



# Mesoporous silica-deoxycholate synergistic substrate, a novel room temperature phosphorescence-sensing platform



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## ABSTRACT

A novel mesoporous silica-deoxycholate (MS-NaDC) synergistic substrate was developed for room-temperature phosphorescence (RTP) sensing and analysis. The substrate exhibited rapid and strong RTP-inducing ability toward 9-bromophenanthrene (9-BrP). The formation mechanism of MS-NaDC synergistic substrate was analyzed and demonstrated. Five MSs with pore size range of 2.73–18.58 nm were synthesized and investigated, and the MS designated as LPMS2 was selected for its rapid RTP protection and good stability in dispersions. RTP in the presence of MS-NaDC substrate also shows good thermostability. Assistant inducers, such as cyclohexane, can be used together for further RTP enhancement. Finally, 9-BrP holds a fairly wide linear concentration range of 2 nM–3  $\mu$ M, and a detection limit of 0.5 nM. All the results demonstrated the feasibility and application potential of the MS-NaDC substrate in RTP.

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## 1. Introduction

Room-temperature phosphorescence (RTP) has attracted much attention because of its good selectivity and sensitivity. Phosphorescence may be easily quenched by dynamic collision from oxygen or solvent molecules when detection is carried out at room temperature [1,2]. To solve this problem, researchers often focus on developing phosphorescence protective methods. For example, deoxidants were added into samples to remove the dissolved oxygen [3,4]. Analytes were adsorbed on the surface of solid substrates (SS-RTP, such as filter paper) for protection; the limit of detection (LOD) can reach nM level [5–8]. Macrocyclic compounds (e.g.  $\beta$ -cyclodextrin) have been used to induce RTP by forming clathrates with phosphors [4,9,10]. In micelle-stabilized RTP (MS-RTP), surfactants also served as protective medium by forming ordered micelle with inner hydrophobic cavity [11,12]. In latest researches, some new materials were prepared as solid substrates [13–15], phosphors were encapsulated in the materials for better emission conditions.

Although these strategies effectively reduce the quenching effect and have been successfully applied in different circumstances, some limitations remain [1,2,16]. Deoxidant such as

$\text{Na}_2\text{SO}_3$  may react with sample components, and the quenching from solvent molecule remain inevitable. Hydrophobic cavities in macrocyclic compounds often exhibit a fixed size, which may limit the application range, because various analytes possess different molecular sizes and structures. In MS-RTP, micelle structure may be influenced by temperature variation. For SS-RTP, phosphorescence emission may be affected by the multi-step sample preparation procedures, such as the pointing and drying operations. Even for new material substrates, complex operations were still ubiquitous. For instance, PMMA amorphous polymer [13] should be fabricated in a special shaped device; and in the synthesis of supramolecular gel [14], a gelling reaction under 353 K is required to pre-encapsulate phosphor, the high temperature may also cause unexpected side reaction of analytes.

Thus, we can deduce that an ideal RTP substrate exhibits the following features: rigid structure with better tolerance to detection conditions; facile and simple detection steps for better analytical precision; and appropriate hydrophobic cavity size for wider application range. What's more important, detections can be preferably carried out on general instrumental platform.

Given its excellent adsorption properties, mesoporous silica (MS) has been widely applied as an analytical substrate. Various MSs and derivatives are used for drug loading/release [17,18] and the determination of heavy ions [19] and biomacromolecules [20]. At the same time, few applications of MS have been reported in RTP, mainly because most phosphors often contain two or more aromatic rings and various groups in their molecules, which indi-

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cate large molecular size and poor water solubility. MS pores with hydrophilic surface cannot easily adsorb these phosphors, and is unable to provide effective protection as a RTP substrate. Even for the surface-modified MS, effectively loading target analytes remain a challenge [21–23].

Sodium deoxycholate (NaDC) micelle was reported for its remarkable RTP-inducing ability [24,25]. Unlike many other surfactants, the NaDC molecule possesses a hydrophilic side and an opposite hydrophobic side, and these molecules may aggregate with their hydrophobic side face to face to form sandwich like micelles [26]. In this work, we developed a novel “hard-soft” RTP substrate. In the process, we dispersed MS in a water solution as the hard framework; and added NaDC to the solution as the soft substrate to form a MS–NaDC synergistic RTP substrate. 9-BrP was used as a phosphorescence probe to investigate the RTP-inducing mechanism of MS–NaDC substrate. Five MSs with different pore sizes ranging from 2.73 nm to 18.58 nm were synthesized and compared. Experimental conditions, including temperature, adsorption dynamics, and additives, were optimized. Analytical performance experiments were also carried out to identify the applicative feasibility of the method.

## 2. Experimental section

### 2.1. Materials and instruments

Cetyltrimethylammonium bromide (CTAB, 98%, TCI) and triblock copolymer Pluronic F-127 (EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, 98%, Sigma) were used as structure directing agents for MCM-41 type and 3D face-centered large pore MSs, respectively. Mesitylene (TMB, 99%, Aladdin) was used as a swelling agent. 9-BrP, NaDC (Acros organics), Tetraethoxysilane (TEOS, Aladdin), and other reagents were of analytical grade. Deionized ultrapure water (Milli-Q UV-Plus) was used throughout the experiment.

MS morphology was characterized by MAIA3 field emission scanning electron microscopy (SEM, Tescan), and the mesoporous structure was characterized by JEM-2100 transmission electron microscopy (TEM, JEOL). Small angle X-Ray diffraction detections were conducted on a D8 Advance XRD system (Bruker). Porosity analysis was carried out on an Autosorb IQ automated gas sorption analyzer (Quantachrome). All RTP detections were performed under the phosphorescence mode on a LS-55 spectrometer (Perkin Elmer); the delay and gate times were set at 1 and 5 ms, respectively. Excitation and emission slits were set to 5–20 nm. Ultraviolet (UV) absorption detections were conducted on a Lambda-35 spectrometer (Perkin Elmer).

### 2.2. Synthesis of mesoporous silica

The Synthesis strategy for MCM41-style MSs adopted in this study was modified from a published procedure [27,28]. Accordingly, 1.0 g of CTAB, 480 mL of water, and 7.0 mL of 1.0 M NaOH were added into a Teflon bottle, and stirred to clear at 353 K in an oil bath. TMB (0, 2, and 6 mL) was added to the surfactant solution under vigorous stirring. TEOS (5.0 mL) was added dropwise, and a white precipitate was formed. The mixture was continually stirred for 2 h, and then cooled to room temperature. These as-synthesized samples were collected by filtration and named as MCM41, LPMS1, and LPMS2. After an overnight drying at 323 K in a vacuum oven, these samples were calcined at 823 K for 6 h to completely remove CTAB.

For the synthesis of 3D face-centered MS [18,29,30], 2.5 g of KCl, 1.0 g of F127, and 60 mL of 2.0 M HCl solution were mixed and stirred gently in a Teflon bottle at 293 K, followed by the addition of TMB (0 and 3 mL) under stirring. After 12 h of stirring, 4.0 g of

TEOS was added dropwise to the solution. After another 24 h of stirring, the obtained mixture was homogenized by an ultrasonic disintegrator, placed in a Teflon-lined autoclave, and subjected to hydrothermal reaction for 24 h at 373 K. These as-synthesized MSs were filtered, washed with water and ethanol in turn, and dried at 323 K under vacuum. These MSs were designated as LPMS3 and LPMS4.

### 2.3. General procedure

To prepare samples, MS powder was added to deionized water, shaken for 5 min under ultrasonic homogenization to obtain dispersions. The dispersion was mixed with NaDC and 9-BrP stock solutions, diluted to 10 mL with water, agitated well followed by 2 h of standing, and then sampled for phosphorescence detection.

In UV detections, the MS–NaDC–9-BrP ternary dispersion was further centrifuged for 10 min at 5000 rpm after the 2 h of standing to separate MS; leaving the supernatant to be used for comparing the 9-BrP content in the ternary solution with that in the single NaDC solution. Single NaDC samples were prepared by adding 9-BrP to NaDC stock solution and diluted to 10 mL with water.

## 3. Results and discussion

### 3.1. Characterization of MS

The SEM and TEM characterizations of LPMS1–4 are listed in Fig. 1 and the supplement information. The LPMS1 and LPMS2 particles were mainly spherical and short capsular in shape; these particles exhibited an average diameter of 120 nm (Fig. 1A and B). Two characteristic features can be clearly identified, namely, hexagonal structures along the channel system and 2D pores arranged in well-organized parallel stripes. LPMS3 and LPMS4 (Fig. 1C and E) particles were shaped as hexagonal blocks with average diameters of 4 and 5  $\mu\text{m}$ , respectively. These two MSs exhibited cage-type and interconnected pore structure which arranged orderly in three dimensions. The small angle X-ray diffraction spectra of the five MSs are shown in Fig. 2. The strong diffraction peaks at 2.28, 1.98, 0.88, and 0.74 $^\circ$  also indicate the ordered porosity of the MSs.

The N<sub>2</sub> adsorption-desorption results of the five MSs in Fig. 3 clearly conform to the IUPAC type IV isotherm. Although MCM41 and LPMS1 showed small hysteresis loops, LPMS2, LPMS3, and LPMS4 with larger pores possessed hysteresis loops within the relative pressure ranges of 0.4–0.98, 0.45–0.7, and 0.45–0.98, respectively. The porosity parameters of five MSs calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method are listed in Table 1 and Fig. 4.

Given that the five MSs held different particle sizes, the larger MSs may easily settle down in dispersion. The sedimentation of the five MSs was evaluated by the RTP decrease of 9-BrP in the presence of each sufficiently adsorbed MS–NaDC substrate. After 9-BrP addition, sufficient shaking, and a 60 min of standing, sedimentation of the five MSs was achieved and the related data are listed in Table 1. LPMS3 settled down fast because of inherent particle agglomeration occurred in the synthetic process. LPMS4 is monodispersed, it still showed apparent sedimentation effect due to the micrometer level particle size. By comparison, the other three MSs exhibited good stability in dispersion benefited from the small particle diameter.

### 3.2. RTP in single NaDC medium

The RTP-inducing ability of NaDC is offered by its primary micelle. However, in our previous study [25], we found that the formation of NaDC primary micelle is a slow process. NaDC stock

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