Chemical Engineering Journal 321 (2017) 195–206

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Shape effect on the fabrication of imprinted nanoparticles: Comparison between spherical-, rod-, hexagonal-, and flower-shaped nanoparticles

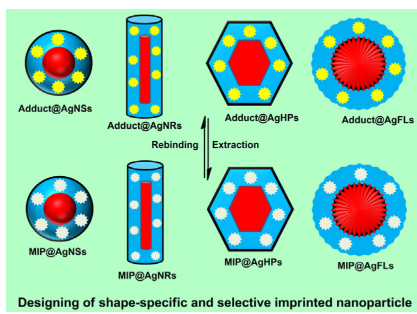
Ekta Roy [a], Santanu Patra [a], Shubham Saha [a], Deepak Kumar [b], Rashmi Madhuri [a,*], Prashant K. Sharma [c]

[a] Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand 826 004, India
[b] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
[c] Functional Nanomaterials Research Laboratory, Department of Applied Physics, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand 826 004, India

HIGHLIGHTS

- Different shaped (spherical, rod, hexagonal, flower) AgNPs were prepared by green-chemistry.
- AgNPs were modified with 2-bromoisobutyl bromide and used as nanoinitiator.
- Effect of different shaped-AgNPs on the performance of MIP was studied.
- Among the different formats, the flower shaped AgNPs@MIPs win the race.
- Shape-specific MIPs was developed for selective detection of phenformin in real samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 October 2016
Received in revised form 3 March 2017
Accepted 13 March 2017
Available online 27 March 2017

Keywords:
Anisotropic nanoparticles
Nanoinitiator
Phenformin
Shape effect of nanoparticles
Real sample analysis

ABSTRACT

In this work, we prepared four different shaped silver nanoparticles (AgNPs) (spherical, rod, hexagonal, and flower shaped) by using the green synthesis approach. The synthesized AgNPs were characterized by UV–vis spectroscopy, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, which showed that AgNPs have a very narrow size distribution with visible and confined geometry and shape. The synthesized AgNPs were modified by 2-bromoisobutyryl bromide, developed as a nanoinitiator, and then used for the synthesis of phenformin-imprinted polymers (MIP@AgNPs). A comparative study was performed between different shaped MIP-modified AgNPs; in addition, the effect of AgNPs on electrocatalytic activity, surface area, adsorption capacity, and electrochemical and photoluminescence sensing of phenformin was also explored. Among the different shaped MIP@AgNPs, the anisotropic AgNPs have multiple facets and planes, i.e., the flower-shaped AgNPs showed the best performance and were successfully applied for trace-level detection of phenformin in an aqueous sample. Furthermore, the MIP@AgNPs were also applied for the detection of phenformin in human serum, plasma, and urine samples without any cross-reactivity effect, suggesting a bright prospect for the use of anisotropic nanomaterials in future clinical trials.

1. Introduction

Noble metal nanoparticles (NPs) represent one of the most remarkable areas of modern nanoscience and nanotechnology because of their biocompatibility, lower toxicity, and higher

* Corresponding author.
E-mail address: rshmmadhuri@gmail.com (R. Madhuri).

http://dx.doi.org/10.1016/j.cej.2017.03.050
1385-8947/

affinity with a wide range of biomolecules [1]. The outstanding properties of noble metal NPs are attributed to their easy stabilization, quantum size effect, plasmon resonance, and large surface/volume ratio [2–4]. During the early research days, the word nanoparticle was related to spherical materials having a size in the nanoscale range. However, in the beginning of the 20th century, Zsigmondy noted that metal NPs in the size range of 40 nm or less are not necessarily spherical and discovered different colored anisotropic gold NPs [5]. Subsequently, it was reported that nanomaterials having nonspherical shapes may exhibit unique physical and chemical properties compared to their spherical counterparts [5]. A dramatic enhancement in properties can be achieved by a simple geometric alteration in the shape and size because different crystal surfaces have different surface atom densities and electronic structures, which lead to different physical and chemical properties [6]. For example, carbon nanotubes (CNTs) having one-dimensional tube shape possess unique physiochemical properties owing to their different shapes and sizes [7]. In contrast, zero-dimensional NPs (such as spherical) having similar confinement of electrons in all the three dimensions possess similar properties regardless of directions [6]. According to the literature, many peculiar properties of the anisotropic nanomaterials may arise owing to a change in their shape due to the spatial confinement of electrons, excitons, phonons, plasmons, and electric fields around the particles and due to changes in their surface to volume ratio. Such changes may affect or introduce some new physiochemical properties such as enhanced chemical reactivity, hardness, and magnetic, catalytic, biological, and optoelectronic properties. Therefore, the current research is more focused on producing nanosized materials of well-defined morphologies with improved properties. Among the various anisotropic noble metal nanoparticles, silver nanoparticles (AgNPs) have received a huge interest during the last decade, owing to their biocompatibility, stability, and low cost in comparison to gold and platinum nanoparticles [6]. Synthesis of anisotropic AgNPs has attracted immense interest among researchers because the structural, optical, electronic, magnetic, and catalytic properties of anisotropic AgNPs are different from and most often superior to those of spherical AgNPs, and therefore, anisotropic AgNPs have tremendous potential applications [8]. The synthesis of anisotropic AgNPs is mainly carried out by seed-mediated synthetic methods, in which a small presynthesized seed particle is introduced into a growth solution containing the metal precursor, a reducing agent, surfactants, and some additives. The shape of the resulting nanoparticles depends on the interaction of precursor compounds with stabilizers, inductors around them, and the preparation method (i.e., reaction conditions) [9–12]. Xu et al. synthesized three different shaped AgNPs (semi-circular, triangular plate, and cube) and used them for oxidation of styrene [13]. They found that the reaction rate in cubic nanoparticles is 14 times more than that in triangular nanoplates and 4 times higher than that in semi-spherical nanoparticles. Similarly, Tak et al. reported the effect of different shaped AgNPs in terms of skin permeability, diffusion coefficients, penetration rates, and depth of penetration through intercellular pathways by using an *in vivo* or *in vitro* model [14]. Although several works have been reported for the synthesis of anisotropic AgNPs via chemical [15], electrochemical [16], radiation [17], photochemical [18] and Langmuir-Blodgett [19] methods, the role of green synthesis approach is not well explored this area. However, green synthesis approach is at their prime phase and in the current demand of market. Recently, Singh et al. reported the synthesis of nanosphere, nanoprism, triangular, rod, pentagonal, hexagonal, and octagonal shaped AgNPs using the green synthesis approach and compared their antibacterial property [20]. Green synthesis of anisotropic AgNPs using pomegranate juice extracts has been already explored by our research group, but their applications for bacterial inhibition and removal remain to be explored in detail [21]. The reported research is confined to the effect of the shape of AgNPs on their own properties, including catalytic, electrochemical, antibacterial, and biomedical properties. However, whether the shape of AgNPs can affect the properties of any other material or polymer is not yet explored and is not available in the literature. Therefore, the present work explores the effect of the shape of AgNPs on the behavior and properties of molecularly imprinted polymers (MIPs). To date, combinations of nanomaterials (such as NPs, graphene, and CNTs) with MIPs are very popular and have already been explored and introduced to solve problems such as poor binding and template leakage. However, it is not yet reported whether the shape of the nanoparticles has any effect on the binding properties of MIPs. In the present work, for the first time, we synthesized four different shapes of AgNPs (spherical, rod, hexagonal, and flower shaped) using starch derived from boiled raw rice as the reducing agent. The green AgNPs were modified through chemical reactions and used to design a nanoinitiator, which was further employed for designing different shaped MIPs.

For the synthesis of imprinted polymers, phenformin was used as the target analyte, which is a biguanide antidiabetic agent used in the treatment of noninsulin-dependent (Type-2) diabetes mellitus [22]. However, recently, the drug is banned because of its high risk of lactic acidosis [22]. Considering the importance of phenformin measurement in real samples in a rapid, sensitive, and selective way, we designed shape-dependent MIPs as a dual probe, i.e., for electrochemical and optical sensing of the target analyte. Using shape-dependent dual-mode MIP format, the drug was successfully measured quantitatively in the real human serum and pharmaceutical samples in a rapid, selective, and sensitive manner.

2. Experimental Section

The materials and instrumentation section along with the procedures for the preparation of starch solution and synthesis of calcein monomers and imprinted polymers are provided in Supporting information, Section S1.

2.1. Synthesis of different shaped AgNPs

2.1.1. Synthesis of spherical AgNPs

To an aqueous $AgNO_3$ solution (50.0 mL, 0.01% by weight), 0.45 mL of starch solution was added, and the solution was heated to boil [23]. The solution was then cooled to the room temperature, and 1.82 g of cetyl trimethyl ammonium bromide (CTAB) was added into the solution, and the mixture was stirred at 27 °C for 12 h. The solid precipitate was collected by centrifugation and was dried and stored in a desiccator.

2.1.2. Synthesis of rod-shaped AgNPs

The seed-mediated growth method was used for the synthesis of rod-shaped AgNPs (AgNRs). For this, the seed and growth solutions were prepared separately [24]. First, the seed solution was prepared by mixing 0.60 mL of hot aqueous starch solution and 0.25 mM $AgNO_3$ (10.0 mL); the mixture was stirred at 40 °C for 2 h. The growth solution was prepared by mixing 0.020 M CTAB (7.0 mL), 10 mM $AgNO_3$ (0.50 mL), and 0.50 mL of starch. To the growth solution, 1.0 mL of seed solution and 0.5 mL 1.0 M NaOH solution were added to make the solution alkaline (pH $\sim$11). The mixture was finally allowed to remain stable for 2 h at 25 °C, and the resulting AgNRs were dried in a vacuum oven and kept in a desiccator.