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The effective of citrate as capping agent on the band gap of γ -Fe₂O₃ nanoparticles

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ABSTRACT

In this study, γ -Fe₂O₃ were synthesis by a chemical route at room temperature in the presence of a capping agent and without a capping agent. The capping agent used for covering Fe₂O₃ was tri-sodium citrate, the absorption spectra obtained by UV-Vis spectrophotometer in the wavelength range of 200 -800 nm. From this, it found that the optical band gap transitions of the γ -Fe₂O₃ nanoparticles in the absence of tri sodium citrate as 3.00 eV and with the present tri sodium citrate capped iron oxide as 2.28 eV. The sizes estimated utilizing observed band gaps data were in the range of 1.37 nm and 1.41 nm respectively the average sizes found to be increased as the band gap declined because of the quantum size effect

Introduction

Nanomaterials *have* attracted *extensive* attention in many *applications* during the last decade because of their unique perspective properties compared to their bulk materials. The exceptional properties of Nano scale materials are caused by varieties in the band structure with the decrease in particle radius (Chakrabart et al.,2004; Fang and Zhang,2006., Fang et al.,2008; Olson and Zhang,2008; Fang et al.,2008; Wang et al.,2009). Magnetic nanoscale materials are the most important materials and have been extensively studied because of their technological scientific importance. Among the most common forms of magnetic nanoparticles are Maghemite (γ -Fe₂O₃) is a semiconductor with a band gap of 2.0 eV (Zhu et al.,2013), which is the most historically interesting iron oxides because of their chemical stability, biocompatibility, and heating ability (Sun et al.,2004). Gamma Fe₂O₃ has been found in nature as maghemite and has attracted attention and especially interesting in biomedical applications because of their biocompatibility and low toxicity in the human body (Hasany et al.,2012; Tartaj et al.,2005) and for potential applications, such as pigment, recording materials, photo catalysis, ferrofluid technology, medical diagnostic and advanced maghemite materials (Anton et al.,1990; Chhabra et al.,1996; Kang et al.,1996; Caruso et al.,2001; Woo et al.,2003; Das and Saha,2012). γ -Iron oxide is ferromagnetic, and its magnetic moment is 430 emu/cc at room temperature (Skomski and Coey,1999), their magnetic moments are oriented in opposite directions on tetra and octahedral (crespo et al.2010). γ -Fe₂O₃, a typical ferromagnetic mineral (oliveira etal.2013) is thermally unstable and is changed at higher temperatures to hematite (α -Fe₂O₃) (Bacri et al.,1986). Several suitable methods have been developed for the creation of maghemite nanoparticles, including co-precipitation (Bacri et al.,1986) microemulsion (Hyeon et al., 2001) electrochemical and hydrothermal synthesis (Pasricha et al.,2006; Basly et al.,2010; Chen and Xu,1998; Sreeja and Joy,2007), sol-gel preparation (Chakrabarti et al.,2004; Casas et al.,2002)

Experimental

Citrate-capped γ -Fe₂O₃ nanocrystals were prepared by Ngo and Pileni with some modification (Ngo and Pileni.,2001 Rao .CN et al; 2005) In a typical preparation, to a 50-mL aqueous solution containing 1.96 g of ferrous ammonium sulfate and 2.78 g of sodium dodecyl sulphate, 40 mL of 40% aqueous solution of dimethylamine was added under vigorous stirring. The brown-black precipitate obtained after stirring for 2 h was centrifuged and washed with 2M HNO₃, followed by water, until it was free from ions. The solid was then re-dissolved in a solution of trisodium citrate (0.06 M, 100 mL) with 30 mins of stirring. To the brown sol obtained, the acetone was added to yield a thin brown precipitate. The precipitate consisting of citrate-capped γ -Fe₂O₃ nanocrystals was centrifuged, washed with acetone, and dried at room temperature. The brown powder so obtained was freely dispersible in water and upon dispersion yielded a brown ferro fluid, which was stable for weeks see (fig.1.). The γ - Fe₂O₃ nanocrystals were characterized by UV microscopy.

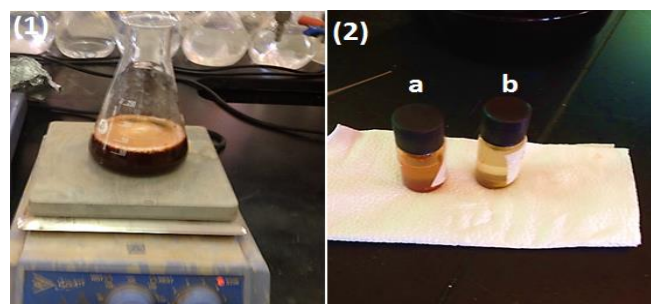


Figure1 : Exhibits photograph of preparation gamma Fe₂O₃ at room temperature.

Results and discussion

Optical properties of Fe₂O₃ samples were characterized through UV-VIS. The optical absorption spectra of the samples were recorded by CE7400-7000 3ERIES Double

Beam UV-vis spectrophotometer manufacture Buck scientific, Inc. The scan distance range was between 200-800 nm (fig.2.). The spectra was recorded at room temperature.



Figure 2: Shows photograph of CE7400-7000 3ERIES Double Beam spectrometer

In this paper, the experiment was prepared in the presence and absence of tri-sodium citrate. the optical absorption spectrum of the synthesized γ -Fe₂O₃ is presented in fig.3. it exhibits absorption in the wavelength range of 543 nm (without citrate). to 572 nm (with citrate capped Fe₂O₃). It is noted that the absorption maximum of iron oxide shifts to a higher wavelength. The observed blue shift of absorption is due to the quantum size effect (Wen et al.,2005). From the absorption data, the band gap energy of γ -Fe₂O₃ was calculated by using the well-known equation for semiconductors (Goudarzi et al., 2014; Manjunath et al.,2016):

$$(\alpha h\nu) = A (h\nu - E_g)^n$$

Here, E_g is band gap, A is constant depending on the material, α is absorption coefficient, $h\nu$ is photon energy, n is 2 for direct transition or 1/2 for indirect transition.

By plotting of $(\alpha h\nu)^2$ against energy band gap (eV) and an extrapolation of the straight-line give the value of absorption edge. The band gap energies(E_g) of the samples are presented as insets of their respective optical spectra (fig.3). The band gap energy (E_g) was calculated to be 3.00 eV, 2.28 eV for Fe₂O₃ without citrate and with citrate capped γ -Fe₂O₃ respectively. The obtained band gap energy for the prepared γ -Fe₂O₃ in the case of citrate capped IONs is bigger than that of the bulk γ -Fe₂O₃ (2.0 eV) which could be indicated to quantum size effects in nano size materials (Manjunath et al.,2016; Bhar et al .,2010; Ajinkya et al.,2020; Arash et al.,2016) thus there is a blue shift relative to the peak absorption of bulk Fe₂O₃. The obtained average diameter of γ -Fe₂O₃ nanoparticles estimated by band gap using burs equation (Purushottam et al .,2016)

$$E_g = E_{\text{bulk}} + \frac{h\pi}{2R^2 \left(\frac{1}{m_e} + \frac{1}{m_h} \right)} - 1.8e^2/\epsilon R \quad (1)$$

In equation 1, E_g is band gap energy of the nanoparticle, E_{bulk} is band gap energy of the bulk of γ -Fe₂O₃ nanoparticles which is 2.0 eV, h is Planck's Constant, R nanoparticles size, m_h and m_e are effective mass for electrons and hole, $e = 1.602 \times 10^{-19}$ unit, ϵ is dielectric constant.

The estimated values of the size for all specimens from the band gap were in the range of 1.37 nm in the case of the absence of citrate and 1.41 nm using citrate capped nanoparticles. Notably, that the space of electronic levels and band gap increase as the decrease in size because of electron confinement at nanoscale so called "quantum size effect".

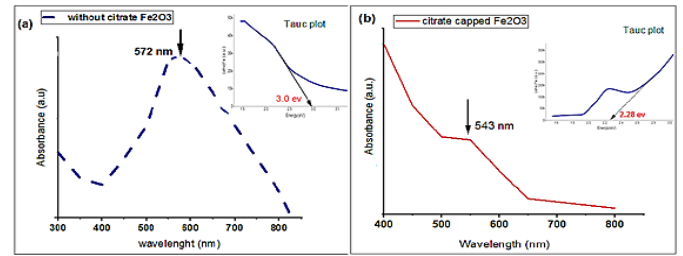


Figure 3: UV-vis spectra of the samples (a) Fe₂O₃ without citrate as capping agent, (b) citrate capped Fe₂O₃. Insets show their representative plots of $(\alpha h\nu)^2$ versus band gap energy (ev) for the direct transition

which is, due to discrete levels of energy band and the electron hole pairs are near together and electrostatic force between them can't be neglected giving higher kinetic energy.

sample	Wavelength (nm)	Band gap (eV)	Particle size (nm)
γ -Fe ₂ O ₃ without citrate	543	3.00	1.37
γ -Fe ₂ O ₃ with citrate	572	2.28	1.41

Table 1: Particle size estimated from band gap energy

The optical band gap and particle sizes values for γ -Fe₂O₃ with and without citrate capped, are shown in table 1. From the table, it is clear that the band edge decreasing as the particles size increasing.

Conclusions

This strategy reports a simple method for creating Fe₂O₃ in the absence and present sodium citrate as a capping agent. The absorption spectra reveal the band gap values were in the absence and present sodium citrate in the range (3.0 - 2.28 eV) respectively. The particles size calculated using the band gaps energy is in the range of 1.37 nm without citrate as capping agent and 1.41 nm in the presence of sodium citrate, it is observed that there was an increase in the particles size during the decreased of band gap energies.

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