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Graphene-mediated self-assembly of zeolite-based microcapsules

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HIGHLIGHTS

- Graphene can be assembled on zeolite surfaces through amorphization.
- Graphene layers mediate the self-assembly of zeolite microcapsules.
- Zeolite microcapsules showed excellent slow-release characteristics.

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ABSTRACT

Porous core–shell microcapsules were obtained by assembling graphene layers on zeolite surfaces during amorphization process. When fused onto the surface, the self-assembled graphene layers played a role as ‘isolation bubbles’ that prevented the vapor releasing from bulk zeolites. The self-steaming of vapor served as the foaming agent of bringing the porous structure inside zeolites but also created an expansive force to form microcapsules. Due to their porous structures, the as-produced microcapsules showed excellent slow-release characteristics. The release of potassium from the microcapsules reaches equilibrium after 27 days, much slower than that from zeolites (2 days). We believe that the new microcapsules can be used as controlled-release agent for delivery of chemical compounds (e.g., fertilizers) as well as be used as microreactors, micro-devices, sensors, and catalysts. In addition, it is anticipated that the new synthesis route, especially using graphene layers to mediate amorphization, may be extended to other reactions.

1. Introduction

Graphene, a one atom-thick material made up of sp^2-bonded carbon atoms exhibits a series of uniqueness, including strong mechanical strength, high thermal and electrical conductivity, massless transportation properties, and so on [1,2]. Many efforts have been spent to fabricate graphene composites, such as graphene/polymer composites [3–7], graphene/metal composites [8–14], and graphene/ceramic composites [15–21], which offer unusual combinations of electrical, thermal, mechanical, optical, and magnetic performances that are difficult to attain separately from the individual components. Because of its unique elasticity and impermeability, it was reported recently that graphene can form bubbles of different sizes and shapes on different substrates using inflation gas or an external electrical field [22,23]. This offers potential opportunities to develop new microcapsules for various applications, including microreactors, templates, slow-release agents, and sensors.

In the past decades, zeolites have been extensively used in the area of gas separation, cation elimination, and numerous catalytic transformations due to their remarkable microporous structure and adsorption ability [24]. The uses of zeolites have recently been extended to life science and environmental protection [25]. Amorphization, which refers to thermally transforming crystalline solids into amorphous materials at temperatures well below those of classical melting [26], provides a facile way to modify zeotype materials to improve their functionalities [27–29]. During the thermal modification, the zeolites are observed to first undergo dehydration, followed by amorphization before SiO_2 phase is observed to form. The thermal collapse of a zeolite structure does not represent a true melting point, but rather a gradual transformation that is dependent not only on temperature but also on the presence of water vapor. Therefore, the dehydration process plays a crucial role in controlling amorphization of zeolites and subsequently determining the structures of the final products. Existing methods for manipulation of dehydration process in amorphization, however, are mainly dependent on steaming, either external steaming or self-steaming. There are disadvantages associated with the two steaming methods, such as additional equipment requirement and potential sample contamination for the external steaming method, and unfeasibility for the self-steaming at high temperatures because water vapor may release completely.

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It was reported that hydrophilic pyrene molecules can be used to heal defects and 'solder' graphene sheets on solid surfaces during annealing [30]. This technology makes it possible to envision using graphene to mediate the amorphization of zeolites, especially to control the self-steaming process. It is anticipated that the graphene sheets on the zeolite surfaces may form bubbles to hold the water vapor at high temperatures to prevent its releasing and thus alter the dehydration process in the bulk zeolites. More importantly, there could be a vapor pressure difference between the inside and outside of the zeolites that may cause the structural changes to graphene layers and bulk zeolites. All these may facilitate the amorphization process to create modified zeotype materials with unique functionalities.

In this work, we report for the first time that graphene can be applied as 'isolation bubbles' to synthesize zeotype microcapsules with a foamed core and an apertured shell through amorphization. This synthesis process is different from the conventional amorphizations induced by external factors, such as pressure, temperature, or ball milling. As shown in Scheme 1, hydrophilic pyrene molecules can be used to disperse and 'glue' graphene sheets on zeolite particle surfaces [30]. When temperature rises, the graphene sheets are fused as graphene layers to wrap the zeolite particles. During the annealing process, water stored in the micropores of the zeolites is vaporized but cannot escape because of the graphene layers, which have excellent mechanical strength, gas impermeability, and elasticity and thermal stability. The expansionary forces of the water vapor can be gradually balanced by the tension force of graphene layers. When temperature increases, the net forces keep expanding the graphene surface to build up inside pressure to facilitate the collapse of the zeolite and eventually to form microcapsules out of the bulk zeolites through a sudden explosion process similar to popcorn expansion. The water vapor inside the collapsing zeolite cores may keep self-steaming and bubbling due to the temperature increases, leading to the formation of foams inside microcapsules. In addition, apertures are created on the graphene layers on the microcapsule surfaces either during the explosion or when the vapor has enough expansionary strength to penetrate the shell. During the amorphization, not only do graphene bubbles act as microreactors, they also provide zeolite surface the isolation layers under which the vapor with increasing pressure inside the zeolites induces the formation of porous core–shell microcapsules.

2. Experimental

2.1. Materials

Synthetic graphite powder (<20 mm particle size), potassium chloride, natural zeolite (stilbite-Ca, $NaCa_4(Si_{27}Al_9)O_{72}\cdot28(H_2O)$), and 1,3,6,8-pyrenetetrasulfonic acid ($Py\text{-}SO_3$) tetrasodium salt hydrate from Fisher Scientific were purchased and used as received. All solutions were prepared using deionized water (18.2 MΩ, Nanopure water, Barnstead), which was also used to rinse and clean the samples.

2.2. Preparation of graphene suspension

A graphene suspension was synthesized from synthetic graphite flakes by a method similar to that described by Zhang et al. [30]. A stock solution of $Py\text{-}SO_3$ with a concentration of 0.2 mg/mL was prepared in deionized water by vigorous stirring for 1 h. Graphite powder was added to the resultant solutions with the weight ratio between the pyrene derivatives to the graphite powder of 2:1. Direct exfoliation of graphite to graphene sheets was performed by sonication of the obtained mixture solution at 42 kHz with Sonics VX-130 (130 W, 80%) in an ice bath. The obtained gray suspension was used directly to prepare microcapsules by annealing.

2.3. Preparation of graphene/zeolite core–shell microcapsules

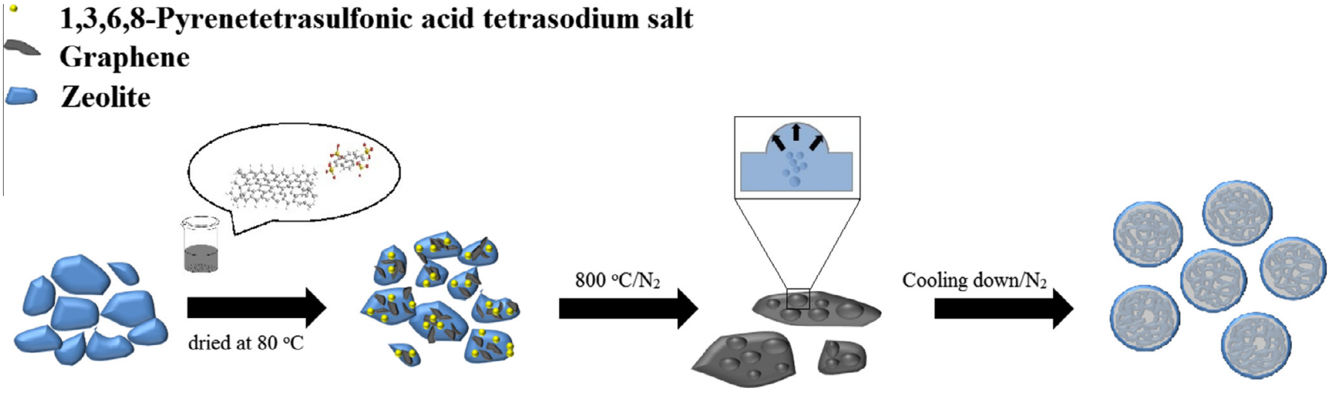
The microcapsules were prepared via two-step procedure. In the first step, 10 g of the zeolite (grounded into powder with mortar and pestle) was dipped into the prepared graphene suspension for 30 s and then dried at 80 °C for 2 h. In the second step, the dry mixture was heated at 10 °C/min and annealed for 5 min at 800 °C under inert gas (N_2) flow.

2.4. Preparation of graphene/zeolite core–shell microcapsules with encapsulated potassium

The potassium was loaded into the microcapsule by treating the zeolite feedstock with KCl solution before annealing process. First, the penetration of KCl into zeolite particles were achieved by soaking zeolite in the KCl solution (10 wt%) for 24 h and then dried at 80 °C for 2 h. Next, the potassium-laden zeolite particles were coated with a thin layer of graphene/pyrene by dipping them into the prepared graphene suspension for 30 s and then dried at 80 °C for 2 h. Some of the potassium-laden zeolite particles without the graphene treatment were used as a control sample. Finally, both the control and the graphene-treated samples then were heated at 10 °C/min and annealed for 5 min at 800 °C under inert gas (N_2) flow.

2.5. Characterizations

The sonicated dispersion of exfoliated graphene sheets was pipetted onto a mica sheet and dried. These sheets were then



Scheme 1. Illustration of strategy for preparation of microcapsules by amorphization.