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Alginate and polyethyleneimine dually mediated synthesis of nanosilver-containing composites for efficient *p*-nitrophenol reduction

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ABSTRACT

Three-dimensional silver/polyethyleneimine/alginate hydrogel beads have been prepared successfully *via* a facile and simple one-pot assembly method, which can be used efficiently in catalytic hydrogenation reaction of *p*-nitrophenol under batch and fixed-bed experiment. Polyethyleneimine is used to reduce and limit the growth of nano-silver particle and alginate microsphere is used as the catalyst carrier, leading to form well silver nanoparticles dispersion. Several characterizations were applied to the materials, such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. As-prepared catalysts only spent 120 s finishing reaction at ambient temperature (20% silver load) and stable catalytic performance with high conversion percentage for *p*-nitrophenol about 90% at 298 K under fixed-bed condition. The relationship between concentration and time was well depicted by Pseudo-first order kinetic model. The catalytic performance for recycled catalyst remained highly efficient, and the conversion efficiency of 96.4% can be maintained after 10 cycles.

1. Introduction

With the development of nano-technology over the decades, metal nanoparticles have been widely used in the field of catalysis and biology, due to the fascinating and tailored surface properties and nano-scale effects. (Wing-Shaná Lin, 2014; An & Somorjai, 2012; Du, Du, & Mao, 2011) However, the existence of surface energy makes metal nanoparticles tend to aggregate, which seriously limits the catalytic activity and efficiency of metal nanoparticles. (Camargo, Li, & Xia, 2007; Yu, Zhang, & Jaroniec, 2010; Pawar, Marathe, & Pattabhi, 2015; Baig & Varma, 2013; Yan, Dai, & Wang, 2016; Corma, Concepción, & Boronat, 2013) Besides, the recyclability of metal nanoparticles is still difficult from a variety of catalytic systems. By way of improving the activity and recyclability for metal nanoparticles, considerable efforts had been devoting to the research of using dispersants and different supporters. (Guo, Yu, & Chu, 2014; Sharma & Sharma, 2014; Amoozadeh, Rahmani, & Bitaraf, 2016; Yan, Gozin, & Zhao, 2016; Bastús, MerkoçI., & Piella, 2014; Jiang, Xie, & Jiang, 2012; Yan, Guo, & Zhang, 2015) For example, Cyril et al. (Aymonier et al., 2002) used polyethylamine with high branched amphiphilical modification to make a silver particle of 1–2 nanometers, effectively adhering to polar substrates of environmentally friendly antibacterial coatings. Recently, Hideyuki et al. (Nagao, Ichiji, & Hirasawa, 2017) made great progress in synthesis of nano-sized platinum by selecting an appropriate usage of polyethyleneimine (PEI), which can reduce Pt ions to generate Pt nanoparticles with diameters in the range of 12.9–70.7 nm and showed the potential of facile synthesis by just adding Palladium ion and PEI. In another research, Kuo et al. (Kuo, Chen, & Jao, 2005) synthesized new alkylated PEIs *via* a facile one-pot method. As prepared PEI chains were localized, to avoid them convolve with each other, by means of applying a lipophile to shape polymer micelles for producing environment of hydrophilic shell, in which the gold nanoparticles were generated. In general, catalytic materials based on nano metal reported in most reports are well-designed but with complex preparation course. Additionally, it is reported that some researchers have used some magnetic carriers as supporting matrices for preparing heterogeneous catalysts, in order to solve the recycling issue. For example, (An et al., 2012) conducted out a detailed study of bimetal catalysts that using solution-phase synthesis of bimetallic nanoparticles was easier than the traditional methods. Under the influence of external magnetic field, the advantages of microsphere in recoverability and reusability are verified by multiple reduction reactions. And the synergistic effect of carbon layer in catalytic reaction is further studied. As-prepared bimetallic nanoparticles were loaded on Fe_3O_4@Carbon microspheres that exhibited excellent catalysis performance for 4-nitrophenol (4-NP). Although the methods demonstrated above have good controllable

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morphology and catalytic performance, there are still several drawbacks such as high cost and complicated preparation process. In spite of the materials mentioned above have good magnetic functions, the loss of catalyst is still inevitable in the process of reaction and recovery, considering the ultra-small particle size and powdery state, leading to an increase in the cost of reactions and possible tiny unfavorable pollutants in final products. Moreover, the application to manufacture on a large scale is still intractable. Therefore, compared with the complex preparation course and high cost of reported catalytic composites, the inexpensive and simple large-scale preparation toward high catalytic activity and stability materials are important trends of development.

Sodium alginate is a kind of natural polysaccharide which belongs to by-products after extracting iodine and mannitol from brown algae or sargasso. Its molecules can be connected with the press (1–4) by β-D-mannose hyaluronic acid (β-D-mannuronic, M) and α-L-gulonic hyaluronic acid (α-L-guluronic, G), which can provide stability, solubility, viscosity and security for pharmaceutical preparations auxiliary materials. (Li et al., 2016; Hernández-Carmona, McHugh, Arvizu-Higuera, & Rodríguez-montesinos, 1998; O'sullivan, 1997) Surely speaking, alginate hydrogel beads have attracted widespread attention due to their environmentally friendly features, sustainable ability, developed network structure, high specific surface area, rich surface groups and stability. (Li et al., 2015; Wang, Vincent, Roux, Faur, & Guibal, 2017; Qu, Zhu, Li, Zhang, & Chen, 2016; Kharkar, Kiick, & Kloxin, 2013; Li et al., 2016; Li et al., 2013) The negatively charged framework ($-COO^-$) in G-rich blocks of the alginate polymers makes it simple to form multivalent cations alginates *via* an ion-exchange process, and their structures have been described by the so-called egg-box model, and consequently further form an insoluble network. (Primo, Liebel, & Quignard, 2009; Chtchigrovsky et al., 2012) In one of our previous researches, our group prepared a series of hydrogel beads *via* nano-silver-loaded glutaraldehyde crosslinked alginate (Ag/CA@GTA) successfully, in consideration of cost and dosage, nano silver is a preferred one for the construction of catalytic composites that aims for 4-NP reduction degradation. (Huang et al., 2014) More recently, the authors used glutaraldehyde as a linking agent to graft PEI onto the calcium alginate hydrogel beads, and this material can be applied to the purification of chromic acid effluent, showing excellent adsorptive ability. (Yan, An, Xiao, Zheng, & Zhai, 2017)

On the basis of our previous research and the multiple capabilities of PEI, we conducted further studies on the construction of a controlled active component-sized metal catalyst with the synergy of PEI and alginate hydrogel. From the perspective of ecological friendliness and sustainability, the catalysts can not only be used in batch experiments but also used in fixed-bed reactor is of practical importance, especially considering the fact that most of metal-based catalyst are expensive and limited resources. (Pavia et al., 2013; Petrucci et al., 2014) As a consequence, we synthesized alginate composite hydrogel beads containing highly dispersed silver nanoparticles (Ag/NPs) at ambient temperature *via* a facile and simple one-pot assembly method, by which it would surely meet for the requirement of large-scale preparation and simultaneously exhibit excellent catalytic performance in batch and fixed-bed experiments.

2. Materials and methods

2.1. Materials and reagents

The reagents and materials used in the experiment were all analytical levels, and no further purification was performed. Sodium alginate (M/G ratio of 1.56, degree of polymerization of 60–400, other details see Table S1) and silver nitrate ($AgNO_3$, ≥99.8%) were provided from Sinopharm Chemical Reagent Co., Ltd., China. Anhydrous calcium chloride ($CaCl_2$, ≥96%) was purchased from Tianjin Kermel Chemical reagent co., Ltd., China. Sodium borohydride ($NaBH_4$, 96%), 4-NP (99%) and polyethyleneimine (PEI, 99%) were supported by Aladdin Chemistry Co., Ltd., China. Ethanol was purchased from Tianjin Fuye Fine Chemical Reagent Co., Ltd., China. Deionized water was produced by self-owned equipment (A Milli-Q system with the resistance of 18.2 MΩ cm).

2.2. Synthesis of multi-functional alginate hydrogel beads (AHB)

Alginate hydrogel beads were prepared by ionic crosslinking theory. For the first step of the preparation, 2 g sodium alginate powder was dissolved in 100 ml deionized water (2%, w/v) under continuous magnetic stirring until form a transparent and viscous solution. Subsequently, we prepared ionic solution for crosslinking, which used 5 g $CaCl_2$ to dissolve with 100 ml deionized water (5%, w/v). Then the homogeneous sodium alginate solution was dripped into the calcium chloride solution by peristaltic pump at a speed of 3 ml/min. After hydrogel beads were formed in $CaCl_2$ solution with 6 h constant magnetic stirring, the aged materials were washed three to five times, 10 min each time with unstinted deionized water. The next step was to transfer as-prepared hydrogel beads into ethanol solution (ethanol: water = 3:7) for 45 min magnetic stirring to further aging and solidification. Finally, the spheroidal materials were treating in freeze dryer about 8 h, and then the product was able to operate on the catalytic process and characterization.

2.3. Synthesis of Ag/alginate hydrogel beads

The approximate synthetic flow chart for the preparation process is shown in Scheme 1. In order to better compare the growth control effect of PEI to silver nanoparticles, we conducted a comparative experiment. Compared to the route of synthesizing the AHB, the synthetic route of Ag@AHB and Ag@PEI@AHB is analogical. As for the preparation of Ag@AHB, the first step is to add the silver nitrate (1.85 mmol) in the sodium alginate solution (2% w/v), while keeping stirring by magnetic force without light, by which can disperse silver ions by connecting with carboxyl groups on alginate and form silver alginate. After forming homogenous hydrogel, the silver-sodium alginate materials were dropped into $CaCl_2$ solution (5%, w/v) to produce 10% Ag@AHB. To obtain different silver load of Ag@AHB, we changed the usage of $AgNO_3$ to 0.555 mmol, 0.925 mmol and 2.77 mmol so that we can produce 3%, 5% and 15% Ag@AHB. In another aspect, in order to further explore the effect of PEI on silver nanoparticles, we adopted the method of controlling the dosage of PEI to synthesize the catalyst. We studied the influence of PEI to the silver nanoparticles and we prepared Ag@PEI@AHB. Firstly, 2.77 mmol $AgNO_3$ was stirred in 100 ml deionized water and double proportional PEI was added until forming homogenous solution under magnetic stirring without light. Subsequently, the solution configured above was mixed up with 2 g sodium alginate under magnetic stirring until forming homogenous hydrogel without light and then the mixture was dropped into $CaCl_2$ solution (5%, w/v). Just like the preparation of different silver load of Ag@AHB, we took different dosage of $AgNO_3$ with 1.85 mmol, 3.7 mmol and 4.62 mmol to obtain 10%, 20%, 25% Ag@PEI@AHB. Besides, we found PEI can improve silver load on the materials. For Ag@AHB, 10% load of silver is the best, with increasing addition of $AgNO_3$, hydrogel solution existed insoluble substance. However, the phenomenon disappeared in the hydrogel with PEI and the load of silver can achieve 25% and the catalysts containing PEI exhibited more excellent properties in subsequent batch experiment and fixed-bed experiment.

2.4. Catalytic performance study of p-nitrophenol under batch condition

For the batch experiment, 4-NP solution (5 mmol/L) was used as the initial reactive concentration and sodium borohydride which is freshly prepared with concentration of 5 mol/L as the reducing agent of the catalytic reaction. The detail steps of batch experiment are shown below. For the first step of the catalytic process, 40 mg catalyst and