Materials Letters 235 (2019) 197–201

Contents lists available at ScienceDirect

Materials Letters

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

In situ formation and immobilization of silver nanoparticles using thermo-responsive microgel particles and their cytotoxicity evaluation

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ARTICLE INFO

Article history:
Received 7 May 2018
Received in revised form 30 August 2018
Accepted 6 October 2018
Available online 8 October 2018

Keywords:
Silver nanoparticles
Thermo-responsive
Glucose
Electron microscopy

ABSTRACT

In this study, a simple environmentally greener "in situ" chemical synthesis has been developed to prepare silver nanoparticles (Ag NPs) from chemically reduced $AgNO_3$ in an aqueous media of thermo-responsive microgel, using glucose as a reducing agent and by adopting a microwave irradiation technique. The thermo-responsive microgel poly-*N*-isopropylacrylamide-co-2-hydroxyethyl acrylate, poly (NIPAM-co-HEA) 200 nm in size was prepared by surfactant free emulsion polymerisation of a selected mixture of *N*-isopropylacrylamide, methylene-bis-acrylamide and 2-hydroxyethyl acrylate. This microgel acts as a mere support to immobilize Ag NPs. The formation of Ag NPs and the thermo-responsive properties of the mixture were studied using UV–visible Spectroscopy. Their structures were characterised by FE-SEM and TEM. The Ag NPs prepared by this approach appear to be monodispersed with sizes which are <15 nm. Excellent biocompatibility, cell viability and environmentally responsive properties suggested that as-prepared composite particles are ideal candidate for antibacterial, biosensors and drug delivery applications.

1. Introduction

Development of bio-compatible composites of metal NPs with polymers are of great interest for providing important building blocks and for the construction of functional structures in biomedical applications [1,2]. Among the various metal NPs, Ag NPs are of particular interest because of their unique properties, i.e., size and shape dependent, optical, and electrical properties which have applications in biosensors, anti-microbial and drug delivery systems. Nanocomposites or hybrid polymer-Ag NPs have also attracted much attention because of their potential applications in the areas of biomedicine, electronics, catalysis, energy, and environment [3]. Poly(NIPAM) is one of the most extensively studied thermo-responsive polymers because of their unique amphiphilic characteristics. It has also been reported that this polymer is a bio-compatible polymer [4,5]. To this end, polymer-NP composites are promising candidates to exploit or enrich the unique properties of nanoparticles, while the polymer matrix can control host-guest interactions to ensure the well-defined spatial distribution of nanoparticles.

To date, many methods have been developed for the synthesis of noble metals, in particular, Ag NPs. A polymer-protected reduction and micro-emulsion method has been widely used for preparing Ag NPs in the presence of polymer-protectors by reducing silver nitrate ($AgNO_3$) [6]. Using thermos-sensitive unimolecular micelles as templates, Liu and co-workers [7] reported "in situ" preparation of Ag NPs with a controllable spatial distribution. Water-soluble gold NPs have also been successfully incorporated into poly(NIPAAm-co-methacrylic acid) microgel particles [8]. Recently, our group [4] reported a method of preparation of Ag NPs (a well stable, monodisperse) in poly(NIPAAm-acrylic acid) using a microwave technique in thermo-responsive microgel solution using the same microgel as a template. Although "in situ" fabrication of Ag NPs has been well documented, no work has been reported yet regarding the synthesis of Ag NPs with poly(NIPAM-co-HEA) microgels using a microwave-assisted heating technique and their cytotoxicity evaluation.

In this work, we describe an easy, environmentally greener approach toward the synthesis of highly monodispersed and stable Ag NPs in a thermo-responsive microgel i.e. poly NIPAM/HEA

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https://doi.org/10.1016/j.matlet.2018.10.041
0167-577X/

copolymer. The synthesis was performed in weakly alkaline solution containing pre-synthesised thermo-responsive microgel solutions in the presence of a non-toxic reducing agent – glucose, using a microwave technique for 50sec. The synthesised microgel/Ag NPs composite materials were characterised by UV-vis spectrophotometer, FE-SEM, TEM and hemolysis test followed by a cytotoxicity evaluation with a cell viability assay.

2. Experimental section

2.1. Preparation of microgel particles

A 9.2 mM of aqueous N-isopropylacrylamide was taken in a 100 ml flask. 63.0 μl of 2-hydroxyethyl acrylate was added to the above solution with a 7 wt% quantity of methylene-bis-acrylamide (MBA). These mixtures were degassed for half an hour, and heated to 70 °C. Then, 50.0 μl (5% w/v) of potassium persulphate was injected into this solution under the same conditions and the reaction was allowed to proceed for 4hr. Finally, the microgel particles were centrifuged, cleaned, dialysed with distilled water and freeze dried for further use.

2.2. Preparation of Ag NPs in microgel particles

12 ml of the prepared microgel particles in aqueous solution (5 mg of microgel diluted with 50 ml of water) was poured into a 25 ml flask and bubbled with nitrogen for half an hour. The pH of the solution was taken to 8.5 by 0.1 M NaOH and a 50 μl aliquot of a 0.20 M $AgNO_3$ solution was added into the microgel solution, the colour of the solution turned to turbid. Finally, a 100 μl aliquot of a 0.20 M aqueous solution of D-glucose was added and then stirred. The mixture was transferred into a Teflon-lined household microwave oven (2.45 GHz) with 1.25 kW power and irradiated for 50sec. Characterizations and experimental procedures of the cell viability (MTT) and hemolysis assays are provided in the Supporting Information section.

3. Results and discussion

Fig. 1a and b shows the TEM and FE-SEM images of the synthesised microgel particles respectively. As depicted in the above images, nanometre size particles inter-connected each other of nearly spherical shape with an average diameter of 200 nm, is

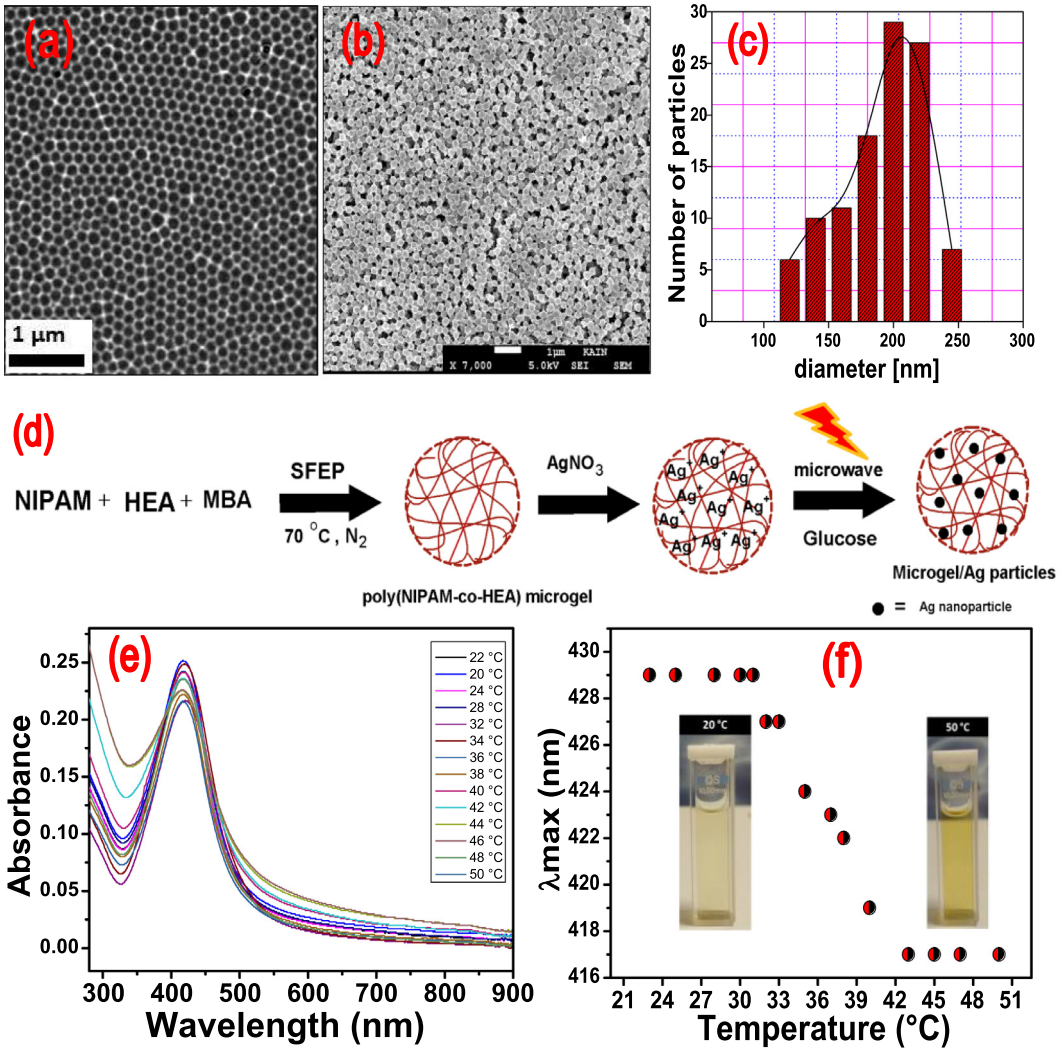

Fig. 1. (a) TEM, (b) FE-SEM image and (c) Particle size distribution histogram plot of the synthesised microgel particles. (d) Schematic illustration of the synthesis of microgel/Ag NPs particles. (e) UV–vis absorption spectra of microgel/Ag composite particles at altered temperatures and (f) is the temperature dependence absorption maximum (wavelength) of Ag NPs in microgel/Ag composites.