Magnetite-silica core-shell nanostructures: application for photodynamic therapy

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Abstract. Magnetite nanoparticles have been synthesized with chemical co-precipitation. The surface of magnetite nanoparticles was coated with an inorganic silica layer by hydrolyzing and condensing tetraethyl orthosilicate. An XRD investigation supports the cubic inverse spinel structure of Fe₃O₄ nanoparticles. The average crystallite size of the magnetite nanoparticles produced by the peak broadening was 13 nm. The UV-visible spectrum of methylene blue-loaded magnetite-silica nanoparticles shows a strong hump at 657 nm. According to TEM examination, the nanoparticles are polydisperse and almost spherical in form. The average size of the nanoparticles is 14.39 nm plus 1.66 nm, and they have a polydispersity index of 0.12%. The size and shape of the core-shell particles are not uniform, according to a SEM examination. There is no distinguishing morphology in any sample. The magnetic results depict the superparamagnetic behaviour of nanoparticles makes them suitable for photodynamic therapy.

1. Introduction

Chemotherapy is the foremost treatment for cancer patients, but application rate is still low. This is largely because drugs are difficult to access in tumour tissue, toxic in high doses, develop multi-drug resistance, and have a dynamic, heterogeneous biology as they grow. Recent advances in tumour biology knowledge and novel targeted drug delivery strategies using various Nano systems and bio-conjugates offer hope for the development of effective cancer treatments. Chemotherapy failure is primarily caused by anti-neoplastic drugs limited tumour accessibility, which necessitates greater doses, and their non-selective nature, which results in severe toxicity [1, 2]. A potential strategy to improve the therapeutic effectiveness and lessen the possibility of systemic toxicity of anti-cancer therapies is to target pharmaceuticals with specifically developed drug delivery systems. Targeted medicine delivery through magnetic fields is currently generating a lot of interest [3-6]. A photosensitive chemical that has accumulated inside of cells is triggered by light in photodynamic treatment (PDT), a form of light-induced chemotherapy that results in

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oxidative harm to the cells. PDT produces a localised effect as opposed to the systemic effect of conventional chemotherapy. In this regard, PDT resembles a surgical procedure or a form of radiation therapy more than a chemotherapeutic regimen [7]. Policard observed that tumour tissue naturally emits more light than healthy tissue in the 1920s. In order to more precisely define the boundaries of the tumour tissue, Ronchese attempted to introduce endogenous fluorescent molecules in the 1950s [8].

Natural porphyrins were given to individuals and animals with tumours[9, 10]. Winkelman employed artificial porphyrins in the 1960s to identify tumour tissue [11]. Sunlight was used by Tappeiner et al. and Jesionek et al. to produce cosin in tumour tissue in vivo. Hematoporphyrin derivative (HpD), which Lipson isolated from hematoporphyrin preparations and later called, is an impurity that can localise tumours. Through the study of hematoporphyrin's intratumoral fluorescence, Lipson sought to identify tumour tissue. He discovered that it might be used as a photosensitizer to eradicate tumour tissue after using it as a tumour identification tool [12]. Dougherty rediscovered fluorescein diacetate's ability to photodynamically kill TA-3 cells in vitro in the 1970s [13].

Heet al used the chemical co-precipitation approach to create superparamagnetic Fe₃O₄ nanoparticles with a thin, adjustable coating of silica that was added to the surface through the condensation and hydrolysis [14]. The silica-coated Fe₃O₄ nanocrystals had a magnetic core that was 6-7 nm in diameter and a silica shell that was about 2 nm thick. They were evenly spread. The nanocrystals that were created have a cubic spinel structure. In order to create contrast agents for potential in-vivo tumour identification utilising MRI, Xie proposes a unique method of synthesising and functionalizing ultra-small Fe₃O₄ nanoparticles [15]. The requisite biocompatibility and selectivity to U87MG tumour cells are displayed by the c(RGDyK)-MC-Fe₃O₄ NPs. Tada describe the creation and evaluation of silica-coated magnetic particles that contain methylene blue [16]. Recently, Mosaddad et. al uses photodynamic therapy to kill tumor cells directly causing inflammatory reactions at targeted sites [17]. Wang et.al has given an extensive review on applications on Fe₃O₄ nanoparticles in the field of biomedicine [18].

2. Synthesis of Fe₃O₄-SiO₂ core-shell nanostructures with MB

For the synthesis of magnetite (Fe₃O₄) nanoparticles co-precipitation technique was selected. During the process ferric chloride (FeCl₃.6H₂O) and ferrous sulphate (FeSO₄.7H₂O) were added in stoichiometric ratio. Ammonium hydroxide was added drop wise along with continuous stirring. The pH was 10.5 maintained by the addition of ammonia solution. Obtained black precipitates were decanted magnetically and washed. Adapting the process of hydrolysis and condensation, previously synthesized magnetite nanoparticles were coated with silica by incorporating TEOS(Tetra ethyl orthosilicate).at different required concentrations. Finally, the mixture of silica coated Fe₃O₄ nanoparticles was loaded with Methylene Blue (MB). Magnetic decantation has extracted Fe₃O₄-SiO₂ core-shell nanostructures with MB loaded from the solution.
3. Results and Discussions

3.1 Structural and phase analysis

Powder X-ray diffraction (XRD) has been used to investigate the structural and phase properties of magnetite nanoparticles and magnetite nanoparticles coated with silica. PANalytical records X-ray patterns. Fig. 1 displays the XRD patterns of the naturally occurring Fe₃O₄ nanoparticles and those coated with TEOS. The creation of the Fe₃O₄ phase is indicated by the six peaks seen at θ 30.25° (220), 35.75° (311), 43.25° (400), 53.70° (422), 57.45° (511), and 62.70° (440) that are all associated with cubic inverse spinel structure.

![XRD patterns of uncapped and TEOS capped Fe₃O₄ nanoparticles.](image)

Thereference number 19-0629 of Joint Committee on Powder Diffraction Standards (JCPDS and all of the peaks in the XRD patterns coincide quite well. Using the Debye-Scherrer formula, the average crystallite size (D) of uncapped and TEOS-capped Fe₃O₄ nanoparticles was determined [19,20].

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]
Table 1 shows the derived values for where is the characteristic wavelength utilised (Cu-K = 1.54016), is the full width at half maximum (FWHM) of the highest peak (311), and θ is Bragg's angle.

Table 1. Crystallite size from x-ray diffraction.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample specification</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe₃O₄</td>
<td>13.20</td>
</tr>
<tr>
<td>2.</td>
<td>TEOS 10</td>
<td>14.10</td>
</tr>
<tr>
<td>3.</td>
<td>TEOS 50</td>
<td>10.05</td>
</tr>
<tr>
<td>4.</td>
<td>TEOS 100</td>
<td>15.47</td>
</tr>
<tr>
<td>5.</td>
<td>TEOS 150</td>
<td>11.72</td>
</tr>
<tr>
<td>6.</td>
<td>TEOS 200</td>
<td>14.00</td>
</tr>
</tbody>
</table>

3.2 FTIR analysis

All of the powder samples’ FTIR spectra were captured on a Perkin Elmer Spectrum BX(II) spectrophotometer in the transmission mode, as shown in figure 2. The asymmetric stretching vibrations of Fe-O are thought to be the cause of the distinctive bands. The splitting of band seen at 570 cm⁻¹ in the spectra of bulk magnetite is what causes the bands at 580 and 620 cm⁻¹.
1, similar to the band at 440 cm$^{-1}$. The Si-O-Si stretching vibrations that correlate to the sharp band at 1088 cm$^{-1}$ are a sign that SiO$_2$ is present in the nanostructures. Although they are present in all samples, the Si-O-Si bond's asymmetric stretching at 1088 cm$^{-1}$ and symmetric stretching at 800 cm$^{-1}$ show that silica has been successfully coated on the surface of Fe$_3$O$_4$ nanocrystals by the hydrolysis and condensation of TEOS. All of the spectra's bands, which are located around 3427 and 1637 cm$^{-1}$, are mostly caused by H$_2$O's -OH vibrations. Peaks at 2851 and 2915 cm$^{-1}$ are caused by -CH$_2$ vibrations that stretch.

### 3.3 UV-Visible Spectra

UV-Visible spectroscopy confirms the incorporation of methylene blue (MB) in nanoparticles. A little sample is dissolved in water for the UV-Visible investigation, and this solution is used for the analysis. The Analticjena Specord 205 captures UV-visible spectra. In fig. 3, the UV-visible spectrum of magnetite-silica nanoparticles loaded with MB is displayed. A prominent hump at 657 nm corresponds to the MB molecule's typical absorption in water.

![UV-Visible spectrum of (a) MB added magnetite-silica nanoparticles and (b) magnetite-silica nanoparticles.](image)

**Fig. 3.** UV-Visible spectrum of (a) MB added magnetite-silica nanoparticles and (b) magnetite-silica nanoparticles.

### 3.4 Morphological study

#### 3.4.1 TEM analysis

TEM has studied the morphology of magnetite nanoparticles. A little sample is dissolved in ethanol for TEM investigation, and a drop of this solution is applied to a copper grid that has been coated with carbon. Fe$_3$O$_4$ nanoparticle TEM images are shown in fig. 4. The fig. 4 makes it abundantly evident that the nanoparticles are polydisperse and have a shape that is
almost spherical. The graphic also includes an inset that displays the nanoparticles' size distribution histogram. The nanoparticles have an average size of 14.39 nm plus 1.66 nm with polydispersity index equals to 0.12% [21, 22].

![TEM micrographs of Fe₃O₄ nanostructures.](image)

**3.4.2 SEM micrographs**

To examine the morphology of synthetic magnetite nanoparticles coated with various TEOS concentrations using scanning electron microscopy. SEM images of synthesised nanoparticles are shown in fig. 5. The shape and size of the particles are not uniform, as shown in fig. 5. In any sample, no distinctive morphology is seen. Agglomeration of nanostructures may be to blame.

![SEM micrographs](image)
Fig. 5. SEM micrograph of Fe$_3$O$_4$-SiO$_2$ core-shell nanostructures with different amount of TEOS.

3.5 Magnetic Study

VSM (vibrating sample magnetometer) has been used to explore the magnetic properties of synthesised nanoparticles. The fig. 6 makes it abundantly evident that as the magnetic field used gets stronger. Due to the super paramagnetic nature of these nanoparticles, this form of saturation is seen. Due to the diamagnetic nature of silica, the magnetism decreases as the amount of TEOS in the capping increases.

Fig. 6. Magnetic curve of Magnetite core-shell nanostructures.

4. Conclusion

Chemical co-precipitation has been used to create magnetite nanoparticles. Tetraethyl orthosilicate (TEOS) was hydrolyzed and condensed to create an inorganic silica coating on the surface of magnetite nanoparticles. The cubic inverse spinel structure of Fe$_3$O$_4$ nanoparticles is confirmed by an XRD analysis. The magnetite nanoparticles derived from the peak broadening had an average crystallite size of 13 nm. A large hump at 657 nm is visible in the spectrum. The nanoparticles are polydisperse with almost spherical shape, according to TEM analysis. The nanoparticles have an average size of 14.39 nm plus 1.66 nm and a polydispersity index of 0.12%. A SEM analysis reveals that the size and shape of the core-shell particles are not homogeneous. The magnetic results show that magnetite nanoparticles are naturally super paramagnetic and have a relatively high saturation magnetization.
Synthesized nanostructures can be considered as a potential candidate for PDT therapy for aggressive tumours. As opposed to isotropic nanostructures, magnetite silica nanostructures provide a number of advantages. Due to its lower size, biocompatibility, and magnetic properties, this drug delivery system is an effective way to treat tumours using photodynamic therapy.

References


