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A Simple Precipitation Method for Synthesis $CoFe_2O_4$ Nanoparticles

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Abstract

Magnetic $CoFe_2O_4$ nanoparticles were synthesized via a simple chemical reaction using precipitation method. The obtained materials consist of ferrite particles with average diameter of 25 nm. The effect of different surfactants such as cationic, anionic and neutral on the morphology of the products was investigated. Scanning electron microscopy was used to study the structure and particle size of $CoFe_2O_4$ nanoparticles. Magnetic properties of the product were also examined by vibrating sample magnetometer at room temperature. By using ammonia and sodium hydroxide cobalt ferrite nanoparticles exhibit different super-paramagnetic and ferrimagnetic behaviors respectively.

1. Introduction

Magnetic nanoparticles have been the subject of intense research because of their potential applications in high-density magnetic recording, magnetic fluids, high coercive force, mechanical hardness, chemical stability and temperate saturation magnetization[1-2]. There is an increasing interest in magnetic ferrite nanoparticles because of their broad applications in several technological fields including permanent magnets, magnetic fluids, drug delivery, microwave devices, and high density information storage [3–5]. Among the various ferrite materials for magnetic recording applications, cobalt ferrite ($CoFe_2O_4$) has been widely studied because it possesses excellent chemical stability and suitable mechanical hardness. In addition to the precise control on the composition and structure of $CoFe_2O_4$, the success of its practical application relies on the capability of controlling crystal size within the superparamagnetic and single domain limits. It is known that the crystal size is related to the relative interdependence between the nucleation and growth steps, which in turn can strongly be affected by the solution chemistry and precipitation conditions [6-8]. Different

chemical synthesis methods, such as precipitation, sol-gel, hydrothermal are used to produce cobalt ferrite. Among the reported methods, the precipitation method is an efficient and economical way to mass production of ultrafine cobalt ferrite powder [9-16]. In the present work, cobalt ferrite ($CoFe_2O_4$) nano-particles were synthesized by the precipitation method at reaction temperature of 60 °C. The obtained samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD). The magnetic properties were investigated using a vibrating sample magnetometer (VSM).

2 Experimental

2.1. Materials and Instruments

$Co(CH_3COO)_2\ 4H_2O$, $Fe(NO_3)_3\ 9H_2O$, cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS), polyvinyl alcohol (PVA), NaOH and NH_3 were purchased from Merck Company. All of the chemicals were used as received without further purifications. XRD patterns were recorded by a Philips, X-ray diffracttometer using Ni-filtered Cu K_α radiation. For SEM images the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM, made by Meghnatis Daghigh Kavir Company) in an applied magnetic field sweeping between ±10000 Oe.

2.2. Synthesis of $CoFe_2O_4$ nanoparticles

1.62g of $Fe(NO_3)_3\ 9H_2O$ and 0.5g of $Co(CH_3COO)_2\ 4H_2O$ are dissolved in 75 ml of distilled water. 0.25g CTAB (or SDS, PVA) is then added to the solution. 4 ml of NH_3 12M (or 14 ml of NaOH 1M) solution is slowly added to the solution and is heated at 60° C for 60 min. A black-brown precipitate is obtained confirming the synthesis of $CoFe_2O_4$. The precipitate of $CoFe_2O_4$ is then centrifuged and rinsed with distilled water, followed by being left in an atmosphere environment to dry. Fig.1 shows the schematic diagram for experimental setup used in this precipitation method.

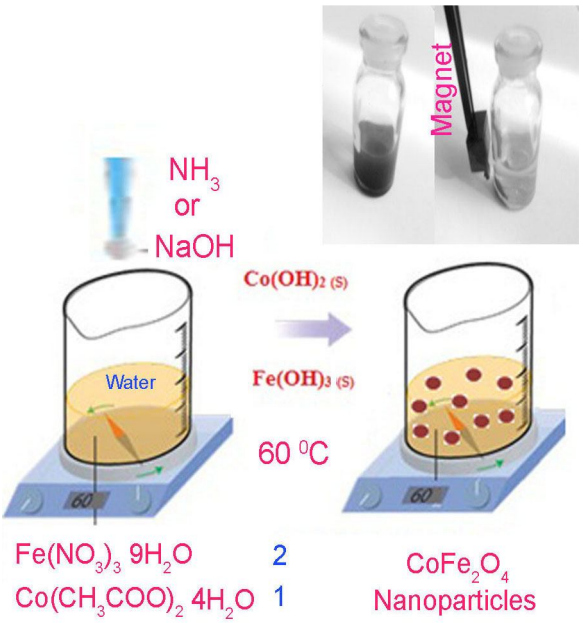

Fig. 1. Schematic of precipitation reaction

3. Results and discussion

The XRD pattern of $CoFe_2O_4$ nanoparticles is shown in Fig. 2. The pattern of as-prepared $CoFe_2O_4$ nanoparticles is indexed as a pure cubic phase which is very close to the literature values (JCPDS No. 01-1121). Space group of cobalt iron oxide is Fd3m with cell constant of 8.39 angstrom. The narrow sharp peaks indicate that the $CoFe_2O_4$ nanoparticles are well crystallized.

The crystallite size measurements were also carried out using the Scherrer equation,

$$Dc=K\lambda/\beta Cos\theta$$

Where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9,

and λ is the X-ray wavelength (CuK_α radiation, equals to 0.154 nm). The estimated crystallite size was about 16 nm.

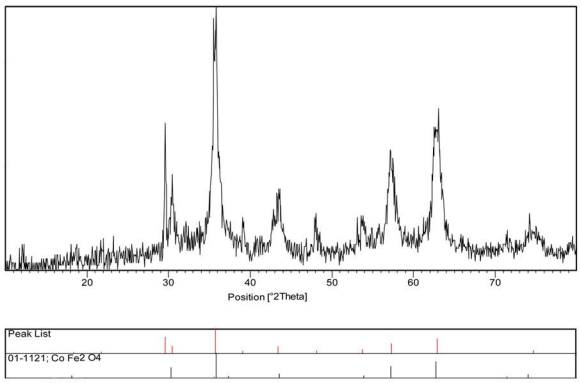

Fig. 2. XRD pattern of the $CoFe_2O_4$ nanoparticles

Fig. 3 illustrates SEM images of nanoparticles synthesized by ammonia and confirms average diameter size product is less than 45 nm. As the images show some agglomeration are observed in the product. Surfactant effect on the particle size and morphology of the products was investigated. Three different water-soluble additives were used as capping agent and surfactant.

The influence of cetyl trimethyl ammonium bromide (CTAB: cationic surfactant) on the morphology of nanoparticles (synthesized by NH_3) is shown in Fig. 4. Using CTAB leads to synthesize of nanoparticles with average diameter less than 100 nm albeit lots of agglomerations were observed and the sample consists of larger particles compare to nanoparticles achieved without surfactant.

The effect of polyvinyl alcohol (PVA: neutral surfactant) on the morphology of nanoparticles (obtained by NH_3) is studied and is illustrated in Fig.5. It seems polyvinyl alcohol remains on the surface of the particles and nanocomposite is formed. For better investigation transmission electron microscopy is needed that shows polymeric matrix remains on the surface of particles.

The effect of sodium dodecyl sulphate (SDS: anionic surfactant) on the morphology of nanoparticles (synthesized by NH_3) is depicted in Fig.6. The image shows that the sample consists of larger particles compare to surfactant-free nanoparticles and bulk particles were synthesized. Outcomes approve in these conditions using various surfactants like cationic, anionic and neutral have negative effect on the size of samples.

It seems by applying surfactants growth stage overcome to nucleation stage and leads to magnetic nucleuses grow together and bigger particles are obtained.

Consequently in these conditions and procedure surfactant-free sample shows smaller particle size.

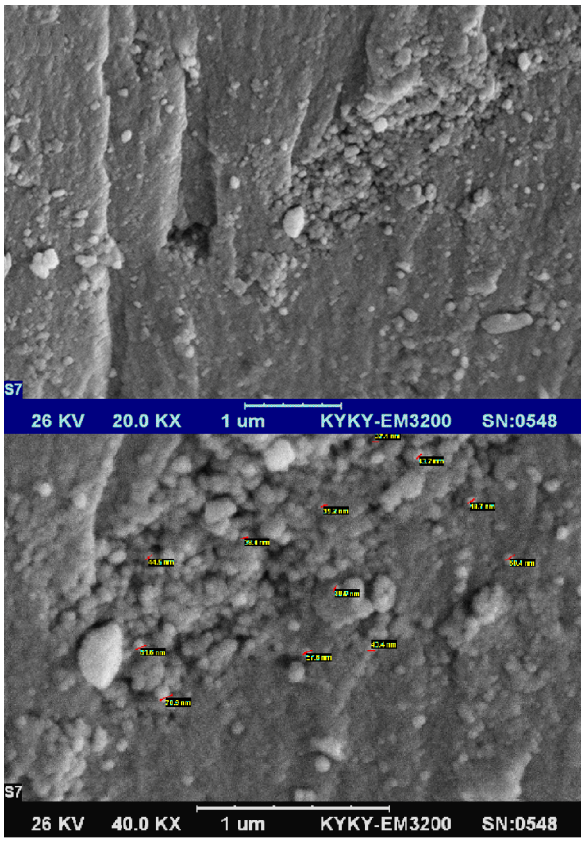

Fig. 3. SEM images of nanoparticles achieved by NH_3

Precursor effect on the morphology of the product was examined and observed by replacing precipitation-agent from ammonia to sodium hydroxide mono-dispersed nanoparticles with average diameter of 25 nm were synthesized.

According to SEM images in these conditions ammonia is not appropriate precipitation-agent in comparison with sodium hydroxide and products with bigger particle size was obtained.

This method proposes easy manipulation in particle size and magnetic properties by a simple change in precursors.

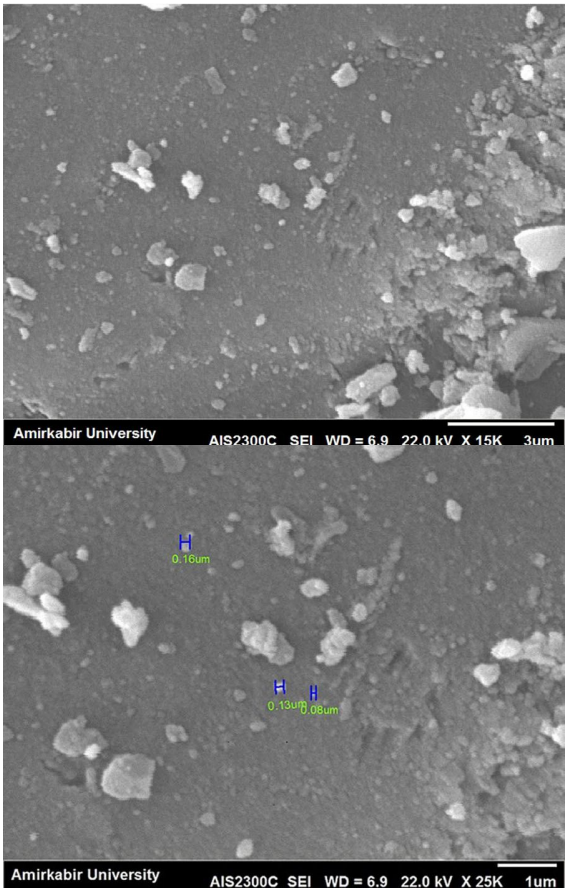

Fig. 4. SEM images of the nanoparticles obtained by CTAB

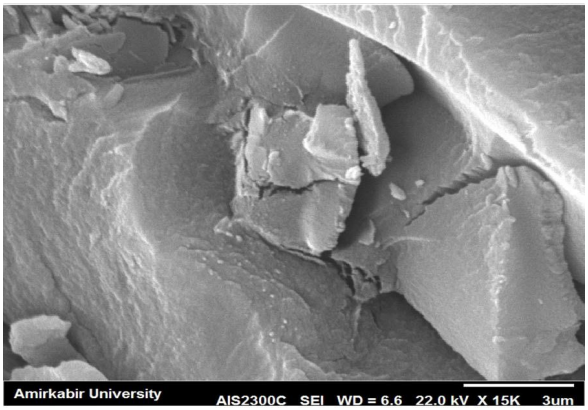

Fig. 5. SEM image of the $CoFe_2O_4$ achieved by PVA

Fig. 7 illustrates SEM image of sample obtained by NaOH and confirms average diameter size of surfactant-free product is about 25 nm.

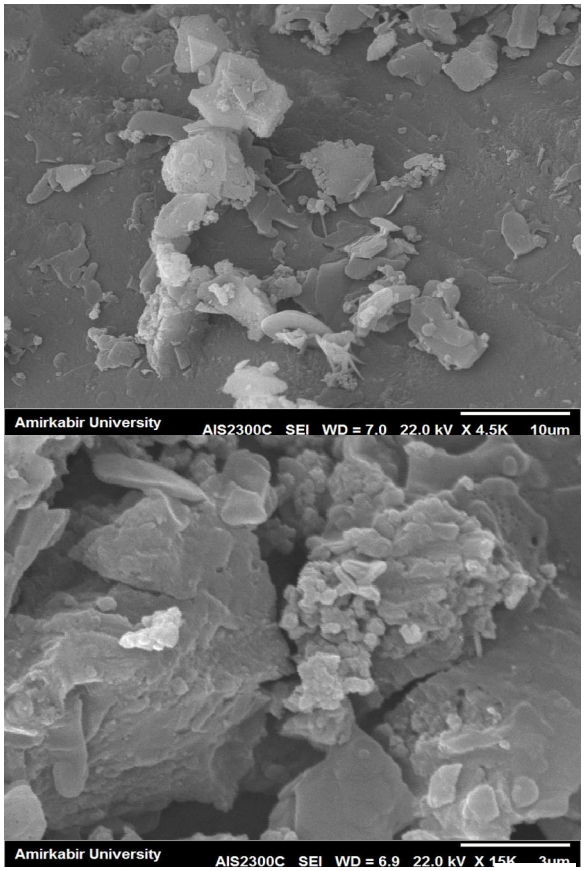

Fig. 6. SEM images of the $CoFe_2O_4$ obtained by SDS

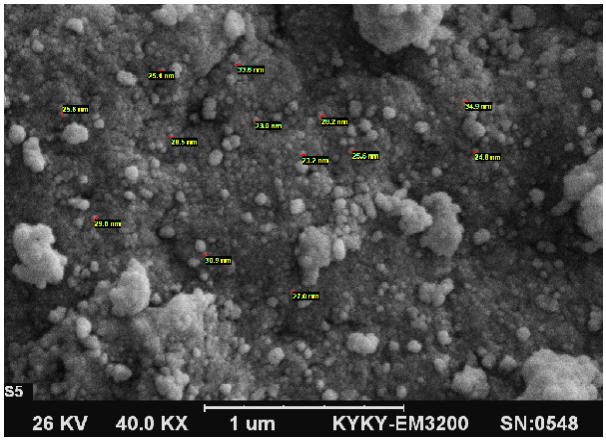

Fig. 7. SEM image of $CoFe_2O_4$ nanoparticles synthesized by NaOH

The annealing effect on the morphology of the products is shown in Fig. 8. Using annealing at 200 °C leads to synthesize nanoparticles with average diameter less than 50 nm and show some agglomeration compare to blank sample.
At 800 °C some bulk products simultaneously were formed besides nanoparticles with average diameter less than 80 nm. Relatively sample consists of bigger particles compare to surfactant-free product (Fig. 9).

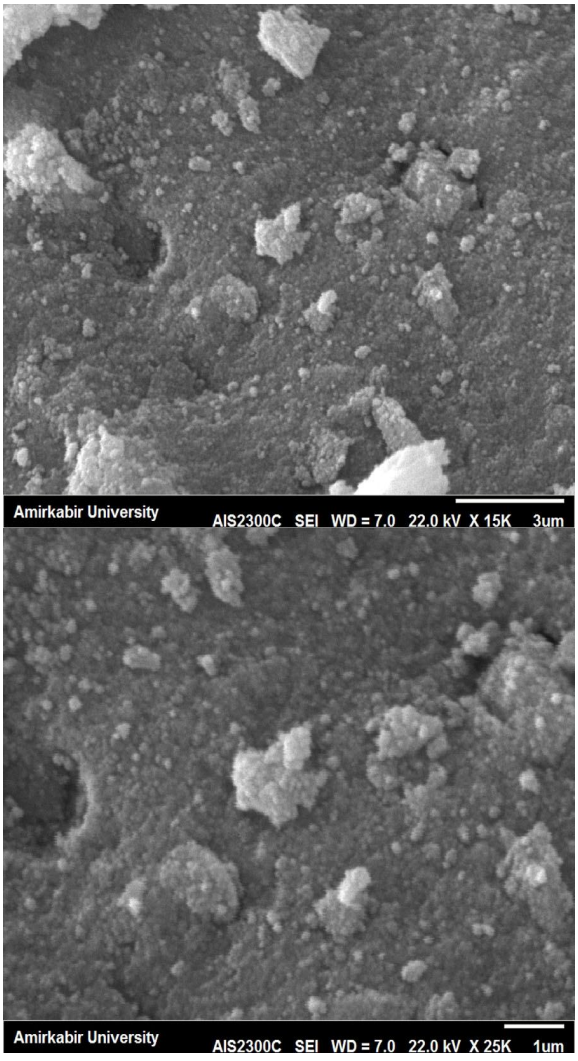

Fig. 8. Nanoparticles that are annealed at 200° C

Room temperature magnetic properties of our samples are studied using a VSM device. Coercivity, remanence and saturation magnetization of the cobalt ferrite nanoparticles which synthesized with sodium hydroxide and ammonia are mentioned in magnetic curves. Hysteresis loops for $CoFe_2O_4$ nanoparticles obtained with sodium hydroxide is depicted in Fig. 10.

$CoFe_2O_4$ synthesized nanoparticles show ferrimagnetic behavior and have a saturation magnetization of 21.05 emu/g, remanence of 3.8 emu/g and a coercivity of 200.9 Oersted.

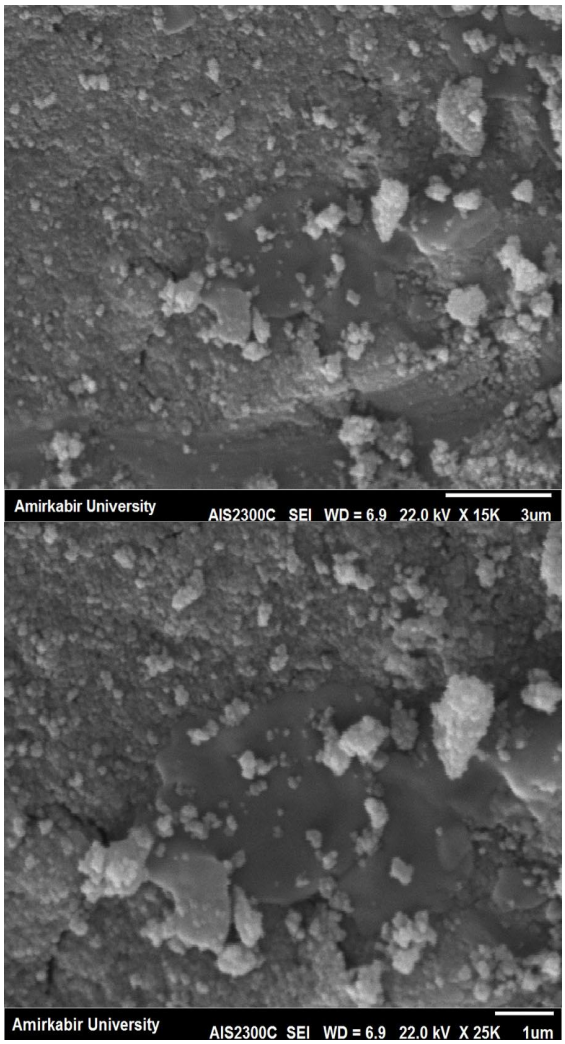

Fig. 9. SEM images of nanoparticles that are annealed at 800 °C

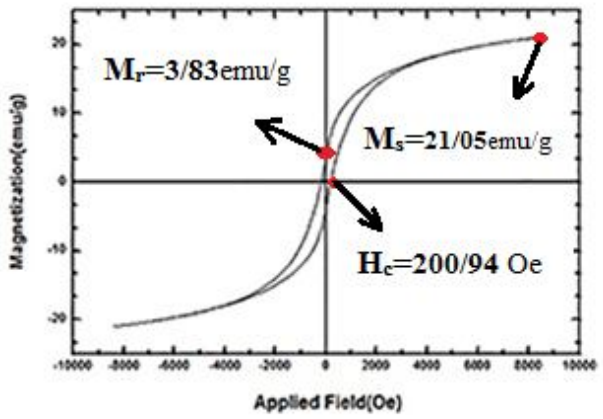

Fig .10. Hysteresis curve of nanoparticles synthesized by NaOH

Fig. 11 shows magnetization curve of $CoFe_2O_4$ nanoparticles (obtained with ammonia) that exhibits super-paramagnetic behavior with a very low coercivity and a saturation magnetization of 5.4 emu/g. It is an interesting outcome because by a simple change in precursor, property of product easily is altered. In this procedure ammonia leads to lower magnetization and coercivity. By using NaOH totally new magnetic product with higher amounts of magnetization and coercivity is synthesized. Applying annealing at higher temperatures also goes to higher coercivity.

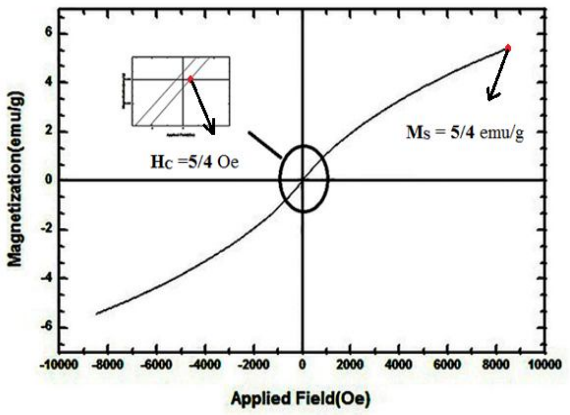

Fig. 11. Magnetization curve of nanoparticles synthesized by NH_3

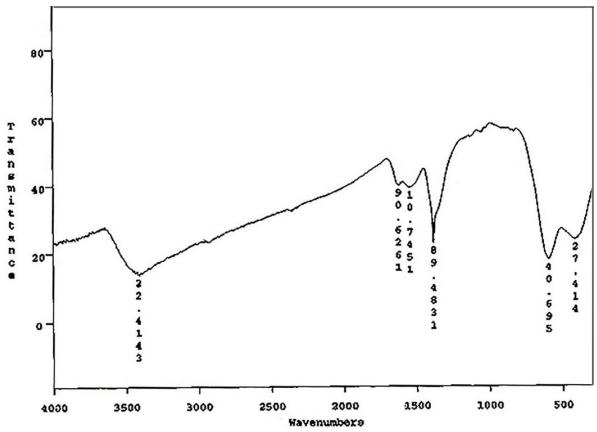

Fig. 12. FT-IR spectrum of nanoparticles

Fourier transform infra-red (FT-IR) spectrum of synthesized nanoparticles was recorded in the range of 400–4000 cm $^{-1}$ at room temperature and results is shown in Fig. 12. The spectrum exhibits absorption peaks between 3400-3500 cm^{-1}, corresponding to the stretching mode of O-H group adsorbed on the surface of nanoparticles. Absorption peaks around 410 and 590 cm^{-1} are related to metal-oxygen (Fe-O, Co-O) bonds.

4. Conclusion

$CoFe_2O_4$ nanoparticles were synthesized via a facile chemical precipitation method. The particle size of products synthesized by sodium hydroxide was smaller than ammonia. By applying surfactants growth stage overcome to nucleation stage and leads to magnetic nucleuses grow together and bigger particles be obtained. The magnetic properties of the product were also investigated using a vibrating sample magnetometer. Interestingly cobalt ferrite nanoparticles exhibit different super-paramagnetic and ferrimagnetic behaviors by changing precipitation-agent. Annealing leads to nanoparticles with average diameter less than 80 nm and also sample consists of bigger particles compare to blank sample.

Acknowledgments

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