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Sequential injection technique as a tool for the automatic synthesis of silver nanoparticles in a greener way



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ABSTRACT

This paper presents a new way to the synthesis of uniform and size-controlled silver nanoparticles by means of microreaction technology. It complies with the philosophy of green chemistry by developing a process that prevents pollution at source—by automation of the manipulations using microtubes manifolds and with the use of benign reagents and photochemistry to enhance the reaction of synthesis of Ag nanoparticles. Effect of hydrodynamic parameters (reagent volumes and volume flow rate) and concentrations (reducer and stabilizer), temperature, pH and UV irradiation time on morphology and size of nanoparticles was studied. The silver nanoparticles has been characterized by transmission electronic microscopy (TEM), electron diffraction X-ray spectroscopy (EDS), UV–vis spectra analysis, dynamic light scattering (DLS) and zeta potential measurements. Particles are mostly spherical in shape and have average sizes between 7 and 20 nm. The particle size can be controlled by changing not only the flow rate and UV light time exposition but also the reducer/AgNO₃ concentration ratio.

This is a sustainable and cost-saving methodology that guarantees not only reproducible synthesis, but also the changing of NPs characteristics at time by simple control of the fluid transport.

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1. Introduction

Silver nanoparticles (AgNPs) use is widespread in diverse areas, including textile engineering, biotechnology, medicine, bioengineering, catalysis, water treatment, optics, electronics and also in food science [1]. The control of their physicochemical properties, namely its size and specific surface area, is a key parameter to determine their application. So, different methods have been reported for the synthesis of silver nanoparticles [2] namely by electrochemistry [3–5], thermal decomposition [6], laser ablation [7], microwave irradiation [8] and sonochemistry [9]. Chemical reduction, however, is the most frequently applied method since stable colloidal dispersions can be obtained [10,11]. The various species of Ag(I) are reduced originating silver atoms (Ag(0)) that then agglomerate into oligomeric clusters. These clusters eventually lead to the formation of colloidal Ag particles [1,11,12]. However, typical redox synthesis methods use, most of the times, hazardous chemicals as reducing agents [13]. So alternatives with the focus in using benign reagents have been growing, not only, regarding the reducing reagents [13] but also the NPs stabilizers [11,14]. However, many green reducer routes are very slow at

room temperature so consequently need long periods of time to be complete [13]. Photoreduction can be an alternative. Harada et al. [15] made the photoreduction of Ag⁺-containing water-in-[BMIm][BF₄] or water-in-[OMIm][BF₄] microemulsions in the presence of the non-ionic surfactant Tween 20 under high-pressure conditions of CO₂ [15]. The surfactant presence in the water-in-ionic liquid microemulsions promotes the stabilization of AgNPs and consequently the suppression of their growth and aggregation. Zhou et al. [16] prepared nanosilver/gelatine/CM-chitosan hydrogels by radiation crosslinking and reduction simultaneously. The formation of nanoparticles and nanorods was also described by Szymanska-Chargot et al. [17] being AgNO₃ in ethanol solution under UV light irradiation.

One of the goals of the present work is then to contribute to the developing of clean, environmental and human benign synthesis, aiming the use of nontoxic chemicals and photochemistry.

However, it is also extremely important to design a synthesis methodology that guarantees control of the experimental conditions as they determine the size, morphology, stability and chemical–physical properties of the AgNPs and consequently their application interest. For that a flow reactor device was used as advantages as scale- out, mass and heat rapid transportation and control, flexibility in space and time kinetic control are achieved [18–21].

The small size of the reaction channel, together with favourable heat and mass transport, allows for precise control of reaction and

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control of particle size, shape and composition, which is not easy to achieve in batch synthesis.

It is also achieved an enhanced efficiency of the UV light irradiation due to the extensive light penetration through the narrow channel compared to batch chamber reactors where the light penetration is not so effective due to the dilutions or the type of vessels used.

Continuous flow synthesis have been tested. However some disadvantages are noticed, namely partial mixing of reagents in batch mode [22–24], use of high temperatures [22,23,25], complex systems with microwaves oven [22,25] or ultrasonic stirring [25], high volumes of reagents [25] or a ineffective control of reagent volumes [24]. Additionally, this kind of systems do not present flexibility for changing volumes or reaction times as they present fixed configurations only physically changeable. Other flow techniques based in the sequential injection flow modes [26] (SIA) can, however, be used contributing to the design of more versatile modules. Its way of functioning is based in a computer-controlled nature that allows modifying the most relevant analytical parameters at run-time. It allows a great operational flexibility and the establishment of distinct strategies without physical reconfiguration. Moreover the bi-directional nature of fluid handling, the robustness, the ease of operation and the low reagent consumption inherent to SIA guarantee a great potential for its application in the silver nanoparticles synthesis. The incorporation of a photo reactor in a SIA module is also advantageous since the system can control precisely the irradiation time that leads to a great reproducibility of synthesis process and consequently of synthesized silver nanoparticles.

So, the objectives of this work were to develop an automatic module, based on sequential injection technique to synthesize silver nanoparticles, using at the same time green reducers and UV light for the reduction process. In addition to the synthesis, the present study was designed to characterize silver nanoparticles and to investigate the effect of different reducers, reagent concentrations, times of UV irradiation and other important parameters in this synthesis.

To the best of our knowledge this is the first report of a rapid, green and automatic protocol for size controlled silver nanoparticles synthesis, based on the sequential injection technique with a photoreactor and green reducers.

2. Experimental section

2.1. Reagents and solutions

All solutions were prepared with analytical reagent grade, high purity water (milli Q) with a specific conductivity $< 0.1 \mu\text{S cm}^{-1}$.

A $5.00 \times 10^{-3} \text{ mol L}^{-1}$ silver nitrate (Merck) and a 0.10 mol L^{-1} tri-sodium citrate (Sigma) solutions were prepared from dissolution in water of appropriate amounts of the commercial powders.

The reducers used were ascorbic acid (Merck), glucose (Sigma) and glycerol (Sigma) in working standard solutions with concentrations between 2.50×10^{-5} and $2.00 \times 10^{-2} \text{ mol L}^{-1}$. It was also used working standard solutions of NADH (Sigma) between 2.50×10^{-5} and $1.00 \times 10^{-3} \text{ mol L}^{-1}$ and of uric acid (Sigma) between 2.50×10^{-5} and $1.25 \times 10^{-4} \text{ mol L}^{-1}$. All of these working standard solutions were prepared in water by dilution of the aqueous stock solutions prepared by dissolution of the appropriate amount of commercial powder or by dilution of the commercial solution in case of glycerol.

The carrier solution was $1.0 \times 10^{-3} \text{ mol L}^{-1}$ NaOH in water.

2.2. Automatic silver nanoparticles synthesis

2.2.1. Apparatus

The automatic SIA system (Fig. 1) consisted of a Gilson Minipuls 3 (VilliersleBel, France) peristaltic pump, equipped with a 1.30 mm

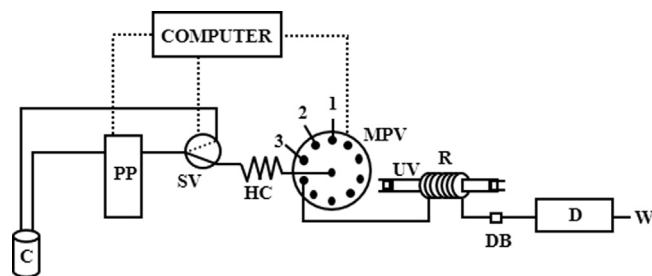


Fig. 1. SIA manifold for the silver nanoparticles synthesis. C, carrier; PP, peristaltic pump; SV, solenoid valve; HC, holding coil (2 m length/0.8 mm i. d.); MPV, multiposition selection valve; 1, AgNO_3 $5.00 \times 10^{-3} \text{ mol L}^{-1}$; 2, tri-sodium citrate 0.10 mol L^{-1} ; 3, reducer; R, reaction coil (1 m, around the ultra-violet lamp); DB, de-bubbler; UV, ultra-violet lamp; D, spectrophotometric detector; W, waste.

i.d. Gilson PVC pumping tube and a 10-port selection valve (Valco, Vici C25-3180EMH, Houston, USA).

In order to guarantee reproducibility in the aspirated and propelled volumes, especially when dealing with reduced volumes, the starting position of the peristaltic pump at the beginning of each cycle was controlled. For that an NResearch 161 T031 solenoid valve (W. Caldwell, NJ, USA) (SV, Fig. 1) and a device placed on the peristaltic pump head were also introduced in the system [27].

Irradiation of the solutions with UV light was performed using a 15 W Philips TUV 15 W/G15T8 low pressure mercury lamp at 253.7 nm. The photochemical reactor was implemented by coiling a PTFE tubing (1 m and 0.8 mm i.d.) around the lamp, which was subsequently placed inside a protecting chamber.

As detection system, a Jenway (Model 6300, United Kingdom) spectrophotometric detector equipped with a flow-through cell of $30 \mu\text{L}$ was used. In the system, before the detector, it was placed a de-bubbler 006BT from Omnifit (Cambridge, England), to avoid that any bubble, formed in the reactor, could reach the detector.

All connections and the holding coil (HC, Fig. 1) that was serpentine-shaped in configuration were made with 0.8 mm i.d. PTFE tubing. This system was controlled by a homemade program written in QuickBasic language and implemented in a microcomputer equipped with an interface card (Advantech Corp., PCL 711B, San Jose, CA).

2.2.2. Automatic procedure

The developed analytical cycle (Table 1) began with the aspiration of $20 \mu\text{L}$ of AgNO_3 to the holding coil, followed by $20 \mu\text{L}$ of tri-sodium citrate and $20 \mu\text{L}$ of reducer solutions (steps 1–3). This aspirated sequence was sent by flow reversal, to the reaction coil (R, Fig. 1) placed around the UV lamp (UV, Fig. 1), through the port 4 (step 4). In the reaction coil the flow was stopped for 30 s (step 5), and thereafter, the fluids were sent to the detector (step 6) at 1 mL min^{-1} and a signal was recorded giving an indication about the yield of the synthesis, measuring the absorption signals in a fixed wavelength of 435 nm. After the detection the fluids resulted from each synthesis were collected for the Ag NPs characterization.

2.3. Characterization of AgNPs

2.3.1. UV-vis spectra analysis

The characterization of AgNPs could be done by UV-vis spectra analysis since their optical properties differ from those of bulk metal AgNPs. This NPs when dispersed in liquid media, display intense colors exhibiting a strong UV-vis absorption band attributed to surface plasmon resonance absorption. Surface plasmon resonance is a collective excitation of the electron in the conduction band near the surface of the nanoparticles [1,2,28]. Electrons are limited to specific vibrations modes by the particle's size

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