Preparation and catalytic performance of temperature-responsive cell-like particles

Qiufeng Yang[1], Zhao Dai[1*], Wenjuan Guo[1], Yuanyuan Chu[1] and Guangping Chen[2]
[1]Key Laboratory of Hollow Fiber Membrane Materials and Processes, School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin, China
[2]Department of Physiological Sciences, College of Veterinary Medicine, Oklahoma State University, Stillwater, USA

Abstract: A novel kind of cell-like particles as temperature-responsive catalysts was presented in this paper. First, uniform α-Fe_2O_3 shuttle-like nanoparticles were prepared by homogeneous hydrolysis. Then, these α-Fe_2O_3 particles were coated by Au nanoparticles (AuNPs), SiO_2 and poly (*N*-isopropylacrylamide) (PNIPAM), respectively. After the removal of SiO_2 layer by etching with HF solution, the cell-like particles were prepared when the α-Fe_2O_3, AuNPs, and PNIPAM were as cell nucleus, catalysts, and cell membranes, respectively. These cell-like particles showed a novel temperature-responsively catalytic performance because the PNIPAM shell could change its hydrophilicity and swelling capacity under different temperature. When the temperature was 25°C, the yield of 4-aminophenol (4-AP) from 4-nitrophenol (4-NP) by reduction of $NaBH_4$ was about 100% in 15 min, while the yield of 4-AP was about 90.5% in 40 min. when the temperature was 40°C.

Keywords: α-Fe_2O_3, *N*-isopropylacrylamide; Cell-Like Particles, Catalyst; Temperature-Responsive

---

INTRODUCTION

Functional micro spheres have great potential applications in drug delivery system, absorption and separation fields, etc. (Fagundes *et al.,* 2012 and Behra *et al*., 2012). As a new category of micro sphere materials, a cell-like micro sphere is different from a core-shell one, in which there exists an interstitial space between the shell and the core particle and therefore the core particle is movable in the hollow shell. Because the cell-like particles can have different functional shells and movable cores, they have various applications in catalysis, batteries, and biomedical fields (Choi *et al.,* 2014).

The cell-like micro sphere with a single noble metal nanoparticle core has a high stability in catalysis because the coalescence tendency of metal nanoparticles can be avoided (Güttel *et al.,* 2010), and exhibit a high capacity and good cycle performance (Zheng *et al.,* 2009). Lee *et al.* prepared tin-encapsulated spherical hollow carbon for the anode material in lithium secondary batteries by a sol-gel polymerization technique with subsequent decomposition of tributylphenyltin (TBPT) at 700°C under an argon atmosphere (Lee *et al.,* 2003). Kamata *et al.* reported that the incorporation of Au nanoparticle (AuNPs) as a movable core into a polymeric hollow sphere to monitor the diffusion of chemical reagent into and out of the shell (Kamata *et al.,* 2003).

The size of core affects the whole size of cell-like micro spheres because the usual preparation method is based on the template-assisted method (Lee *et al.,* 2003 and Kamata *et al.,* 2003). Yang *et al*. prepared poly (*N,N'*-methylenebisacrylamide) (PMBAAm) cell-like micro sphere with a movable AuNP core. The diameters of AuNPs were only about 13 nm and the diameters of hollow micro spheres were about 50-100 nm (Liu *et al.,* 2009). Hou *et al.* demonstrated a facile encapsulation of presynthesized metal nanoparticles (10nm) into carboxylic acid based metal-organic frameworks (300-400 nm) (Liu *et al.,* 2014). The small diameters of cell-like particles will result in the difficulty of the removal of particles from reaction system and the deformation and damage of shell layer under ultra centrifugation.

Therefore, in this work, a novel kind of cell-like particle as temperature-responsive nanoreactors when α-Fe_2O_3 particles self-assembled Au nanoparticles (AuNPs) (Fe_2O_3/AuNPs) are as cores and poly (*N*-isopropylacrylamide) (PNIPAM) hollow micro spheres are shells. The cell-like particles have catalytic activity of AuNPs, magnetic property of α-Fe_2O_3 particles, and temperature sensitivity of PNIPAM shells. The α-Fe_2O_3/AuNPs core has more AuNPs and magnetic property to be removed from reaction system easily, as well as the PNIPAM has the temperature sensitivity to affect the mass transfers of reaction system (Li 2012 and Soleimani *et al.,* 2013).

MATERIALS AND METHODS

Materials

N-isopropylacrylamide (NIPAM), $HAuCl_4$ and tetraethyl orthosilicate (TEOS) were purchased from TCI Ltd. (3-aminopropyl) triethoxysilane (APTS) and [3-(Methacryloyloxy) propyl] trimethoxysilane (MPS) were available from Alfa Aescar Co. 2,2′-

---

Corresponding author: e-mail: daizhao@gmail.com

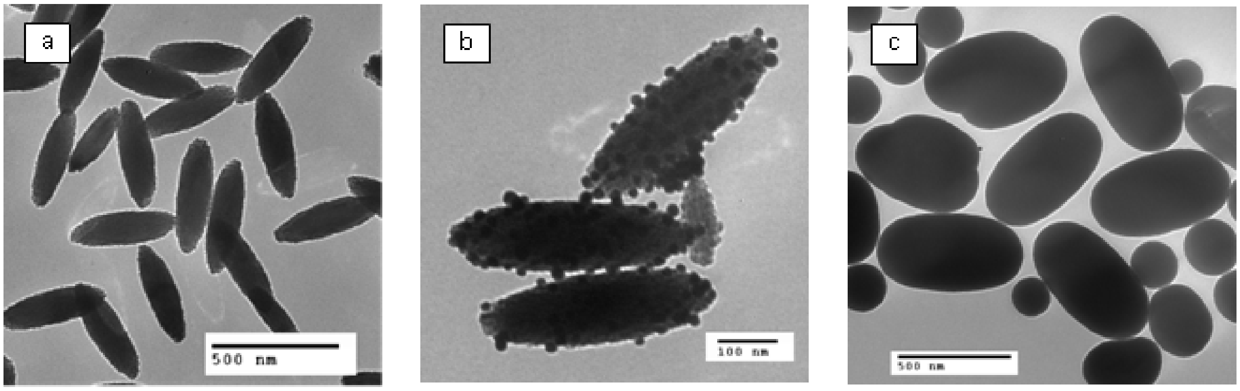

Fig. 1: TEM images of (a) Fe_2O_3, (b) Fe_2O_3/AuNPs and (c) Fe_2O_3/AuNPs/SiO_2 particles

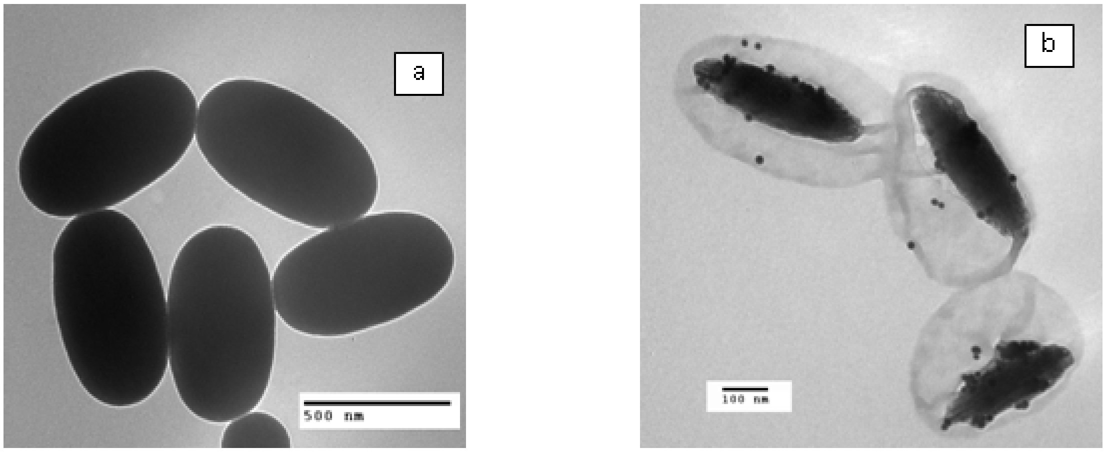

Fig. 2: TEM images of (a) Fe_2O_3/AuNPs/SiO_2/PNIPAM and (b) Fe_2O_3/AuNPs//PNIPAM particles

Azobisisobutyronitrile (AIBN) was available from Tianjin Xida Chemical Reagent Co. and was recrystallized from methanol. Acetonitrile (Tianjin Chemical Reagents II Co.) was dried over 4 Å molecular sieves and distilled prior to utilization. All Other reagents were of analytical grade and used without any further purification.

Synthesis and modification of α-Fe_2O_3 Nanoparticles

The shuttle-like Fe_2O_3 nanoparticles were prepared through a solvothermal reaction (Li *et al.,* 2010). The Fe_2O_3 particles were chemically modified by using APTS. Briefly, Fe_2O_3 particles (0.05g) and APTS (1mL) were dissolved in anhydrous ethanol (30mL) for 24h in digital bath oscillator. The resulting Fe_2O_3 particles were separated by centrifugation, washed with ethanol, and dried in vacuum at 60°C for 24 h.

Self-assembly of AuNPs on α-Fe_2O_3 particles (Fe_2O_3/AuNPs)

AuNPs were prepared according to the standard sodium citrate reduction method (Grabar *et al.* 1995). Then, 10mL of ethanol dispersion of 0.05g α-Fe_2O_3 was mixed with 20mL of the AuNPs solution under ultrasonic bath. Then the mixture was subjected to shaking at room temperature for 24h. Finally, the Fe_2O_3/AuNPs particles were separated by centrifugation, washed with anhydrous ethanol for 3 times.

Preparation of Fe_2O_3/AuNPs/SiO_2 particles

0.05 g of Fe_2O_3/AuNPs particles were employed as seeds and dispersed in solution with 80mL of ethanol, 16mL of deionized water, 2.0mL of ammonia (29%) and 1mL of TEOS. After 6 h reaction, 1mL of MPS was added into it for 24h to introduce the C=C bonds onto the surface.

Synthesis and etching of Fe_2O_3/AuNPs/SiO_2/NIPAM particles

The Fe_2O_3/AuNPs/SiO_2/PNIPAM particles were prepared by distillation precipitation polymerization (Li *et al.,* 2008). The cell-like particles were prepared by removal of the SiO_2 layer from the α-Fe_2O_3/AuNPs/SiO_2/PNIPAM particles. 0.01g of these particles was stirred in 1% HF (10mL) for 2h. The resultant cell-like particles were purified by centrifugation, washed with deionized water for 5 times.

The reduction of 4-nitrophenol (4-NP) by Fe_2O_3/AuNPs//PNIPAM cell-like particles was in a quartz cuvette. Briefly, A 0.1 M 4-NP aqueous solution (80mL) and $NaBH_4$ (0.05g) were mixed in 100mL Erlenmeyer

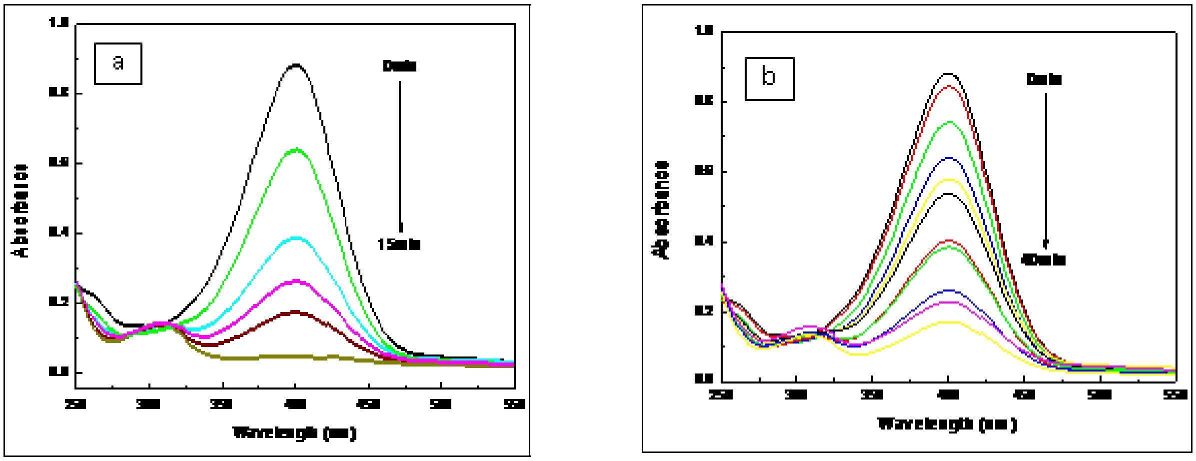

Fig. 3: UV-vis spectra of gradual reduction of 4-NP with α-Fe_2O_3/AuNPs//PNIPAM cell-like particles as catalyst at different temperature a) 25°C; b) 40°C.

flask by quick ultrasonication in a water bath, Subsequently, 1.0mL of the colloidal dispersion containing 5 mg of α-Fe_2O_3/AuNPs//PNIPAM particles was added into the solution. The catalytic performance was measured by a UV-vis spectrometer at 25 and 40°C.

RESULTS

Preparation of Fe_2O_3/AuNPs/SiO_2 particles

Due to the lack of an appropriate interaction between AuNPs and α-Fe_2O_3 particles, the modification of α-Fe_2O_3 particles with $-NH_2$ groups is necessary and the active amino groups on Fe_2O_3 particles can react with AuNPs by coordination bonds (Katz *et al.,* 2004). The TEM of α-Fe_2O_3, Fe_2O_3/AuNPs and Fe_2O_3/AuNPs/SiO_2 particles were shown in fig. 1. The results indicated that the α-Fe_2O_3 particle had an ellipsoidal shape, which had mean lengths of the major and minor axes of 420 and 120 nm (fig. 1a). The AuNPs could be deposited on the surface of NH_2-Fe_2O_3 by the ligand exchange of citrates to the amino groups (Liu *et al.,* 2009). The TEM results indicated that the Fe_2O_3/AuNPs could have a good self-assembly structure and the AuNPs evenly covered the surface of Fe_2O_3 particles (fig. 1b). A modified Stöber reaction associated with the hydrolysis of TEOS was employed to coat the Fe_2O_3/AuNPs particles with an amorphous SiO_2 layer. The TEM results (fig. 1c) showed that SiO_2 could smoothly coat the whole Fe_2O_3/AuNPs particles. These Fe_2O_3/AuNPs/SiO_2 particles had mean lengths of the major and minor axes of 550 and 330 nm, which were longer than those of Fe_2O_3 particles and indicated that these composite particles had a core-shell structure.

Preparation and etching of Fe_2O_3/AuNPs/SiO_2/PNIPAM particles

To functionalize the silica layer, MPS was used as silane coupling agent to reacting with active hydroxyl groups on SiO_2 layer of Fe_2O_3/AuNPs/SiO_2 particles, which led to the particles were functionalized with C=C bonds and allowed further polymerization to form an outer polymeric shell (Li *et al.,* 2010). Therefore, when NIPAM was as monomer, the poly (*N*-isopropylacrylamide) (PNIPAM) could coat the Fe_2O_3/AuNPs/SiO_2 (Fe_2O_3/AuNPs/SiO_2/PNIPAM) particles. After the removal of the silica layer by HF treatment, the cell-like particles (α-Fe_2O_3/AuNPs//PNIPAM) were obtained.

TEM results of fe_2O_3/auNPs/SiO_2 and Fe_2O_3/AuNPs/SiO_2 coated PNIPAM (Fe_2O_3/AuNPs//PNIPAM) particles were shown in fig. 2, which indicated that HF could destroy the SiO_2 layer and result in the form of the cell-like particles (fig. 2b) when α-Fe_2O_3, AuNPs, and PNIPAM were as cell nucleus, catalysts, and cell membranes, respectively.

DISCUSSION

Temperature-responsive catalytic performance of cell-like particles

The AuNPs catalyzed reduction of 4-nitrophenol (4-NP) by $NaBH_4$ to 4-aminophenol (4-AP) was chosen as a model reaction (Wunder *et al.,* 1995) to test the catalytic properties of the cell-like particles. The conversions from 4-NP to 4-AP under different temperatures were monitored by UV-vis spectroscopy and shown in fig. 3.

When the environmental temperature was 25°C, nearly all of 4-NP were convert into 4-AP after 15 min (fig. 3a), while the temperature was 40°C, the conversion of 4-NP to 4-AP was about 90.5% after 40 min (fig. 3b). This behavior were originated from the temperature-dependent swelling transition property of the hollow micro spheres involving the PNIPAM polymers with a lower critical solution temperature (LCST) at around 32°C in aqueous media (Liu *et al.,* 2014). Under the LCST, PNIPAM chains were hydrophilic, leading to a swelling state and opening pores of PNIPAM membrane. Therefore, the transfer of 4-NP molecules across the PNIPAM membrane could be easily. However, above the LCST, the hydrophobic and shrinking sate of PNIPAM membrane could result in the close of pores in PNIPAM membrane.

CONCLUSION

A novel kind of cell-like particles were presented, when α-Fe_2O_3 particles self-assembled AuNPs (α-Fe_2O_3/AuNPs) were as cores and PNIPAM hollow micro spheres were as shells. These cell-like particles could be as temperature-responsive nanoreactors. The catalytic performances of these cell-like particles to reduce 4-NP to 4-AP were investigated under different temperatures and the results indicated that the catalytic activity of cell-like particles was decreased when the temperature was above the phase transition temperature of PNIPAM.

ACKNOWLEDGE

This research is financially supported by the National Natural Science Foundation of China (No. 21172171 and No.21206124) and Tianjin Research Program of Application Foundation and Advanced Technology (No. 11JCZDJC22300 and No.12JCQNJC08600).

REFERENCES

Behra A, Giri TK, Krishna DT and Alexander AA (2012). An exhaustive review on recent advancement in pharmaceutical bioadhesive used for systemic drug delivery through oral mucosa for achieving maximum pharmacological response and effect. *Int. J. Pharm.,* **8**: 283-305.

Choi SH and Kang YC (2014). Ultrafast synthesis of yolk-shell and cubic NiO nanopowders and application in lithium ion batteries. *ACS Appl. Mater. Interfaces,* **6**(4): 2312-2316.

Fagundes DLG, Franca EL, Hara CCP and Honorio-Franca AC (2012). Immunomodulatory effects of poly (ethylene glycol) microspheres adsorbed with cortisol on activity of colostrum phagocytes. *Int. J. Pharm.,* **8**: 510-518.

Grabar KC, Freeman RG, Hommer MB and Natan MJ (1995). Preparation and characterization of Au colloid monolayers. *Anal. Chem.,* **67**: 735-743.

Güttel R, Paul M and Schüth F (2010). Ex-post size control of high-temperature-stable yolk-shell Au, @ ZrO_2 catalysts. *Chem. Commun.,* **46**: 895-897.

Kamata K, Lu Y and Xia YN (2003). Synthesis and characterization of monodispersed core-shell spherical colloids with movable cores. *J. Am. Chem. Soc.,* **125**: 2384-2385.

Katz E and Willner I (2004). Integrated nanoparticle-biomolecule hybrid systems: Synthesis, properties and applications. *Angew. Chem., Int. Ed.,* **43**: 6042-6108.

Lee KT, Jung YS and Oh SM (2003). Synthesis of tin-encapsulated spherical hollow carbon for anode material in lithium secondary batteries. *J. Am. Chem. Soc.,* **125**: 5652-5653.

Li GL, Liu G, Kang ET, Neoh KG and Yang XL (2008). pH-responsive hollow polymeric microspheres and concentric hollow silica microspheres from silica-polymer core-shell microspheres. *Langmuir,* **24**: 9050-9055.

Li JQ (2012). Synthesis of thermoresponsive core-shell microgels cross-linked with acryloyloxyethylami-nopolysuccinim-ide. *Asian J. Chem.,* **24**(1): 150-156.

Li LY, Qin DB, Yang XL and Liu GY (2010). Synthesis of ellipsoidal hematite/polymer/titania hybrid materials and the corresponding hollow ellipsoidal particles. *Polym. Chem.,* **1**: 289-295.

Liu GY, Ji HF, Yang XL and Wang YM (2008). Synthesis of a Au/silica/polymer trilayer composite and the corresponding hollow polymer microsphere with a movable Au core. *Langmuir,* **24**: 1019-1025.

Liu GY, Wang H, Yang XL and Li LY (2009). Synthesis of tri-layer hybrid microspheres with magnetic core and functional polymer shell. *Eur. Polym. J.,* **45**: 2023-2032.

Liu YY, Zhang WN, Li SZ, Cui CL, Wu J, Chen HY and Huo FW (2014). Designable yolk-shell nanoparticle @MOF petalous heterostructures. *Chem. Mater,* **26**(2): 1119-1125.

Soleimani F, Sadeghi H, Shahsavari H, Soleimani A and Sadeghi F (2013). Ammonium persulfate-induced graft copolymer based on carboxymethyl cellulose-g-PMAAm-co-PNIPAAm. *Asian J. Chem.,* **25**(9): 5025-5028.

Wunder S, Polzer F, Lu Y, Mei Y and Ballauff M (2010). Kinetic analysis of catalytic reduction of 4-nitrophenol by metallic nanoparticles immobilized in spherical polyelectrolyte brushes. *J. Phys. Chem. C.,* **114**: 8814-8820.

Zheng R, Meng X, Tang F, Zhang L and Ren J (2009). A general, one-step and template-free route to rattle-type hollow carbon spheres and their application in lithium battery anodes. *J. Phys. Chem. C,* **113**(30): 13065-13069.