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Structural, Morphological, and Vibrational Properties of Porous α-Fe_2O_3 Nanoparticles Prepared by Combustion method

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Iron oxide (α-Fe_2O_3) nano particles are synthesized by solution combustion technique where glycine is used as a fuel. The current work describes role of fuel in the formation of α-Fe_2O_3 phase. Citric acid and glycine is used as a fuel to study the role of fuel in the phase formation and its impact on structural properties. X-ray diffraction spectroscopy is used to study its structural properties. As revealed in XRD, single phase α-Fe_2O_3 is obtained in glycine-assisted combustion. Further, as prepared α-Fe_2O_3 is calcined at different temperature, it is observed that crystallanity of α-Fe_2O_3 is enhanced with the calcination temperature. Raman spectroscopy is employed to study vibrational modes of molecule. Morphology of calcined material is studied by using FESEM. These results reveal that, fuel plays a key role in the phase formation of α-Fe_2O_3 and gases released during combustion are responsible for the morphology.

1. Introduction

Currently, nanosized materials and their applications are the currently attractive areas of research because as the size of material decreases towards the nanometer, the physicochemical properties of materials change and new phenomena will appear.[1] Nowadays, metal oxide nano particles play an important role in the growth of nano science and technology. Among these metal oxides, iron oxide is one of the attractive metal oxides because of its fundamental applications in various fields such as biomedicine, magnetic storage, lithium ion battery, supercapacitor, water treatment, catalyst, gas sensor, optical device, pigment, and drug delivery.[2,3] Further, it shows some additional advantages such as thermodynamic stability, low processing cost, nontoxic nature, etc.[4] Therefore, research is carried out on large extent on the synthesis of iron oxide nanoparticles in material science from past few decades.

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Iron oxide is found in three different forms: i) FeO ii) Fe_2O_3 and iii) Fe_3O_4. From these phases, Fe_2O_3 has two different crystallographic phases α-Fe_2O_3 and γ-Fe_2O_3[5] Where, α-Fe_2O_3 is the most stable iron oxide in ambient condition.[6] However, its physicochemical properties are very sensitive and are governed by its chemical composition, structure and particle size, etc.[7] In the current decade, several research articles shows increasing efforts to control these properties. Desired properties of iron oxide are achieved by using several synthesis techniques such as hydrothermal, sol gel, combustion, etc. Crystalline size, agglomeration, composition, and structure of material are easily controlled by using solution combustion technique. Therefore, compared with the several techniques, this technique is more attractive for bulk formation of material with desired properties.[8] This technique involves two-step processes, 1) formation of precursor and 2) auto ignition. Both steps are equally important in the phase formation of material. Generally, in this technique, metal nitrates act as oxidants and organic compounds such as glycine, urea, citric acid, hydrazine, and ethyleneglycol, etc., are used as a fuel. Among the various parameters, nature of fuel and its amount determines desired properties of final product.[9] It plays a major role in formation of homogeneous mixture, heat generation, and evolution of gases during combustion. Therefore, choice of fuel is an important task in this technique; it controls morphology, phase, crystalline size surface area, and nature of agglomeration.

During past few years, researchers in the field of academia and industry have significantly focused synthesis of Fe_2O_3 nano particles for various applications like as an anode material for Li-ion battery,[10] supercapacitor,[11] gas sensing,[12] etc. Different techniques are used for this purpose, however there is need to correlates synthesis technique with various physiochemical properties of synthesize material. The aim of the present study is to obtain phase pure iron oxide (Fe_2O_3) by using solution combustion technique and study the influence of fuel on the phase formation of material.

2. Results and Discussion

The XRD pattern of as prepared (a) C-Fe_2O_3, (b) G-Fe_2O_3 and calcined G-Fe_2O_3 at (c) 700°C, (d) 800°C, and (d) 900°C for 5 h

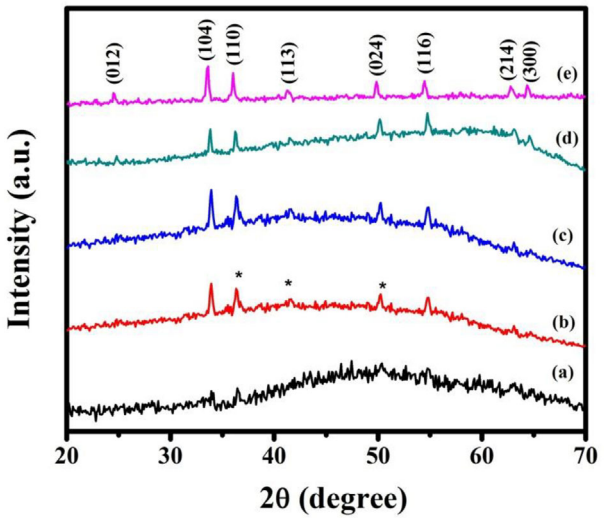

Figure 1. XRD patterns of a) C-Fe_2O_3, b) G- Fe_2O_3, and G-Fe_2O_3 calcined at c) 700°C, d) 800°C, and e) 900°C.

is shown in **Figure 1**. In pattern (a), diffraction peaks are not observed due to the amorphous nature of C-Fe_2O_3. On the contrary, G-Fe_2O_3 (pattern b) shows crystalline nature. The observed diffraction peaks are matched well with JCPDS card no. 33–0664 of Fe_2O_3. It shows rhombohedral structure. Furthermore, hump centered at 45° in G-Fe_2O_3 is observed due to presence of residual carbon and non-combusted residue. To make material more crystalline, as prepared powder must be calcined at higher temperature. Compared to citric acid (-2.76 kcal g^{-1}), glycine has more negative combustion heat (-3.24 kcal g^{-1}), therefore, glycine produces more heat during combustion. This self-propagated combustion at a higher temperature leads crystallization of G-Fe_2O_3 and removes non combusted residue. It is inferred from the above results that the phase purity as well as residual content are governed by the type of fuel used. Compared to citric acid, glycine gives single phase powder. The presence of residues can be minimized by calcination at higher temperatures. To study the evolution of crystallinity with higher temperature, we selected only G-Fe_2O_3 sample.

To make material more crystalline and to remove residual carbon, G-Fe_2O_3 is calcined at 800°C and 900°C for 5 h. Figure 1c-e shows XRD pattern of G-Fe_2O_3 calcined at 700°C, 800°C, and 900°C for 5 h. Major change in the crystal structure is not observed; however, crystallinity increases with the temperature. Crystalline size (D) was calculated using Scherrer formula. The observed crystalline size for highest intense peak (104) is 29.39 nm for 700°C, 32.76 nm for 800°C, and 38.73 nm for 900°C.

From XRD, it is concluded that after calcination of G-Fe_2O_3 at 700°C, presence of some carbon in the powder detected. Therefore, powder is calcined at higher temperature, i.e., at 800°C and 900°C.

Raman spectroscopy is used to study the type of residual carbon in the calcined powder at 900°C and it is shown in **Figure 2**a. The Raman spectrum exhibits six lines of α-Fe_2O_3 at ~ 222, 290, 406, 496, 605, and 1311 cm^{-1}. All these peaks are matched well with the reported data; it reveals the formation of α-Fe_2O_3 phase. The peaks observed at 222 and 496 cm^{-1} are assigned to the A_{1g} mode.[13,1] The peaks observed at 290, 406, 605 are assigned to E_g mode. The peak observed at 1311 cm^{-1} is assigned to the hematite two magnon scattering.[1]

In combustion synthesis technique, morphology of obtained material is governed by gases evolved during combustion and combustion temperature.[14] The morphology of Fe_2O_3 calcined at 900°C is studied by using FESEM and it is shown in Figure 2b. Uniform grains are observed in the FESEM image. The observed average grain size is 164.4 nm. These results reveal that, carbon and hydrogen are present in the fuel complexes metal ions and produce homogeneous gel. In addition, variation in nature of combustion is observed and it is governed by the fuel used. A large amount of gases, heat, and light energy released during combustion; these parameters are also controlled by the fuel. In view of these, the observed results reveal that fuel plays major role in the physicochemical properties of Fe_2O_3.

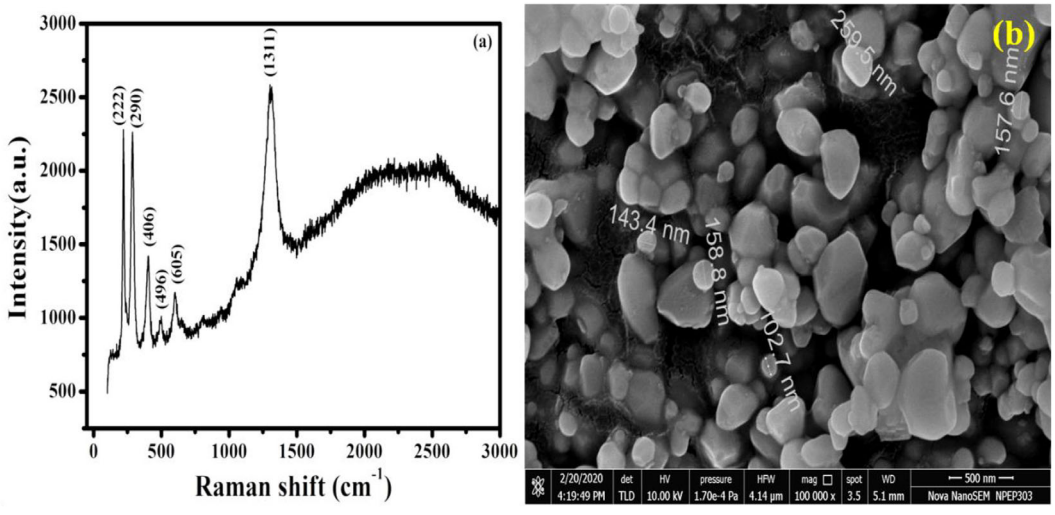

Figure 2. a) Raman spectra and b) FESEM image of G-Fe_2O_3 calcined at 900°C.

3. Conclusion

In summary, single-phase rhombohedral α-Fe_2O_3 is successfully synthesized by solution combustion technique. Citric acid and glycine is used as a fuel to study their role as a fuel in the phase formation. During combustion, released gases, heat and light energy is controlled by fuel. Therefore, compared to citric acid as fuel, glycine gives single phase Fe_2O_3 nano particles due to self-propagated higher temperature in glycine-assisted combustion, which leads to more crystallization and less non-combusted residue. It is observed that crystalline size of material increases from 29 to 38 nm if the calcinations temperature is increased from 700°C to 900°C, respectively. The Raman spectrum exhibits six lines of α-Fe_2O_3, which reveals formation of α-Fe_2O_3 phase. Uniform grains with average grain size is 164.4 nm is observed in FESEM image.

4. Experimental Section

Fe_2O_3 powder was synthesized by solution combustion synthesis (SCS). Iron nitrate ($FeN_3O_9.9H_2O$, LOBA CHEMIE PVT LTD 98%) was used as metal precursor. Glycine ($C_2H_5NO_2$, Himedia 99%) and citric acid ($C_6H_8O_7$,LOBA CHEMIE PVT LTD 99.5%) were used as fuel.

The iron nitrate ($FeN_3O_9.9H_2O$) was dissolved in the minimal amount of double distilled water and kept on hot plate for constant stirring and heating. Then, the aqueous solution of fuel was added into the solution of iron nitrate, it helped mixing metal nitrates at molecular level to make a homogeneous mixture. The stoichiometric oxidant to fuel ratio for glycine ($C_2H_5NO_2$) was 1:2 and for citric acid ($C_6H_8O_7$) 1:3. The gel was formed by removal of excess water during the process of constant heating and stirring. This gel was kept in a pre-heated furnace and was decomposed forming ash. The powders were named G-Fe_2O_3 and C-Fe_2O_3 for glycine and citric acid respectively. After grinding and homogenation in agate mortar, the powders were calcined in the muffle furnace. The G-Fe_2O_3 and C-Fe_2O_3 powders were calcined at 700°C with heating rate of 10°C min^{-1} for 5 h. To enhance crystallanity of G-Fe_2O_3, as prepared material is calcined again at 800°C and 900°C with heating rate of 10°C min^{-1} for 5 h.

The study of crystalline properties of calcined Fe_2O_3 powders was carried out by using X-ray diffractometer (PHILIPS PW-3710) with Cu-K_α as radiation source. The morphological properties were analyzed using field emission scanning electron microscope (FE-SEM, Hitachi S-4200). The vibrational spectroscopic studies were carried out by Raman spectroscopy (Bruker AXE Analytical Instrument PVT. Germany).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

combustion technique, Fe_2O_3, nanoparticle, RAMAN, XRD

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