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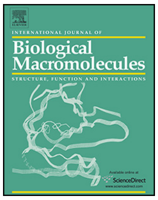

Short communication

In situ generation of silver nanoparticles within crosslinked 3D guar gum networks for catalytic reduction

Yian Zheng[a], Yongfeng Zhu[a,b], Guangyan Tian[a,b], Aiqin Wang[a,*]

[a] Center of Eco-materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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ABSTRACT

The direct use of guar gum (GG) as a green reducing agent for the facile production of highly stable silver nanoparticles (Ag NPs) within this biopolymer and subsequent crosslinking with borax to form crosslinked Ag@GG beads with a 3D-structured network are presented here. These crosslinked Ag@GG beads were characterized using UV–vis absorption spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy, and then tested as a solid-phase heterogeneous catalyst for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of excess borohydride. The results indicate that these crosslinked Ag@GG beads show excellent catalytic performance for the reduction of 4-NP within 20 min and can be readily used for 10 successive cycles.

1. Introduction

In recent years, metal nanoparticles (NPs) have been investigated extensively to understand their physical and chemical properties, due to their potential applications in emerging areas of nano-science and nano-technology. In the nano size regime, metal NPs have received special attention because of their characteristic optical, electronic and catalytic properties [1–4]. Generally, the preparation of metal NPs involves the reduction of metal ions with a suitable reducing agent, such as hydrazine, dimethyl formamide (DMF), and sodium borohydride ($NaBH_4$). All of these are highly reactive chemicals and will pose potential environmental and biological risks. Following the principles of "green chemistry", the primary challenges in this regard are the maximization of usage of environmentally friendly materials and adoption of sustainable processes in the generation of nano-sized metal particles.

It is now well established that polymers are excellent host materials for the preparation of metal NPs and serve also as a surface-capping agent when those NPs are embedded or encapsulated in a polymer. Due to large reserves, biodegradability and eco-friendly "green" processing [5,6], the use of biopolymer such as starch [5], alginate [7,8], chitosan [9,10] and cellulose [11] in research and industry has significantly increased. The biopolymers can provide a size-confined micro-environment where the reduction of metal ions into NPs can be achieved by biopolymer itself *via* adsorption coupled reduction pathways [12,13], or by external assistance *via* chemically [9,14], photochemically [8], by heating [15–17], by laser ablation [18] or by high-energy radiation [19]. Some biopolymers (such as chitosan) not only show a better ability to stabilize the resulting metal NPs by anchoring them, but also act as the reducing agent for the surrounding metal ions [20], but this *in situ* reduction requires heating and controlled pH.

Guar gum (GG) is an edible carbohydrate polymer extracted from the seeds of *Cyamopsis tetragonoloba* and is considered as a polysaccharide with one of the highest molecular weights of all naturally occurring water soluble polymers. It is a nonionic, branched-chain polymer, consisting of straight-chain mannose units joined by β-D-(1-4) linkages having α-D-galactopyranose units attached to this linear chain by (1-6) linkages. Galactose and mannose are the repeating units in GG. Compared with native GG, sulfated or phosphorylated GG shows better antioxidant activities [21,22]. Grafting GG with acrylamide irradiated by microwaves can be used as a better drug delivery system in colon [23]. GG has a strong hydrogen bond forming tendency in water which makes it an excellent thickener and stabilizer [24]. GG has also a strong tendency to form gel in the presence of borax, an efficient crosslinker for polymers bearing hydroxyl groups [25]. These characteristics enable GG to entrap, protect and stabilize the synthesized metal

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* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.
E-mail address: aqwang@licp.cas.cn (A. Wang).

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NPs by acting as an excellent surface capping agent [26]. GG solution is stable over time, not prone to coagulation over a wide range of salinity and pH. Therefore, GG can be used to effectively improve stability and mobility of zerovalent iron NPs used for *in situ* remediation of groundwater [27,28]. Actually, GG has been testified as a suitable candidate to effectively stabilize iron NPs than starch and alginate [29,16]. Furthermore, the inherent biocompatibility and biodegradability in the presence of specific enzymes and microorganisms makes GG are potential alternatives used widely in a variety of applications in biotechnology and in environmental protection.

Based on above backgrounds, we present a totally green approach toward the direct synthesis and stabilization of metallic Ag NPs in this study using GG as the reducing agent for the *in situ* production of Ag NPs as well as their stabilizer. Followed by granulation and crosslinking with borax, we further explore the possibility of the resulting Ag@GG beads as an eco-friendly heterogeneous catalyst for the conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). 4-NP is one of the most common organic pollutants in wastewater, while the resulting 4-AP is an important intermediate for the preparation of many analgesic and antipyretic drugs such as paracetamol, acetanilide, phenacetin, and so forth [30]. With the rapid development of nanotechnology in the past two decades, the borohydride reduction of 4-NP to 4-AP with the assistance of metal NPs has been considered to an effective approach and received increasing attention owing to its fast, simple and mild characteristics [31,32].

2. Materials and methods

2.1. Materials

Guar gum (GG, food grade, number-average molecular weight of 220,000) was purchased from Wuhan Tianyuan Biology Co. (Wuhan, China). Sodium borohydride, silver nitrate, 4-nitrophenol (4-NP), sodium tetraborate and acetone were of analytical grade and used as received. All solutions were prepared with distilled water.

2.2. Preparation of crosslinked GG or Ag@GG beads

A 100 mL beaker containing 50 mL distilled water was kept at room temperature with constant mechanical stirring (500 rpm), which was followed by addition of an appropriate amount of GG powder into the beaker. After 30 min, an accurately weighed amount of $AgNO_3$ was added according to its final concentration in the solution (0, 5, 10, 20, 30 and 40 mmol/L), and then stirred at 500 rpm for another 30 min. After 24 h, the color of GG solution from yellow to brown was observed according to different silver concentration. By dropping this mixture with a syringe into a beaker containing 100 mL acetone, many beads can be formed and stayed for 2 h in the solution. Afterwards, these beads with an average size of 3.2 mm were collected from acetone by filtration, transferred to 100 mL 1 wt% borax aqueous solution and stayed for 4 h for enough crosslinking between GG and borate ions. After crosslinking, the average size of these beads shows a slight increase to 3.3 mm. Finally, these beads were collected from the solution, washed with acetone and dried at room temperature for further use. The dried beads show a reduced size to 50% of its original size.

2.3. Catalytic reduction

In a typical experiment, an accurately weighed amount of 10 mg crosslinked GG or Ag@GG was added into 3 mL of mixed solution containing 10 mg/L 4-NP and 20 mmol/L $NaBH_4$ in a quartz cell with a 1 cm path length, which was quickly placed in the cell holder of the spectrophotometer. The progress was monitored by recording the time-dependent absorbance with a UV-vis spectrophotometer to follow the evolution of the reaction in a scanning range of 250–550 nm at room temperature.

2.4. Reusability

Typically, 10 mg crosslinked Ag@GG beads were added into 3 mL of mixed solution containing 10 mg/L 4-NP and 20 mM $NaBH_4$. The reaction was followed at set time intervals using a UV-vis spectrophotometer at the maximal absorbance of 400 nm for 4-NP in the presence of $NaBH_4$. Then, the crosslinked Ag@GG beads were filtered using 100-mesh stainless sieve, washed with 100 mL distilled water, and placed into another 3 mL of mixed solution containing 10 mg/L 4-NP and 20 mM $NaBH_4$. The consecutive time interval was 20 min for the reduction of 4-NP.

2.5. Characterization

UV–vis absorption spectra of the liquid samples as well as samples for catalytic studies were recorded using a TU-1900 double-beam UV-vis spectrometer in the range 250–600 nm. XRD patterns were acquired on a Philip X'Pert Pro diffractometer using Cu-Kα radiation of 1.5406 Å (40 kV, 30 mA). The surface morphologies of crosslinked Ag@GG beads before and after the catalytic reaction were observed by a field emission scanning electron microscope (FESEM, JSM-6701F, JEOL) after coating the samples with gold film. The transmission electron microscopy (TEM) image was performed on a TECNAI G2 TF20 transmission electron microscope. The samples were dispersed in absolute ethanol by sonication and then dropped onto a carbon-coated copper grid. FTIR spectra were recorded on a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets in the range of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Formation of Ag@GG beads

GG is a nonionic and branched-chain polymer with repeating units of galactose and mannose (Supplementary Fig. S1a). However, the incompatibility of GG with water miscible solvent, such as acetone in this study, is observed. The acetone can rapidly deprive the GG of water causing the GG's precipitation. Therefore, when the GG solution was injected into acetone using a syringe, a large amount of beads immediately occur at the droplet surface, which are further crosslinked by borate ions (Supplementary Fig. S1b). It is observed that the shape of these beads can be adjusted by varying the concentration of GG solution (Supplementary Figs. S2 and S3), and the shape of these beads transforms from sphere to rod as a result of increasing viscosity (Supplementary Fig. S2). The granulation results indicate that the concentration range of 0.7–0.8% (0.75% was chosen in this study) is more appropriate for further mixing with Ag^+ ions. Upon the addition of $AgNO_3$ into GG solution, the semitransparent solution turned yellow gradually and darkened to brown with the time indicating the formation of Ag NPs (Supplementary Fig. S4), which is attributed to the increased amount of Ag NPs produced. Due to the presence of a large amount of hydroxyl groups, GG is expected to react with borate ions to form a crosslinked structure (Supplementary Fig. S1b) [33]. A great number of crosslinks between GG and borate ions is favored for securing those Ag NPs within the 3D networks against leakage.