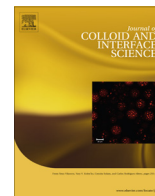




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## Azide-functionalized hollow silica nanospheres for removal of antibiotics



Jinsuo Gao<sup>a,\*</sup>, Jingjing Chen<sup>a</sup>, Xiaona Li<sup>a</sup>, Meiwen Wang<sup>c</sup>, Xueying Zhang<sup>a</sup>, Feng Tan<sup>a</sup>, Shutao Xu<sup>b,\*</sup>, Jian Liu<sup>c,\*</sup>

<sup>a</sup> Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

<sup>b</sup> National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

<sup>c</sup> Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia

### GRAPHICAL ABSTRACT



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### ABSTRACT

Antibiotics, which are hardly removed from polluted water by conventional water-treatment technologies, adsorption has been deemed as one of the efficient and promising method to resolve the problems of antibiotics pollution. Herein, we reported a synthesis of filtration separable hollow nanostructured silicas (HNSs) with efficient click functionalization property for antibiotics adsorption. The clickable HNSs were synthesized by the co-condensation and assembling of tetramethoxysilane (TMOS) and 3-azidopropyltrimethoxysilane (AzPTMS) around F127 single micelle template. Alkynyl compounds such as phenylacetylene (Ph), propargyl alcohol (PA), 1-heptyne (Hep), and 2-butyne-1,4-diol (BD) have been linked to the materials through click reaction with high efficiency. Antibiotic adsorption results reveal that functional groups play an important role in adsorption properties of adsorbents and phenyl was found to be the optimal functional group due to the  $\pi$ - $\pi$  stacking effect. Excellent adsorption capacity and recyclability indicate that the clickable hollow nanostructured silicas exhibit potential application for antibiotics removal.

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### 1. Introduction

Antibiotics pollutants have been considered as one of the emerging contaminants in regards to their potential risks to human health, which have been detected in aquatic environment [1] including surface water, ground water, and even drinking water. To date, various treatment technologies including photocatalysis

[2,3], advanced oxidation [4], ozonation [5] and adsorption [6,7] have been developed for antibiotics removal. From these diverse treatment methods, adsorption is recognized as one of the reliable methods owing to its recyclable nature and simplicity; and more importantly, is its relatively low energy consumption and operation costs. However, the traditional adsorbents used in industries such as active carbons have many shortcomings such as flammability, regeneration difficulty and pore size inconformity for antibiotics. Therefore, exploring new adsorbents with low cost and high efficiency, is of scientific and technological importance.

\* Corresponding authors. Fax: +86 411 84707965.

E-mail addresses: jsgao@dlut.edu.cn (J. Gao), xushutao@dicp.ac.cn (S. Xu), jian.liu@curtin.edu.au (J. Liu).

Hollow nanostructured silicas (HNSs) have shown promising applications as drug delivery carriers [8–12], catalyst supports [13–16], electrodes for energy storage [17] and adsorbents [18] due to their low density, large surface area, high thermal and mechanical stability, and short diffuse lengths. To date, various templates [19–23] including vesicles, polymer micelles, emulsion, and polystyrene spheres (PS) were involved to fabricate HNSs either through a soft templating or hard templating method. However, centrifugation is usually needed to separate HNSs from the synthetic solution. Considering application of HNSs as adsorbents, ideal HNSs should be easily separated from the adsorption solution by filtration rather than centrifugation. For instance, a single micelle template method has been developed to fabricate HNSs with various functionalities [13–15,24–26].

The Huisgen [3 + 2] azide-alkyne cycloaddition, termed as one typical click reaction [27–29], has been widely used to incorporate organic functional groups onto mesoporous silicas for diverse applications [30–33]. Recently, we have synthesized clickable mesoporous SBA-15 silicas and PMOs as functional groups screening materials and excellent adsorbents for antibiotics adsorption [34,35]. Inspired by the above work, herein, we further extend the strategy to develop filtration separable clicked hollow silica nanospheres for antibiotics adsorption. Azide-functionalized HNS ( $N_3$ -HNS), has been firstly prepared by a co-condensation method, using tetramethyl orthosilicate (TMOS) and 3-azidopropyltrimethoxysilane (AzPTMS) as silica precursors, as shown in Scheme 1. The clickability of the obtained azido HNS is evaluated by click reaction between azido HNS and different alkynyl compounds, such as phenylacetylene (Ph), propargyl alcohol (PA), 1-heptyne (Hep), and 2-butyne-1,4-diol (BD) (Scheme 1). Finally, the clicked HNSs have been evaluated by the adsorption of ciprofloxacin hydrochloride.

## 2. Results and discussion

Co-condensation method has been adapted to synthesize azide-functionalized HNS, an advantage of which is that the organo-functional groups would distribute uniformly on the surface of the hollow nanospheres as shown in Scheme 1. A TEM image shows azide-functionalized HNS ( $N_3$ -HNS) have hollow spherical morphology with an average size of 25 nm (Fig. 1), the average cage size is 16 nm. After click reaction, as a typical example, Ph- $N_3$ -HNS maintains the hollow nanostructure as evidenced from TEM image (Fig. 1), which indicated the click reaction with phenylacetylene (Ph) did not alter the morphology and structure.

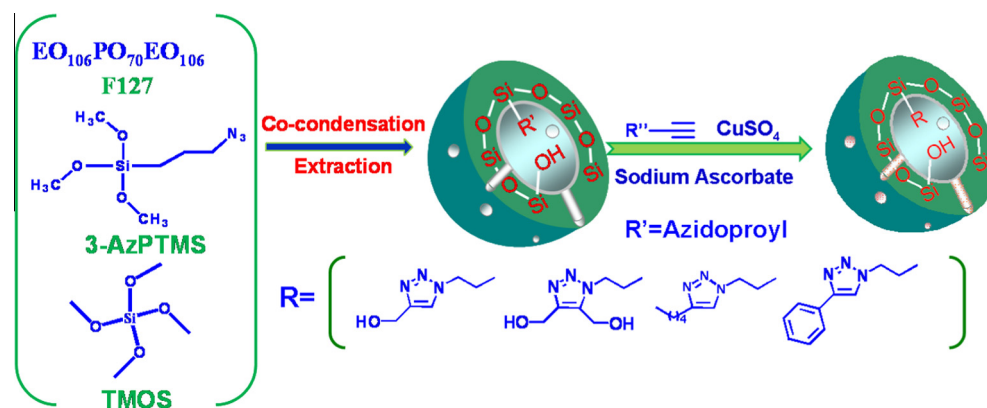
Nitrogen sorption isotherms and pore size distribution curves of the hollow spheres before and after click reaction are shown in Fig. 2. The shape of the isotherms is similar to previous reported

HNSs: a typical IV isotherms with a H2 hysteresis loop. [13,24,25] The similarity of the isotherms of  $N_3$ -HNS and click HNSs indicates the click reaction has little influence on the nanostructure of the materials. The pore size distribution shown in Fig. 2 calculated from BJH method is with a peak centered at 14–15 nm, which is attributed to the inner void of hollow nanospheres [24]. It should be noted that BJH model is usually more suitable for calculating size of cylindrical channel like pore. For cage-like pore, BdB or DFT method is more suitable. However, in this case, the pore size calculating from the BJH model is more close to the hollow cage size determined by TEM images similar as the previous report [13,14,24,25]. The  $N_3$ -HNS show a high specific surface area of  $437 \text{ m}^2 \text{ g}^{-1}$  and total volume of  $1.94 \text{ cm}^3 \text{ g}^{-1}$ . After click reaction, the surface area of the resultant clicked HNSs is decreasing, indicating the successful introduction of organic functional groups using click chemistry (Table S1) [35].

The integration of organic functional groups were further evidenced by composition characterization methods including IR and  $^{13}\text{C}$  CP-MAS NMR. An obvious adsorption peak at  $2100 \text{ cm}^{-1}$ , which is characteristic stretching vibration of azido groups, is observed in the FTIR spectrum (Fig. 3). The peaks at 2976,  $2940 \text{ cm}^{-1}$  are attributed to the stretching vibration adsorbance of the CH of propyl, whose bending vibration can be observed at  $1407 \text{ cm}^{-1}$ . The IR spectrum shows the clickable organosilane, AzPTMS, has been incorporated into the materials. After the click reaction, the adsorbance corresponding to the azido group decreases significantly and even disappears in the IR spectra of clicked materials. A new peak at  $763 \text{ cm}^{-1}$  corresponding to phenyl is observed in the spectrum of Ph- $N_3$ -HNS. The decrease of azido groups adsorbance together with the appearance of organic groups adsorbance indicate the facile process of click reaction for introducing organic functional groups.

The solid-state  $^{13}\text{C}$  cross-polarized magic angle spinning (CP-MAS) NMR spectra of  $N_3$ -HNS and Ph- $N_3$ -HNS are presented in Fig. 4. For  $N_3$ -HNS, the peaks at  $\delta = 9.4$ , 22.3 and 53.9 ppm are ascribed to the C signals of azidopropyl. After the click reaction, new peaks ascribed to the reaction products are observed at around  $\delta = 127$  and 147 ppm. The  $^{13}\text{C}$  CP-MAS NMR characterizations further confirm that phenylacetylene has been anchored onto the hollow nanospheres during the click reaction.

Thermogravimetric (TG) analysis was also used to confirm the incorporation of organic functional groups. As shown in Fig. S1, the first weight loss stage below  $170 \text{ }^\circ\text{C}$  is caused by the loss of physical adsorbed water. The second weight loss stage between 170 and  $250 \text{ }^\circ\text{C}$  is ascribed the decomposition of the residual surfactant. The weight loss stage from 250 to  $600 \text{ }^\circ\text{C}$  can be ascribed to the decomposition of the functional groups. TG analyses show Ph- $N_3$ -HNS has 35 wt% weight losses in compare with  $\sim 20 \text{ wt}\%$



Scheme 1. Schematic description of the synthesis of clickable HNS and clickable modifications.

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