocalized π -electrons [1–4]. In particular, the polydiacetylene (PDA), one of the conjugated polymers, has been applied to bio/chemosensors because it exhibits strong "turn-on" optical responses with color changes, photoluminescence (PL) and resonance Raman shift to various stimuli [5–10]. When diacetylene (DA) monomers are well aligned and packed with individual molecules, they can form a conjugated domain under UV irradiation and show strong optical properties [6,9]. PDA-based sensors are typically developed by the self-assembly of various colloidal structures (e.g., vesicles, sheets, or wires) in each medium [11–13]. The optical properties

of such colloids depend on the domain size and shapes and the components [11,12]. However, the industrial application of colloid-type sensors is limited because their structures are unstable during long-term storage, during which the colloid dispersibility is easily influenced by environmental conditions such as pH, temperature, and medium [14–16].

To overcome the limitations of colloid-type PDA-based sensors, several strategies have been developed, such as the use of sensor chips, where immobilization of PDA during drying on a substrate is achieved via surface modification or by embedding PDA in polymer matrices by a mixing process [17–21]. In contrast to colloids, sensor chips are useful in different applications because of their long-term storage capability owing to their insensitivity to environmental variations. In addition, sensor chips can be applied to various types of sensor devices such as patterned devices, electrical devices, and attached devices, facilitating increased recognition, and multiplexing in sensors [20–26]. However, the structure of DA must be modified to enhance its interaction with a given surface for the preparation of sensor chips. This requires complex modification steps, wherein the DA structure of sensor chips may change or collapse during processing or storage.

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Abbreviations: DA, diacetylene; PL, photoluminescence; PDA, polydiacetylene; LbL, Layer-by-Layer; TCDA, 10,12-Tricosadiynoic acid; PAH, Poly(allylamine hydrochloride); TMOS, tetramethylorthosilicate; APTES, (3-aminopropyl) triethoxysilane; α -CD, alpha-cyclodextrin.

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