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Molecularly imprinted fullerene-silica nanocomposite particles for sensitive and selective recognition of diethylstilbestrol

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ABSTRACT

A highly sensitive, molecularly imprinted fluorescent sensor was fabricated using a C_{60} fullerene as the signal transducer and silica as the imprinting matrix. The incorporation of C_{60} and the formation of diethylstilbestrol (DES) imprinted sites in the silica network were achieved by the sol–gel method. C_{60} has a narrow band gap between the ground and excited states, resulting in a weak photoluminescence. However, C_{60} showed a strong emission when it was incorporated into a molecularly imprinted silica matrix. DES imprinted fullerene-silica nanocomposite particles (MIFSNCs) showed an intense fluorescence emission with the peak maximum at ~600 nm. The fluorescence intensity of MIFSNCs significantly decreased with increasing DES concentration. MIFSNCs exhibited a linear Stern–Volmer relationship for DES and its structural analogs. The quenching constant of MIFSNCs for DES was about five times higher than those for DES analogs, indicating the highly selective recognition property.

1. Introduction

Molecularly imprinted polymers (MIPs) are widely used in sensing applications as a synthetic receptor [1,2]. In particular, MIPs are well applied to fluorescent sensing in combination with fluorophores as a signal transducer [3]. MIP-based fluorescent sensors detect changes in the emission of a fluorophore upon molecular binding. A variety of fluorophores such as quantum dots [4], organic dyes [5], and lanthanide ions [6] have been used for this purpose.

Recently carbon dots have emerged as a promising fluorophore owing to their unique optical and physical properties [7]. They are also biocompatible, which is a big advantage for their use in biosensing over cytotoxic semiconductor quantum dots [8]. Carbon dots are prepared by breaking down carbonaceous materials or by the carbonization of small organic molecules. They usually have quasi-spherical shapes with a size of less than 10 nm in diameter.

Fullerenes are spherical carbon molecules with a compact size of about 1 nm. They have been a subject of a great interest owing to their potential applications in electronics/photovoltaic devices [9]. C_{60} powders are very weakly photoluminescent under normal conditions because of their small band gaps between the ground and excited states [10]. When incorporated in silica or polymer matrix, however, they often show a strong emission, resembling carbon dots [11–13]. Although C_{60} has yet to be investigated in detail as a fluorescent probe, it has a possibility to be widely used in sensing applications [14].

We report molecularly imprinted fullerene-silica nanocomposite particles for fluorescent sensing of diethylstilbestrol (DES). The rapid and reliable detection of DES at low concentrations is of great importance in clinical pathology and chemistry. DES is a synthetic form of the hormone estrogen and is well-known as an endocrine disrupting chemical. DES has been quantified by conventional analytical approaches such as gas/liquid chromatography-tandem mass spectrometry [15–17]. However, tedious sample treatment and preparation limit the rapid and facile detection of the analyte. In this study, the sol–gel chemistry was used to incorporate C_{60} and simultaneously form delicate imprinted sites in the silica network [18]. A core-shell type silica particle consisting of a C_{60}-containing core and a DES imprinted shell was also prepared and its performance toward the molecular recognition was investigated.

2. Experimental

2.1. Preparation of DES embedded fullerene-silica nanocomposite particles (DES-FSNCs)

FSNCs were synthesized according to the reported procedure with minor modifications [13]. C_{60} fullerene (100 mg in 20 mL toluene) was added to a microemulsion solution containing cyclohexane (50 mL), hexanol (20 mL), distilled water (5 mL), and Triton X-100 (17 mL). After the addition of ammonium hydroxide

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(28 wt%, 0.6 mL), the dark purple solution turned a dark brown color within 5 min. TEOS (1 mL) and TES-DES (0.138 g) was added to the solution and the reaction mixture was stirred at room temperature for 24 h. The mixture was suspended in ethanol (150 mL) and the precipitated product was filtered, washed with distilled water and ethanol. The resultant particles were re-suspended in ethanol and centrifuged at 3000 rpm. After the supernatant removal, the nanoparticles were dried in a vacuum oven at 60 °C for 24 h.

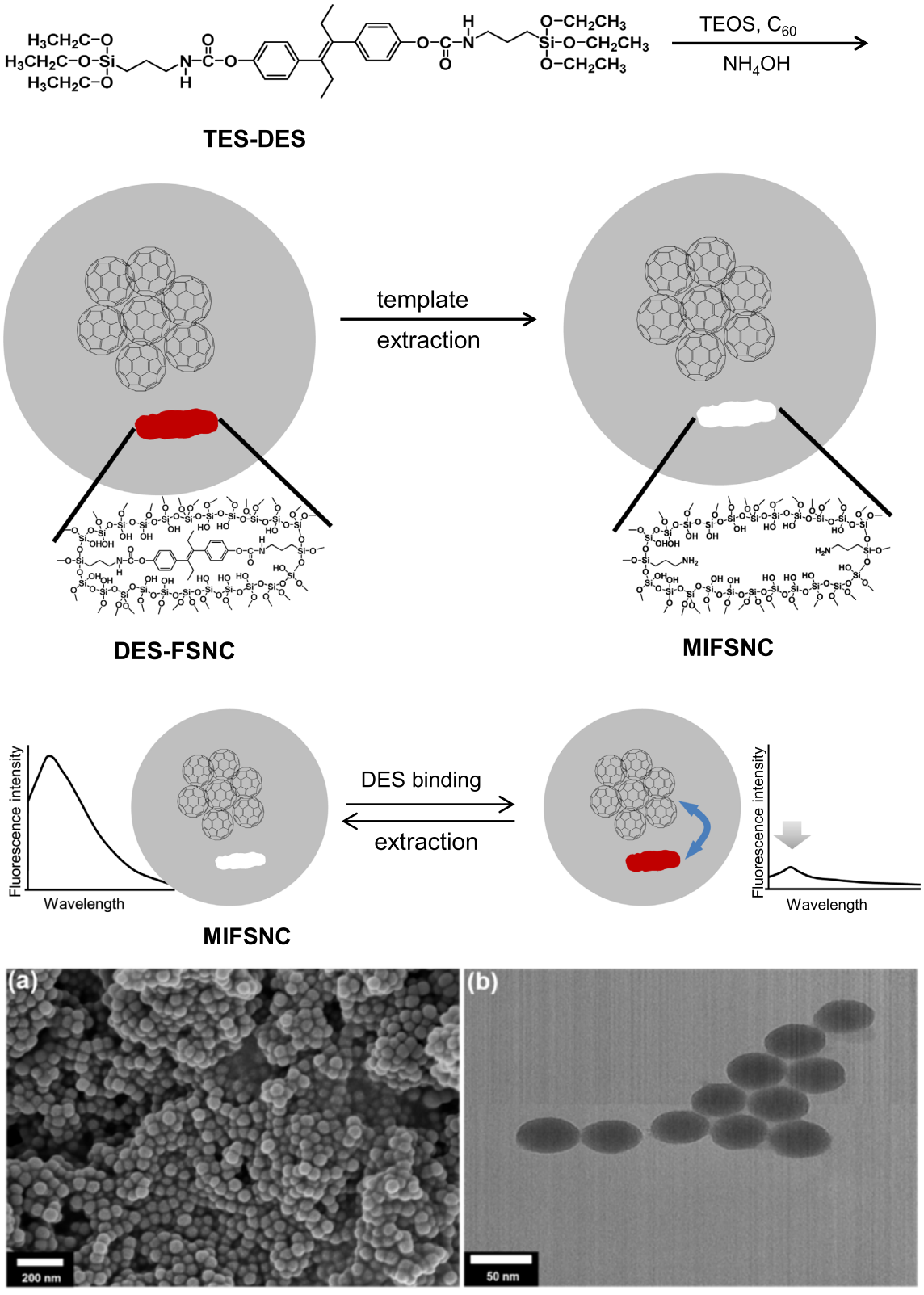

Fig. 1. Schematic representation of the process for the preparation of a DES imprinted fullerene-silica nanocomposite particles (MIFSNCs) *via* the sol-gel reaction. (a) SEM and (b) TEM images of MIFSNCs.