#### Materials Chemistry and Physics 173 (2016) 161-167

Contents lists available at ScienceDirect

### Materials Chemistry and Physics

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

# Synthesis and characterization of thiolated pectin stabilized gold coated magnetic nanoparticles



CHE

Varun Arora<sup>a</sup>, Ankur Sood<sup>a</sup>, Jyoti Shah<sup>b</sup>, R.K. Kotnala<sup>b</sup>, Tapan K. Jain<sup>a,\*</sup>

<sup>a</sup> University School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, Sector 16-C, Dwarka, New Delhi 110078, India <sup>b</sup> National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi 110012, India

#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- Use of side group of tyrosine (phenol) as a pH dependent reducing agent to synthesize gold coated magnetic nanoparticles.
- Successful coating of gold shell on magnetic nanoparticles core.
- Synthesis of thiolated pectin and stabilization of aqueous dispersion of core-shell nanoparticles with thio-lated pectin.
- The superparamagnetic behaviour of magnetic nanoparticles is retained after shell formation.

#### A R T I C L E I N F O

Article history: Received 1 December 2014 Received in revised form 18 December 2015 Accepted 23 January 2016 Available online 5 February 2016

Keywords: Nanostructures Composite materials Magnetic properties Polymers Electron microscopy Surface properties

#### ABSTRACT

Core–shell nanoparticles, magnetic core and gold shell, were synthesized by reduction of gold chloride on the surface of magnetic nanoparticles; using tyrosine as a reducing agent. The formation of gold shell on magnetic nanoparticles was confirmed by X-ray diffraction (XRD) and UV-Visible spectroscopy. The core–shell nanoparticles (CSn) were conjugated with thiolated pectin to form a stable aqueous dispersion. The hydrodynamic size of thiolated pectin stabilized core–shell nanoparticles (TP-CSn) measured by Dynamic light scattering (DLS) was 160.5 nm with a poly dispersity index (PDI) of 0.302, whereas the mean particle size of TP-CSn calculated by high resolution transmission electron microscopy (HRTEM) was  $10.8 \pm 2.7$  nm. The value of zeta potential for TP-CSn was -13.6 mV. There was a decrease in the value of saturation magnetization upon formation of the gold shell on magnetic nanoparticles. The amount of thiolated pectin bound to the surface of core–shell nanoparticles, calculated using Thermogravimetric analysis (TGA), was 6% of sample weight.

© 2016 Elsevier B.V. All rights reserved.

Abbreviations: MRI, magnetic resonance imaging; CSn, core-shell nanoparticles; TP, thiolated pectin; TP-CSn, thiolated pectin stabilized core-shell nanoparticles; DLS, dynamic light scattering; HRTEM, high resolution transmission electron microscopy; XRD, X-ray diffraction; FT-IR, fourier transform infrared spectroscopy; TGA, thermogravimetric analysis; VSM, vibrating sample magnetometer; MNPs, magnetic nanoparticles; SSPE, saline sodium phosphate EDTA buffer; SPR, surface plasmon resonance.

<sup>c</sup> Corresponding author.

*E-mail addresses*: varun.arora3986@gmail.com (V. Arora), ankursood02@gmail. com (A. Sood), shah.jyoti1@gmail.com (J. Shah), rkkotnala@nplindia.org (R.K. Kotnala), tapankjain@gmail.com, tapan.jain@ipu.ac.in (T.K. Jain).

http://dx.doi.org/10.1016/j.matchemphys.2016.01.056 0254-0584/© 2016 Elsevier B.V. All rights reserved.

#### 1. Introduction

Magnetic nanoparticles, magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), have been the focus of research over the last decade due to their expansive applications in the field of targeted drug delivery [1], magnetic resonance imaging (MRI) [2], cell labelling and separation [3,4], and hyperthermia treatment of cancer [5]. Magnetic nanoparticles are superparamagnetic in nature; they are magnetized only upon application of an external magnetic field [6]. Due to large surface area, magnetic nanoparticles are prone to oxidation by



air [7] and aggregation [8]; this limits their use in biomedical applications. Various coating strategies have been employed to protect magnetic nanoparticles from oxidation and aggregation by using polymers [9] and noble metals like gold [10], silica [11]. Out of them, gold coating offers advantage of being chemically stable and biocompatible [12]. It also provides the possibility of conjugating targeting ligands [13], drugs [14] using gold-thiol chemistry, and for photothermal destruction of cancer cells [15]. In gold coated magnetic nanoparticles, superparamagnetic nature of magnetic nanoparticles is retained with either a decrease [16] or an increase [17] in the value of saturation magnetization.

Various methods have been reported to synthesize core—shell nanoparticles (CSn), gold shell and magnetic core, like in reverse micellar solution [18], in organic solvents [19], and in aqueous solution [20], but the strategy employed is same i.e. reduction of gold chloride on the surface of preformed magnetic nanoparticles. Low yield and toxic nature of materials used limits the application of reverse micelles and organic solvents in the synthesis of core—shell nanoparticles [21].

The core—shell nanoparticles have also been synthesized using gold nanoparticles as seeds and subsequent formation of gold shell [22], but this method requires multiple steps, making the process control difficult. Here, we report a single step aqueous phase synthesis of gold coated magnetic nanoparticles using tyrosine as a reducing agent and capping agent. Tyrosine is a non-toxic, eco-friendly chemical and is found in various plants and animals based foods. Tyrosine has been used as a reducing agent to synthesize silver nanoparticles from silver ions and in the formation of silver shell on gold nanoparticles core [23]. However, tyrosine has not been reported to be used in the synthesis of gold shell on magnetic nanoparticles.

The aqueous dispersion of core—shell nanoparticles was stabilized by thiolated pectin (TP).Thiolated pectin stabilized core—shell nanoparticles (TP-CSn) were characterized for size, dispersion stability, purity, coating, and magnetic properties using Dynamic light scattering (DLS), High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), and Vibrating sample magnetometer (VSM) respectively.

#### 2. Material and methods

#### 2.1. Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 99%) and Gold chloride (HAuCl<sub>4</sub>·3H<sub>2</sub>O, Au > 49–50%) were purchased from Thomas Baker (Chemicals). Ferrous sulphate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, 98%), Sodium hydroxide (NaOH, 97%), and Hydrochloric acid (HCl, 37%) were purchased from Merck Chemicals. Pectin (D-galactouronic acid minimum 65%, degree of esterification 65–70%), L-Tvrosine (>99%) were from Himedia Laboratories and Mercaptopropionic acid (MPA, 99%) was from Alfa Aesar. All chemicals were of analytical grade and used as received without any further purification. All experiments were carried out using double distilled water.

#### 2.2. Synthesis of magnetic nanoparticles

Magnetic nanoparticles (MNPs) were prepared by coprecipitation of Fe (II) and Fe (III) salts in the presence of NaOH [24]. Briefly, FeSO<sub>4</sub>·7H<sub>2</sub>O (5 mmol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mmol) were dissolved in a solution of 5 mmol HCl in 20 ml nitrogen purged water. The above solution was added dropwise to a rapidly stirred solution of 125 ml of 1.5 M NaOH under nitrogen gas atmosphere. A black precipitate was observed instantly and stirring was continued



**Fig. 1.** UV-absorption spectra of (a) Bare magnetic nanoparticles (black); (b) Gold nanoparticles (red); (c) Magnetic nanoparticles with gold nanoparticle seeds (green); (d) Gold coated magnetic nanoparticles, CSn (blue). Inset image: - (a) Bare magnetic nanoparticles; (b) Gold nanoparticles; (c) Magnetic nanoparticles with gold nanoparticle seeds; (d) Gold coated magnetic nanoparticles, CSn. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for 30 min. The precipitate was separated from excess reactants by using an alloy magnet (FeNdB, 2500 Gauss); washed thrice with nitrogen purged water and stored in nitrogen purged water for further use. For obtaining dry powder, the precipitate was washed with acetone and dried in an oven at 50 °C for 24 h.

#### 2.3. Synthesis of gold shell on magnetic nanoparticles

For formation of gold shell on magnetic nanoparticles, gold chloride was added to an aqueous dispersion of magnetic nanoparticles and tyrosine. The ratio of magnetic nanoparticles and gold chloride was 1:3 (w/w) and that of magnetic nanoparticles and tyrosine was 1:4 (w/w). After adjusting the pH of the dispersion to 10.5, it was stirred at 80-85 °C for 2 h and cooled to room temperature. The core–shell nanoparticles formed were separated from excess reactants by using the magnet, washed thrice with water and stored in water for further use.

#### 2.4. Synthesis of thiolated pectin (TP)

Thiolated pectin was synthesized by esterification of hydroxyl groups of pectin with carboxyl groups of Mercaptopropionic acid [25]. Briefly, 1 g of pectin was dissolved in 100 ml water and 600  $\mu$ l of MPA was added to it. The solution was acidified by addition of 3 ml of 2 N hydrochloric acid, heated at 80 °C for 3 h, and cooled to room temperature. After cooling, the solution was added into excess methanol to precipitate thiolated pectin, washed several times with methanol to remove excess MPA, and dried at room temperature. Degree of thiolation of pectin was determined by Ellman assay.

### 2.5. Stabilization of magnetic core–gold shell nanoparticles in aqueous media

For stabilization, the core-shell nanoparticles were dispersed in a solution of thiolated pectin (w/w, 1:5) in Saline Sodium Phosphate Download English Version:

# https://daneshyari.com/en/article/1520678

Download Persian Version:

# https://daneshyari.com/article/1520678

Daneshyari.com