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Morphology-controlled synthesis of Ag nanoparticle decorated poly(o-phenylenediamine) using microfluidics and its application for hydrogen peroxide detection

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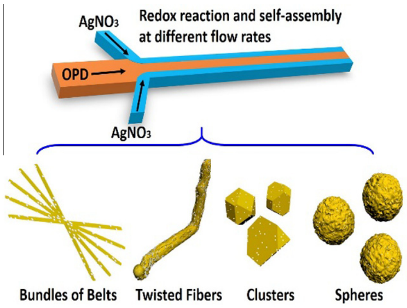
HIGHLIGHTS

- Shear rate was utilized for the morphology controlled synthesis.
- The composition of AgNPs-PoPD can also be controlled.
- A phase diagram of AgNPs-PoPD morphology against flow rate was obtained.
- A H_2O_2 sensor was fabricated based on the AgNPs-PoPD spheres.

GRAPHICAL ABSTRACT

A new method for the morphology-controlled synthesis via tuning shear rate in microfluidic channels.



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ABSTRACT

Shear rate was utilized for the morphology-controlled synthesis of silver nanoparticle decorated poly(o-phenylenediamine) (AgNPs-PoPD) using microfluidics. The morphology of AgNPs-PoPD, such as bundles of belts, twisted fibers, clusters, and microspheres, as well as the composition of AgNPs-PoPD clusters can be easily controlled by changing shear rates, which may provide a new potential method for the property control of materials. The phase diagram of AgNPs-PoPD morphology against reactant flow rate was obtained. The formation mechanism of different morphology of AgNPs-PoPD were analyzed and discussed based on numerical simulations. A H_2O_2 sensor based on AgNPs-PoPD spheres was fabricated, due to its good catalytic activity toward the reduction of H_2O_2. The linear detection range is determined to be from 20 μM to 180 μM, with the detection limit of 5.7 μM at a signal-to-noise ratio of 3.

1. Introduction

Microfluidic technology has been developed as a powerful platform for various applications including bioanalysis [1,2], tissue engineering [3], and chemical assembly or synthesis [4–8]. Several advantages of microfluidics have been proved over conventional bulk reaction, such as continuous and automatic processing, unprecedented precise control over synthetic conditions, and excellent reproducibility [9]. Microfluidics have been used for a wide range of synthesis or assembly such as organic chemicals [10,11], inorganic nanoparticles [12], and organic/inorganic hybrid

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materials [6]. As we know, the morphology control over materials is really significant, because it may provide new properties of the materials with different shapes. However, it is worth noting that there are only several reports about morphology control over microcapsules or polymer particles using microfluidics [13–16], in which droplets were mainly utilized as templates or a microreactor for the final products. Additionally, Doyle and coworkers introduced a new class of microfluidic particle synthesis method using photolithography to define particle shape, which relies on transparent masks to provide shape-definition [17,18]. Recently, we reported a template-free method for morphology control over hybrid self-assemblies comprised of polymer-tethered amphiphilic inorganic nanoparticles [6], which is based on the building blocks fabricated in bulk solution rather than in the chip. To date, there is no report on producing the building blocks first and then self-assembling in one go within the chip, without using any template. Furthermore, to the best of our knowledge there is no report of controlling over the morphology of microfluidic products using shear rate in microchannels.

Conducting polymers have drawn a lot of attention due to their applications in optical and microelectronic devices [19], biosensors [20–24] and chemical sensors [25–27]. Poly(o-phenylenediamine) (PoPD) is a typical conducting polymer, which can be prepared in a fiber or sphere format using chemical oxidation polymerization [28–34]. For example, Wang and coworkers reported the synthesis of PoPD fibers with high quality in aqueous solution without any surfactant using $HAuCl_4$ and $AgNO_3$, respectively [29–31]. Furthermore, other oxidizing agents were also utilized for PoPD synthesis, such as $HPtCl_4$ [35], ferric chloride [36] and ammonium persulfate [32,37]. Metallic nanoparticle modified PoPDs were obtained as well [30,34,38], which showed a good performance in their catalytic activity. However, there is still no report on the morphology control of PoPD hybrid with metallic particles using only one oxidizing reagent.

The accurate detection of hydrogen peroxide is of great significance in the fields of chemistry, pharmaceutical, clinical control, industrial and environmental protection [39–41]. Hence, many different techniques were developed for the determination of hydrogen peroxide, such as photoacoustic spectroscopy [42], chemiluminescence [43] and electrochemistry [44]. Amongst all the techniques, electrochemistry is quite promising, due to its high sensitivity, good reproducibility, excellent selectivity and low cost. Hence, many materials were obtained and utilized to detect hydrogen peroxide using electrochemical techniques. Those materials can be categorized into three classes. One is pure material, such as Au nanoplate [45], graphitic carbon nitride nanosheets [46]; the other is the composite based on metal nanoparticle and reduced graphene oxide or graphene, such as Au NPs/reduced graphene oxide [47], AgNPs/reduced graphene oxide [48], AgNPs/graphene nanosheets [49–51], AgNPs/SiO_2-coated graphene oxide nanosheets [52]; the third is based on the combination of metal nanoparticles and conducting polymers, *e.g.*, AgNPs/2,4,6-tris(2-pyridyl)-1,3,5-triazine nanobelts [53], AgNPs/polyaniline nanofibers [54], AgNPs/poly(m-phenylenediamine) [55], AgNPs/coordination polymer nanobelts [56], AgNPs/polypyrrole colloids [57]. Although all the materials above have the ability to detect hydrogen peroxide, their morphologies cannot be easily well controlled or changed.

Herein, we demonstrated an easy and effective way to synthesize morphology-well-controlled AgNPs modified PoPD with only one oxidizing reagent in the absence of template using microfluidics by simple adjusting the reactant flow rates. We realized redox reaction (forming building blocks of oPD oligomers and AgNPs) and self-assembly (forming AgNPs-PoPD) in one microfluidic chip. The composition of PoPD clusters can be controlled as well. The formation mechanism was proposed based on the simulation using COMSOL software. We found the shear rate was the main factor for different morphology of AgNPs-PoPD, since large assemblies can be obtained under low shear rates, while small assemblies can be obtained under high shear rates. AgNPs-modified PoPD spheres exhibit good catalytic activity toward the reduction of H_2O_2, based on which a H_2O_2 sensor is developed.

2. Experimental

2.1. Chemicals and equipments

$AgNO_3$, o-phenylenediamine (OPD), H_2O_2, NaH_2PO_4, and Na_2HPO_4 were all purchased from Sigma (China) and used as received. An Autolab electrochemical workstation (PGSTAT320N, Switzerland) was applied to carry out the electrochemical experiments using a conventional three-electrode system at room temperature. The electrodes were a modified ITO (indium tin oxide) working electrode with a 5 mm diameter working area, a platinum wire counter electrode and a saturated calomel reference electrode (SCE), respectively. The measurements were conducted in a nitrogen-saturated solution containing 0.2 M PBS (pH 7.0). Ultrapure water (18.2 MΩ cm) was used throughout. Microfluidic experiments were conducted using AL-1000 syringe pumps from world precision instruments (USA).

The PoPD structures were imaged using a Scanning Electron Microscope (SEM; XL 30 Philips, Philips, lnc., Netherlands). Mapping EDS (Energy Dispersed Spectrum) analysis was performed using an EX-250 (Horiba, Japan) attachment. TEM images were recorded on a JEOL JSM-6700F instrument (Hitachi). Raman spectra were obtained using an FT-Raman 960 spectrophotometer with an argon ion laser with a wavelength of 514.5 nm.

2.2. Fabrication of microfluidic devices

Clewin 4 software was utilized for the design of a photomask pattern. The master was fabricated with SU 8 photoresist on a silicon wafer using traditional photolithography technique. The microfluidic chips were fabricated with soft lithography. In brief, silicone elastomer oligomer and crosslinker with a weight ratio of 10:1 (Sylgard 184 Silicone Elastomer Kit, from Dow Corning) were mixed together under strong stirring. The PDMS precursor was poured onto a silicon master in a Petri dish followed by degassing in a vacuum oven and curing in an oven at 65 °C overnight. The PDMS replica peeled off from the silicon master were treated by an O_2 plasma for 30 s, and then bonded with another plasma-treated glass substrate.

2.3. Simulation details

COMSOL Multiphysics software (Version 4.3) was applied to carry out the numeric simulations. The microfluidic flow focusing device was modeled using steady incompressible Navier–Stokes Equations in the convection and diffusion application models [58,59]. Eqs. (1) and (2) are the governing equations that the solver executes, while Eq. (3) is a solution in the convection and diffusion application modes:

$$\rho(u \cdot \nabla)u = \nabla\left[-PI + \mu(\nabla u + (\nabla u)^T)\right] + F \tag{1}$$

$$\nabla \cdot u = 0 \tag{2}$$

$$\nabla \cdot (-D\nabla S) = R - u \cdot \nabla S \tag{3}$$

where ρ is the fluid density (kg/m^3); u denotes the velocity vector (m/s); P is the pressure (Pa); μ equals the dynamic viscosity (Pa·s); F is the body force term (N/m^3); I represents the identity matrix; D equals the diffusion coefficient; S and R are a transported scalar and