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Facile synthesis and characteristics of gold coated superparamagnetic iron oxide nanoparticles via sonication

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Abstract

We reported a simple protocol for synthesizing small-scale gold coated superparamagnetic iron oxide nanoparticles (SPION). The synthesis of the core-shell nanoparticles of the SPION-gold nanoparticles (GNP) was through chemical reduction method in an ultrasonic field environment. The SPION was produced by co-precipitating iron (ii) and (iii) chloride salt in sodium chloride solution as a c o-precipitating agent. The surface of the SPION was sonochemically functionalized with a 3-aminopropyltriethoxysilane (APTES) which served as a linker. Gold precursor was chemically reduced with chilled sodium borohydride in the presence of the APTES functionalized SPION seed. The GNP covalently binds and assembles on the terminal amine groups on the SPION. Physical characterization with Energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction pattern (XRD) and Ultraviolet–visible spectroscopy (UV-Vis) confirmed the composite nanoparticles to be GNP coated SPION.

Keywords: SPION; GNP; APTES; CORE-SHELL; GNP coated SPION.

1. Introduction

Gold nanoparticles (GNP) and superparamagnetic iron oxide nanoparticles (SPION) are the most widely used nanoparticles in medical and related applications. The inexpensiveness, biodegradability and superparamagnetic properties (ability not retain any magnetism in the absence of magnetic field) of the latter made it a promising material for many biomedical researches and developments [1]. In addition, Lee et al., [2] reported SPION can be broken down to form blood haemoglobin. Furthermore, easy synthesis, tuneable surface plasmon resonance (SPR) and stable properties of GNP are favouring it uses in most biomedical applications and researches [3]. In addition, literatures had revealed both GNP and SPION to be biocompatible and of low-level toxicity [4, 5].

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Unlike GNP, the use of SPION for biomedical purposes has encountered main drawbacks; it agglomerates easily in ionic medium and inability to conjugate it with biomolecules. However, many works have reported that surface modification of SPION with biocompatible materials as an effective option to improve on these limitations [6].

Several reports indicate that gold is one of the preferred coating materials due to its stable surface, affinity for biomolecules and functional groups such as thiol and amine moieties [7]. Successful localization of gold's surface plasmon resonance (SPR) on superparamagnetic properties of SPION could enhance multimodal applications of the composite nanoparticles in biomedical, electrochemical sensor, catalysis, electronics and energy applications [8-10].

Many works had reported the synthesis of GNP coated SPION [11, 12] that are time consuming and laborious. Therefore, easy protocol for small-scale synthesis of GNP coated SPION will be of importance to research and development. We present a simple synthesis of GNP coated SPION that employs the use of both sodium borohydride as a reducing agent and the high thermal energy and pressure generated from ultrasonic field. This facile synthesis of GNP coated SPION involves two steps. Firstly, the surface of the SPION was sonochemically functionalized with a 3-aminopropyltriethoxysilane (APTES). The APTES serves as a linker between the GNP and SPION. Lastly, is the sodium borohydride reduction of gold precursor to GNP and covalent binding of the GNP to the terminal amine group on the APTES functionalized SPION under continuous ultrasonic field.

2. Experimental

2.1 Materials

Ferric chloride hexahydrate, ferrous chloride tetrahydrate, ammonium hydroxide, sodium chloride salts, sodium hydroxide, 3-aminopropyltriethoxysilane, sodium borohydride and gold (III) chloride hydrate were bought from Sigma-Aldrich and used directly without further purification.

2.2 Co-precipitation Synthesis of SPION

Magnetite nanoparticles were prepared as reported in our previous work [13]. Briefly, in an inert nitrogen gas environment, a uniform 1M Fe^{2+} and 2M Fe^{3+} solutions were co-precipitated at room temperature, pH of 10 and mechanically stirred at 500rpm. After 2 hours of continuous agitation, the magnetic particles were collected in a beaker using a 1.5T magnet. The particles were thoroughly washed with distilled water, peptized in $HClO_4$ and redispersed in 60ml of distilled water.

2.3 Sonochemical Synthesis of APTES Functionalized SPION

The APTES functionalized SPION was synthesized according to our work that is under review. Briefly, in an ice bath environment, colloidal suspension of the SPION was sonicated using Vibra Cell (750) ultrasonic horn for 2 min and further for 30 min with of APTES solution at the ratio of 4 to 1. The product was left overnight, separated with magnet and washed with distilled water. The supernatant was removed and the APTES functionalized SPION were dispersed in water.

2.4 Sonochemical Synthesis of GNP Coated SPION

1ml of the APTES functionalized SPION was dispersed in 90ml of deionized (D.I) water for 1 minute via sonication. 10ml of 0.01M of gold solution was added and sonicated for another 1 minute. The mixture was continuously sonicated for 3 minutes during which 25ml of 0.01M chilled (4^0c) sodium borohydride was added in drops. The product was placed on a 1.5T magnet to separate the uncoated SPION from the GNP coated SPION. The GNP coated SPION was washed and dispersed in ethanol.

2.5 Characterization

The XRD of the particles were characterized by (D/Max-IIIC, Japan) using Cu, K radiation. Distances between peaks of the GNP coated SPION were compared to the JCDPS 3-065-2870. The various elements presence in the composite nanoparticles were determined with SEM model JSM-6460LV. Ultraviolet–visible spectra were acquired with a Shimadzu UV-3600. The spectra of the GNP coated SPION were collected over the range of 400–800 nm.

3. Result and Discussion

In this work, we exploited the covalent affinity of GNP to amine (NH_2) moiety [14] to achieve easy coating of GNP onto the SPION. The hydroxyl group on the surface site of the magnetic nanoparticles was replaced with an organometallic coupling agent (APTES) which contains alkoxysilane and amine group. Through the methoxy group ($O–CH_3$) present in the alkoxy molecule, the organosilane is attached to the surface of the SPION. The $O–CH_3$ of the alkoxysilane hydrolyses with the hydroxyl (OH) groups on the surface site of the SPION to form silanol (Si-O-H) group. The terminal amine group on the surface of the APTES functionalized SPION provides the binding site for the GNP [15].

From the illustration in Figure 1, the chilled sodium borohydride reduced the gold ions (Au^{3+}) present in the mixture of the gold solution and APTES functionalized SPION to neutral gold atoms (GNP). The GNP covalently bond onto the terminal amine (binding site) on the surface of the SPION. Immediately the composite nanoparticles formed, the colour of the mixture changed to dark-purple. The dark-purple physically indicates the formation of the gold coated SPION [16, 17]. The observation of purple colour is because of the red to blue or purple shift in the SPR of the GNP. The shift is due to the assembly and attachment of the GNP on the amine functionalized SPION. However, since this work is an ongoing research the role of the ultrasonic field in this facile synthesis of GNP coated SPION is not presented here.

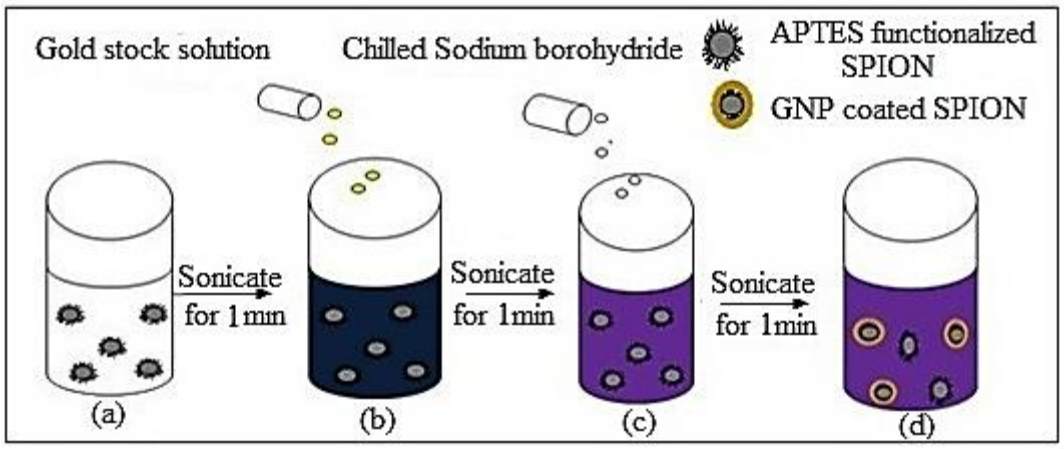

Fig. 1: Illustration of GNP coated SPION (a) dispersion of APTES functionalized SPION in water (b) addition of gold precursor solution (c) addition of reducing agent, sodium borohydride in drops (d) formation of GNP coated SPION.

The EDS spectra in Figure 2a proved that the composite nanoparticles consist of gold, iron and oxygen. The silicon and the carbon present are from the substrate used in preparing the sample and contaminant from the SEM respectively. The optical characterization of the composite nanoparticles (Figure 2b) with UV-VIS confirmed the successful localization of the GNP's SPR on the superparamagnetic properties of the SPION. The peak of the composite nanoparticles was found at 547nm, which correspond, to band of GNP.

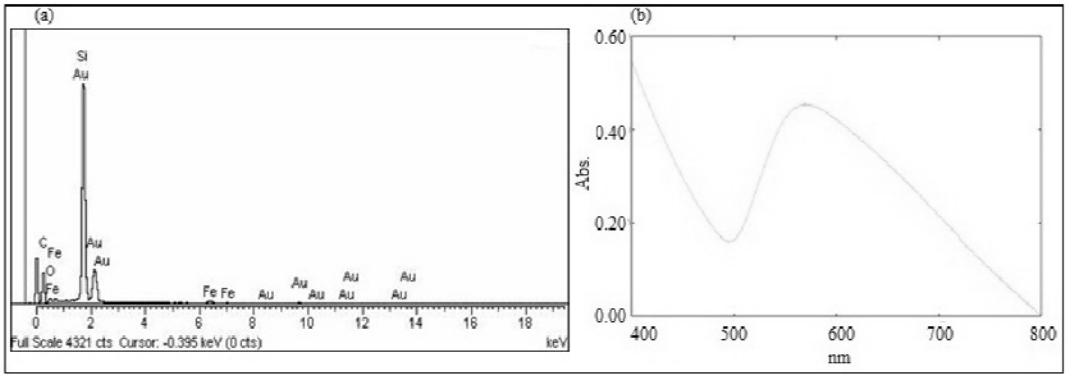

Fig. 2: (a) EDS spectrum, confirmed the presence of the Fe, O and Au in the composite nanoparticles (b) UV-VIS result, showing the SPR peak of the composite nanoparticles to be 547nm which correspond to the band of GNP.

The XRD pattern (Figure 4), further confirmed the successful formation of the core-shell of GNP-SPION. Unlike XRD pattern of the APTES functionalized SPION in figure 4a whose peaks correspond to magnetite, the pattern in Figure 4b further confirmed the composite nanoparticles to be GNP coated SPION. The presence of prominent peaks - (111), (200) and (220) – corresponding to GNP were observed in the Figure 4b pattern.

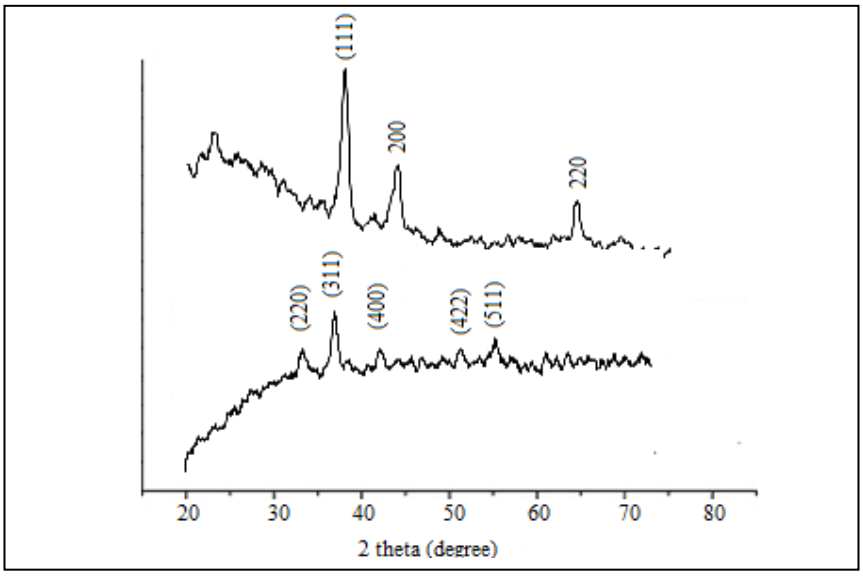

Fig. 3: (a) APTES functionalized SPION, peaks corresponding to magnetite (b) showing the three prominent peaks corresponding to GNP when compared with JCDPS 3-065-2870.

4. Conclusion

We presented a facile synthesis of GNP coated SPION that exploited the covalent affinity of GNP to amine group, the chemical reduction of Au (111) to Au (0) by sodium borohydride and the high thermal energy and pressure generated from acoustic cavitation effect. Within a period of 5 minutes, gold nanoparticles is simply coated on the APTES functionalized SPION. The various physical analyses conducted on the composite nanoparticles confirmed the successful localization of the GNP's SPR of on the superparamagnetic property of the SPION.

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