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Light-stimulated cargo release from a core–shell structured nanocomposite for site-specific delivery

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ABSTRACT

This paper reported a core–shell structured site-specific delivery system with a light switch triggered by low energy light (λ=510 nm). Its core was composed of supermagnetic Fe_3O_4 nanoparticles for magnetic guiding and targeting. Its outer shell consisted of mesoporous silica molecular sieve MCM-41 which offered highly ordered hexagonal tunnels for cargo capacity. A light switch N1-(4aH-cyclopenta[1,2-b:5,4-b′]dipyridin-5(5aH)-ylidene)benzene-1,4-diamine (CBD) was covalently grafted into these hexagonal tunnels, serving as light stimuli acceptor with loading content of 1.1 μM/g. This composite was fully characterized and confirmed by SEM, TEM, XRD patterns, N_2 adsorption/desorption, thermogravimetric analysis, IR, UV–vis absorption and emission spectra. Experimental data suggested that this composite had a core as wide as 150 nm and could be magnetically guided to specific sites. Its hexagonal tunnels were as long as 180 nm. Upon light stimuli of "on" and "off" states, controllable release was observed with short release time of ~900 s (90% capacity).

1. Introduction

For their potential application in drug transportation field, site-specific delivery systems have been insensitively explored and reported [1,2]. An ideal delivery system is supposed to release therapeutic drug level at specific tissues, organs or even cellular structures. Before reaching target organs or tissues, no cargo molecules should be released since some of them are generally toxic and harmful to normal organs as well as to abnormal ones. In addition, a perfect delivery system should be highly stable to experience various physiological conditions, holding cargo molecules tightly and safely. So far, some candidates have been proposed. However, few of them can meet all above requirements well [3,4]. For example, biodegradable polymers have been reported as a delayed release supporting host for drug molecules. In this case, their release process is controlled by their hydrolysis-induced erosion [3]. Their drawback localizes at the fact that such release process happens immediately upon dispersion in water, which makes them unsuitable for toxic drug delivery such as antitumor medicament. What's more, it is nearly impossible to request a site-specific release from them. Thus, it is needed to explore and develop smart delivery systems with both controllable release and site-specific character.

Core–shell structured nanocomposites are then proposed to meet above requirements since they can combine advantages of each component without compromising individual character [4–7]. A representative core–shell structured site-specific delivery system usually has a magnetic core which is responsible for magnetic guiding [8,9]. Its outer shell is usually composed of mesoporous or amorphous silicates which are here used to support cargo molecules and other functional components.

Aiming at controllable and active release, stimulus-sensitive switches should be embedded into such core–shell structured nanocomposites, such as light, pH, competitive binding, enzymes and chemical reactions [10–12]. Of all these candidates, light switch has been considered promising owing to its virtue of noninvasive therapy, which makes it free of biological interferences, giving instant and controllable release. Some precursive efforts have tried azobenzene and its derivatives as light switch owing to their trans/cis iso-merization and high compatibility with supporting hosts [13,14]. However, these light switches need high energy light peaking at 450 nm which causes server light damage to live body is nearly impenetrable for live tissues and is nearly impenetrable for live tissues. Thus, core–shell structured site-specific delivery system with light switch triggered by low energy light should be explored and developed.

Guided by above consideration, in this effort, we decide to construct a core–shell structured site-specific delivery system with light switch triggered by low energy light. To achieve this goal, magnetic nanoparticles were used as core, mesoporous silicate

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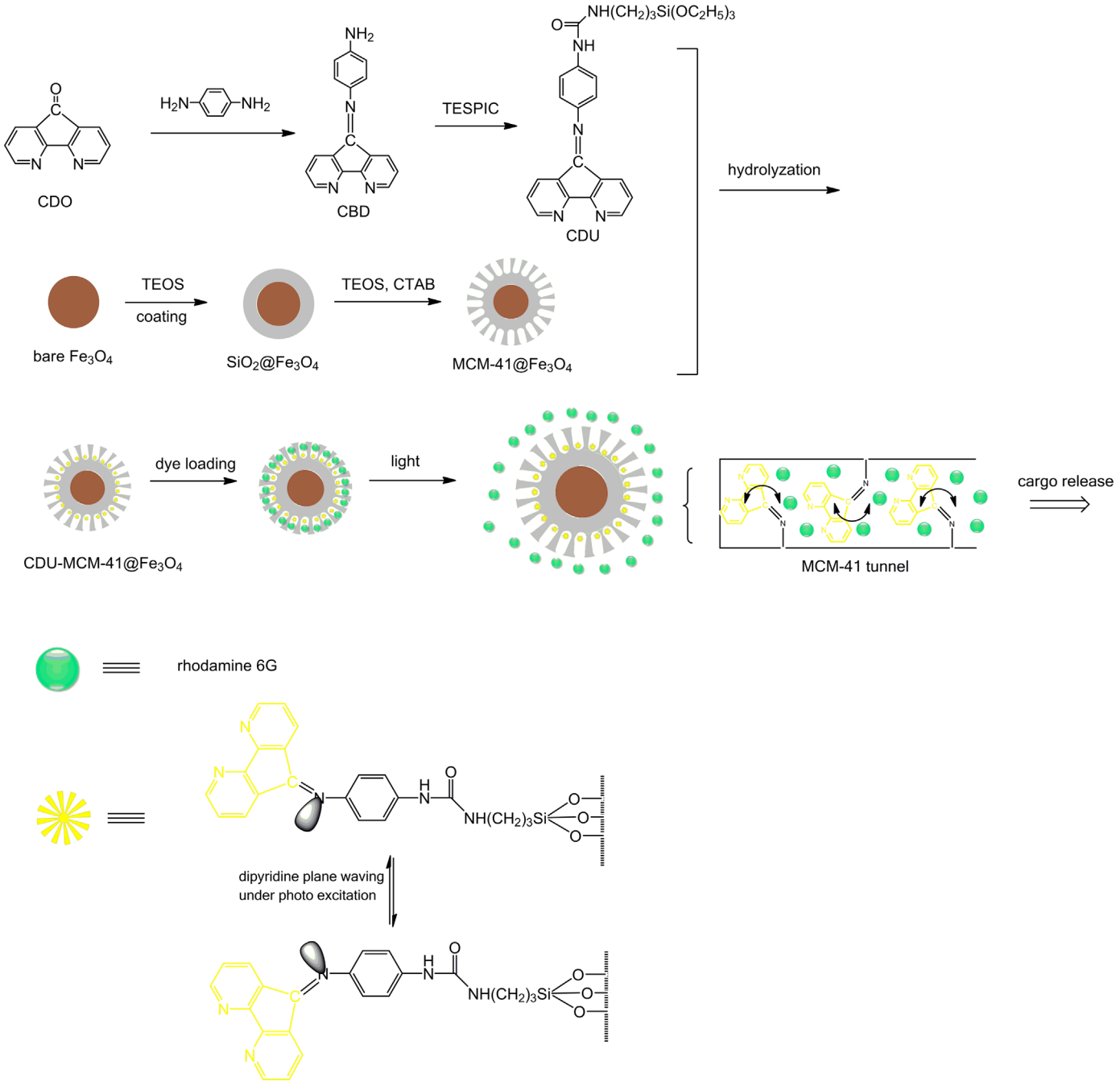

Scheme 1. Synthetic route for CDU and construction strategy for CDU-MCM-41@Fe_3O_4.

MCM-41 was grew onto this core, serving as supporting host. As shown in Scheme 1, a light switch derived from 1,10-phenanthroline was grafted into MCM-41 shell so that it could be triggered by low energy light. The resulting nanocomposite was characterized in detail, along with its controllable release character.

2. Experimental details

2.1. General information

Construction route and operating principle of our nanocomposite (denoted as CDU-MCM-41@Fe_3O_4) are shown in Scheme 1. Starting compounds, 1,10-phenanthroline, benzene-1,4-diamine, 3-(triethoxysilyl)propyl isocyanate (denoted as TESPIC) and rhodamine 6 G, were obtained from Aldrich Chemicals Co. and used as received with no purifications. Other chemicals, including $NH_3 \cdot H_2O$, HCl, NH_4AC, *N*,*N*-dimethylformamide (DMF), cetyltrimethylammonium bromide (denoted as CTAB, AR grade), tetraethoxysilane (denoted as TEOS), $FeCl_3 \cdot 6H_2O$, anhydrous sodium acetate, ethylene glycol, *p*-toluene sulfuric acid, *n*-hexane, chloroform, toluene and ethanol, were bought from Tianjin Chemical Company. All organic solvents were purified through standard procedures. Solvent water used in this work was deionized.

Equipments used for sample characterization are listed as follows. NMR, mass and IR spectra were obtained from a Varian INOVA 300 spectrometer, a Agilent 1100MS series/AXIMA CFR MALDI/TOF (matrix assisted laser desorption ionization/time-of-flight) MS (COMPACT) and a Bruker Vertex 70 FTIR spectrometer (400–4000 cm^{-1}, KBr pellet), respectively. Elemental analysis was finished on a Carlo