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Fabrication and Characterization of Nanoporous Co Oxide (Co_3O_4) Prepared by Simple Sol-gel Synthesis

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Cobalt oxide (Co_3O_4) nanorods were prepared by a simple co-precipitation method using ethanol solution of cobalt nitrate as precursor and cetyl trimethylammonium bromide (CTAB) as surfactant. Morphological properties of the nanoparticles were characterized. XRD measurement exhibited the structure of Co_3O_4 nanocrystals for annealed samples. The SEM images revealed that the particles changed from spherical shape to rod-like shaped by increasing annealing temperature. The TEM results exhibited that the size of cobalt oxide nanoparicles decreased from 25 nm for as-made particles to 50 nm for annealed samples with increasing temperature. The FTIR analysis confirmed the functional group presents in the cobalt oxide nanoparticles. The sharp peaks in FTIR spectrum determined the purity of Co_3O_4 nanoparticles and existence of Co-O group. Absorbance peak of UV-Vis spectrum showed the band gap energy of 3.69 eV corresponding to wavelength about 335 nm for as-prepared samples and the band gap energy of 3.49 eV corresponding to wavelength about 355 nm for annealed Co_3O_4 nanoparticles. The results of magnetic measurements indicated a good coercive field and saturation magnetism around 447.81 G and 17.295 emu g^{-1}, respectively.

Keywords: Cobalt oxide (Co_3O_4), Nanorods, Sol-gel, CTAB surfactant, Synthesis

INTRODUCTION

In recent years, much attention has been paid to the synthesis and study of nanoparticles because of wide range of potential applications [1,2]. Nanomagnetic materials are of considerable interest because of their application in magnetic recording media, catalysis and sensors [3,4]. Recently, cobalt (Co) nanoparticles have attracted much attention for various industrial applications [5,6]. There are three kinds of structures for Co nanoparticles depending upon the synthetic route: Co hcp, ε-Co cubic [7] and fcc structure [8]. Over the past decades, many studies in synthesis and fabrication of the Co nanoparticles have been reported [9,10]. Chemical synthesis is a simple route for the fabrication instead of physical methods due to its low cost, easy preparation and industrial viability [11]. Cobalt nanoparticles have been fabricated by different routes including precipitation method [12,13], reverse microemulsion [14,16], sol-gel [16], gas vapor condensation [16-18] and thermal decomposition [19]. When nanoparticles are annealed to change their structure they are close to each other and agglomerated. To prevent sintering and control the particle growth, protective agent such as surfactant and polymers are used which provide steric hindrance and prevent agglomeration [20-23]. In this paper, Co oxide nanorods were successfully fabricated by using cobalt nitrate as precursor and cetyl trimethylammonium bromide (CTAB) as surfactant using sol-gel method. The morphology properties of the samples have been studied by XRD, SEM, FTIR, UV-Vis, VSM and TEM analyses.

EXPERIMENTAL

Cobalt oxide samples were successfully synthesized according to the following manner. First, 5 g of

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$Co(NO_3)_3.6H_2O$ was dissolved into 100 ml de-ionized water with stirring. Then, 100 ml ethanol solution was slowly added to the solution and stirred for 5 min at room temperature. By adding the cetyl trimethylammonium bromide (CTAB) surfactant the solution changed to blue color. The pH was maintained to 5 during the process. Resulting Co solution were dried at 80 °C for 2 h and cooled to room temperature and then calcined at 600 °C for 3 h. The Cobalt oxide nanocrystals powder was later obtained. The samples were characterized without any washing and purification.

Structural features of the as-synthesized and annealed cobalt nanoparticles, such as the size, structure and surface morphological properties, were thoroughly examined. All of the measurements were carried out at room temperature. X-ray diffractometer (XRD) analysis was accomplished to determine the lattice parameters and crystalline phase. Crystallography of the particles was performed by the XRD measurement with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 Å. The samples were characterized by field emission scanning electron microscopy (FESEM) with type KYKY-EM3200, 25 kV and field emission transmission electron microscopy (FETEM) with type Zeiss EM-900, 80 kV. The absorption picks were measured by ultraviolet-visible spectrophotometer (UV-Vis) with optima SP-300 plus, and Fourier transform infrared spectroscopy (FTIR) with WQF 510. Magnetic properties were measured using vibration sampling magnetometer with type VSM 7400 Lake Shore.

RESULT AND DISCUSSION

Figure 1a shows the XRD morphology of as-made Co oxide nanoparticles and Fig.1b indicates the annealed one. Well-defined diffraction peaks at about 19.52°, 31.50°, 37.05°, 38.77°, 44.96°, 55.80°, 59.53°, 65.30°, 74.55°, 77.50° and 78.60° are observed, corresponding to the (111), (220), (311), (222), (400), (422), (511), (440), (620), (533) and (622) planes of Co_3O_4 crystals. The mean size of the ordered Co_3O_4 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The size of

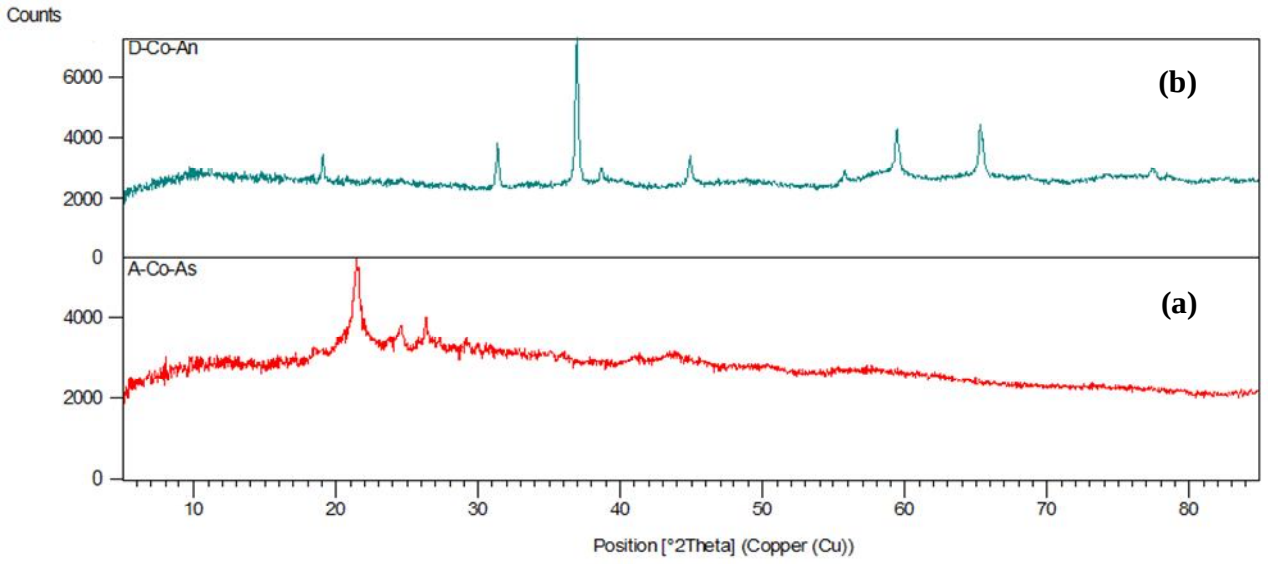

Fig. 1. XRD pattern of (a) as-made and (b) annealed Co_3O_4 nanoparticles.

as-prepared Co_3O_4 nanoparticles was in the range of 15-30 nm from this Debye-Sherrer equation.

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of Co_3O_4. These figures show cobalt oxide nanorods emerged on the surface of the samples by increasing annealing temperature. Figure 2a shows the SEM image of the as-prepared cobalt oxide nanoparticles prepared by sol-gel method. It can be seen that the particles were aggregated together with particle size in the range of 15-30 nm. Figure 2b shows the SEM image of the annealed Co_3O_4 nanoparticles at 600 °C for 3 h in presence of CTAB surfactant. It can be seen that the rod-like shaped Co_3O_4 nanocrystals were formed with good uniformity in size and shape when CTAB surfactant was used. The average diameter of crystallite size of annealed samples is about 50 nm.

To determine the exact size of the particles, their growth pattern and distribution of the nanoparticles TEM analysis was performed. Figure 3 shows TEM images of cobalt oxide nanoparticles before and after annealing. Figure 3a

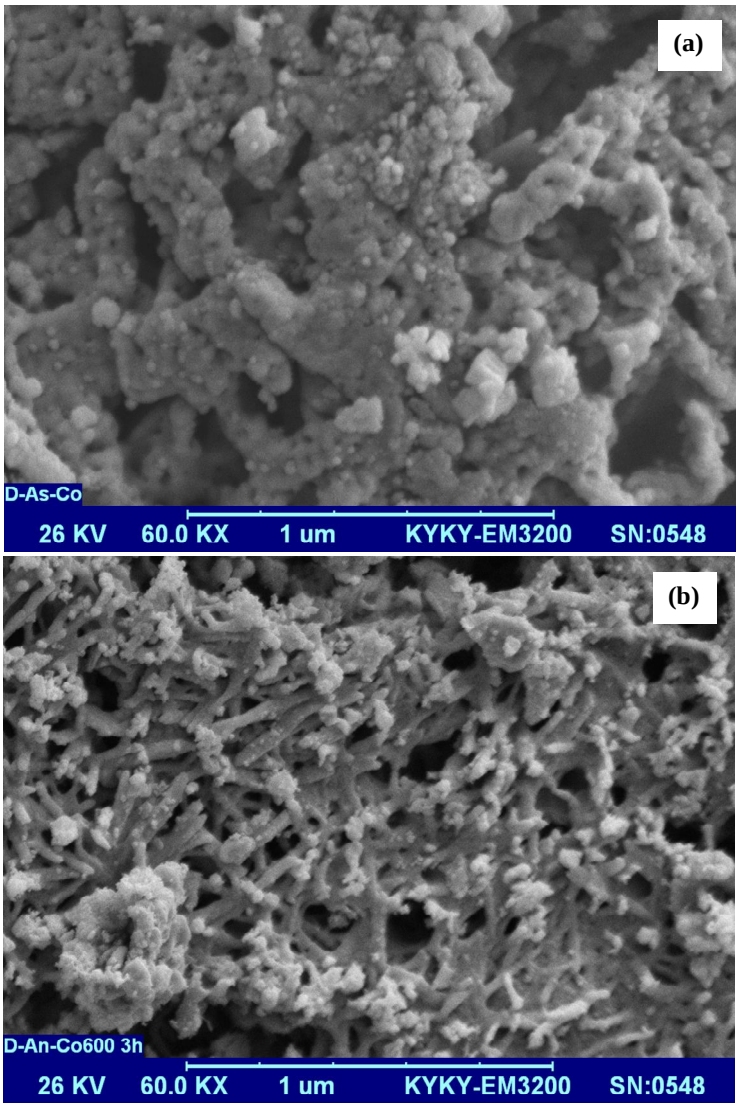

Fig. 2. SEM images of the (a) as-prepared and (b) annealed Co_3O_4 nanorods.

shows the nanoparticles before heat treatment. The spherical particles size is in a range of 20-30 nm, and the mean particle diameter is 25 nm. Figure 3b shows the nanoparticles after annealing with mean particle size of 50 nm. In fact the CTAB surfactant was removed after annealing and the particles were close to each other and their size was increased.

According to Fig. 4, the infrared spectrum (FTIR) of the synthesized Co_3O_4 nanoparticles was in the range of 400-4000 cm^{-1} wavenumber which identify the chemical bonds as well as functional groups in the compound. The sharp bands at 1450 cm^{-1} and 879 cm^{-1} can be assigned to the bending mode C-H group. The sharp bands at 1139 cm^{-1} can be assigned to the streching mode C-O group. The low energy region and large broad band at 621 cm^{-1} indicates the stretching mode of Co-O bond of a Co_3O_4 network.

UV-Vis absorption spectra of as-prepared and annealed Co_3O_4 nanoparticles are shown in Fig. 5. The absorbance peak of UV-Vis spectrum showed the band gap energy of 3.69 eV corresponding to wavelength about 335 nm (Fig. 5a) for as-prepared samples and the band gap energy of 3.49 eV corresponding to wavelength about 355 nm (Fig. 5b) for

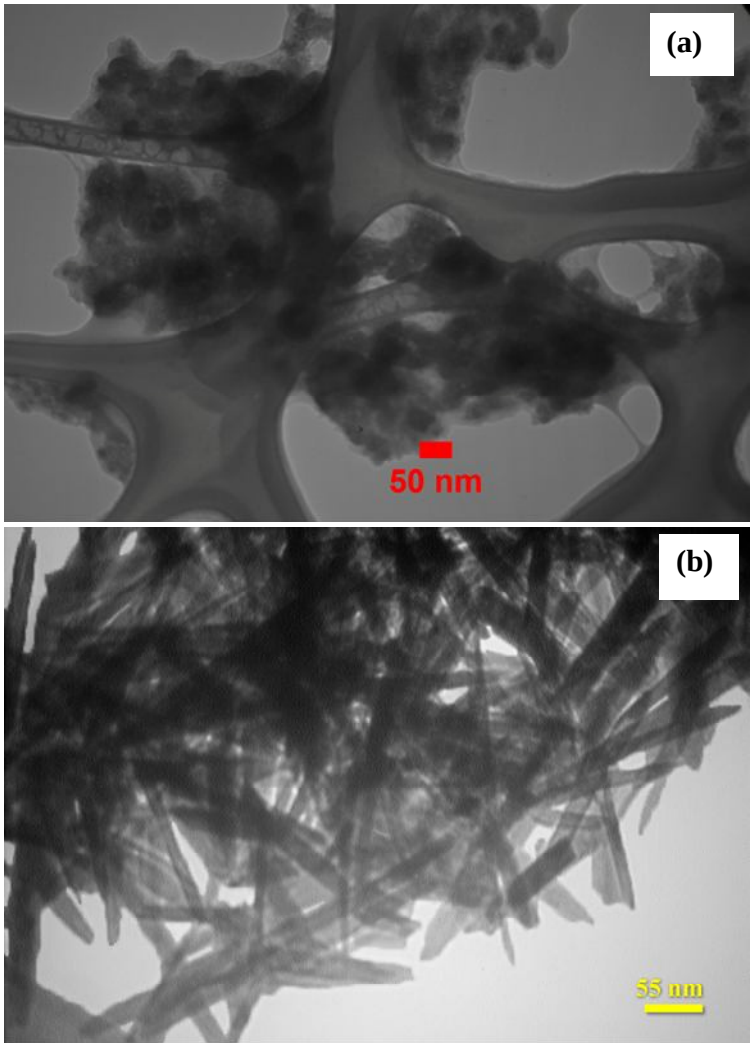

Fig. 3. TEM images of the (a) as-prepared and (b) annealed Co_3O_4 nanoparticles.

annealed Co_3O_4 nanoparticles under heat treatment at 600 °C. Strong absorption band in the UV-light region is clearly observed. In fact, the absorption edge extends to longer wavelengths for Co_3O_4 nanoparticles, and absorption tail in the visible-light region over 330-500 nm [24].

Magnetic properties were measured to identify the magnetic behavior of the nanosized particles. Magnetizations *M* versus applied magnetic field *H* for powders of the samples are measured at room temperature by cycling the magnetic field between -20k to 20k G. Figure 6a shows the magnetization curve hysteresis of as-made samples and Fig 6b shows the loop for annealed samples. The magnetic measurements showed a good coercive field and saturation magnetism of annealed one around 447.81 G and 17.295 emu g^{-1}, respectively.

CONCLUSIONS

Cobalt oxide (Co_3O_4) nanorods were successfully fabricated by simple and new sol-gel synthesis method using ethanol solution of cobalt nitrate as precursor and CTAB as surfactant. The size of Co_3O_4 particles was measured in the range of 15-30 nm for as-prepared particles and 50 nm for annealed ones. SEM images revealed that the particles changed from spherical shaped to rod-like shaped with less agglomeration by increasing annealing temperature. XRD pattern of cobalt oxide samples nanoparticles exhibited the structure of Co_3O_4 nanoparticles. TEM image revealed the sphere-like shaped cobalt oxide nanoparticles for as-made samples. FTIR spectrum indicated the stretching mode of Co-O bond of a Co_3O_4. UV-Vis spectrum indicated the band gap energy of 3.69 eV corresponding to wavelength about 335 nm for as-prepared samples and the band gap energy of 3.49 eV corresponding to wavelength about 355 nm for annealed Co_3O_4 nanoparticles under heat treatment at 600 °C. Magnetic measurements studies showed a good coercive field and saturation magnetism around 447.81G and 17.295 emu g^{-1},

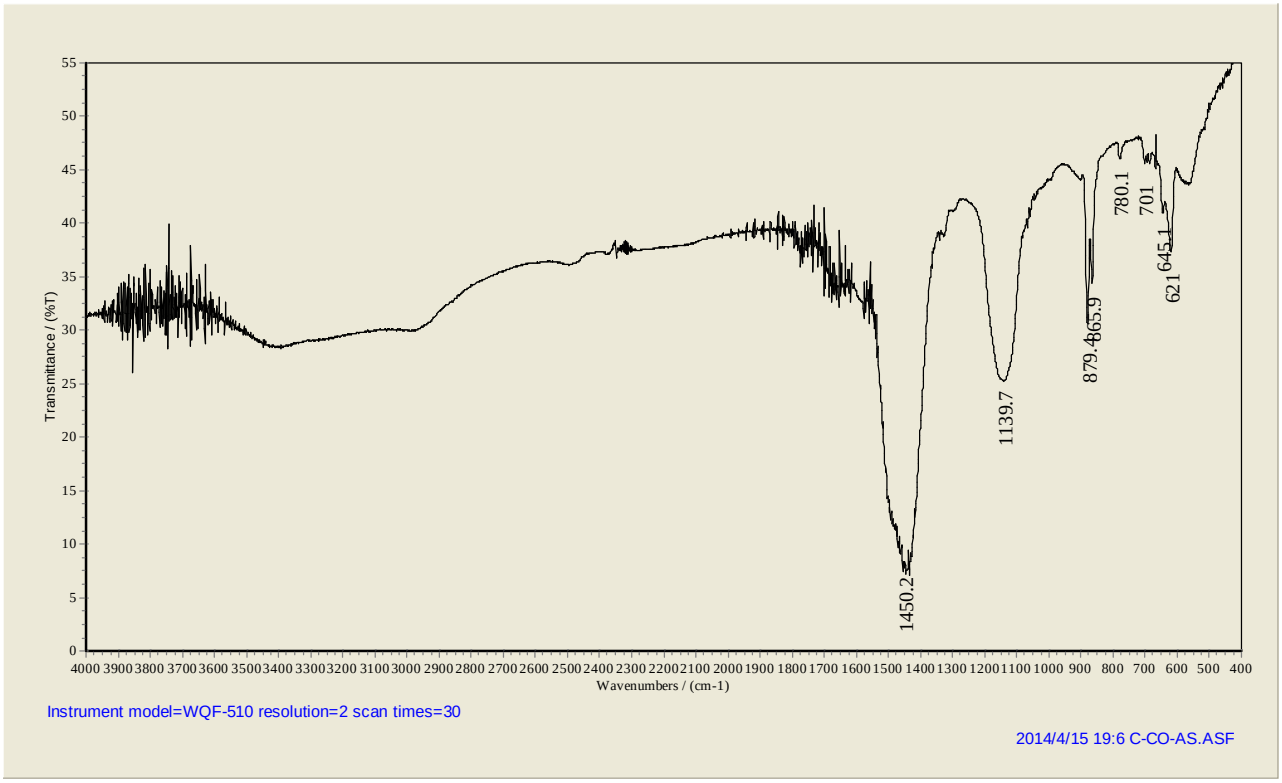

Fig. 4. FTIR spectrum of Co_3O_4 sample.

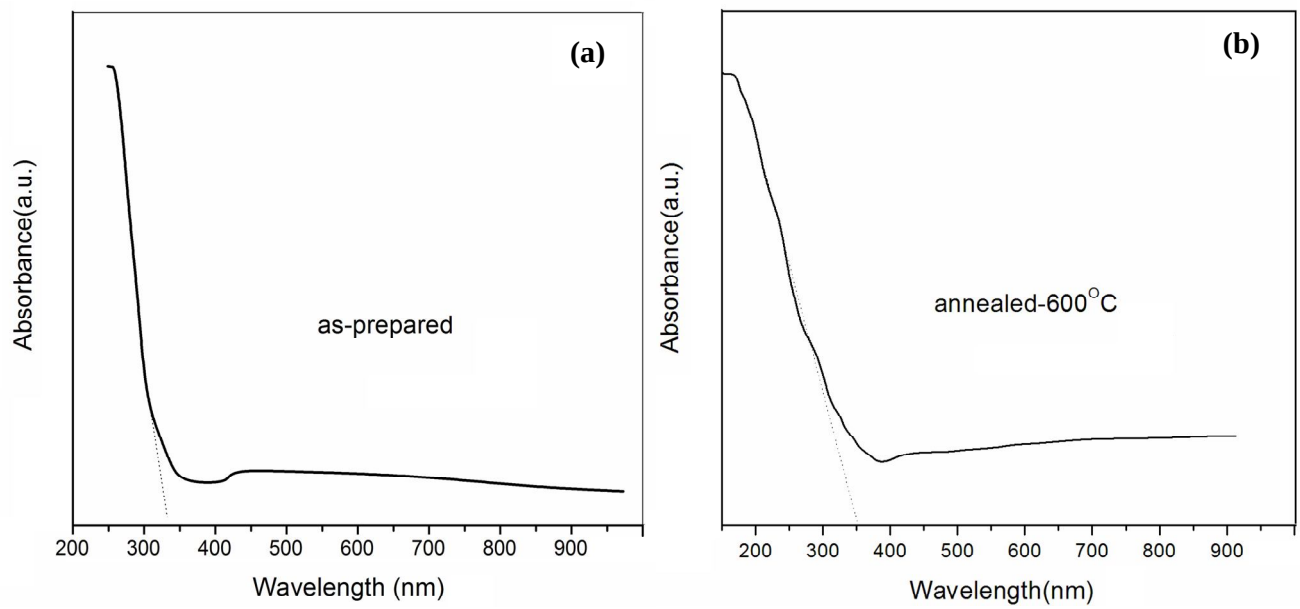

Fig. 5. UV-Vis absorption spectra of Co_3O_4 (a) as-prepared and (b) annealed at 600 °C.

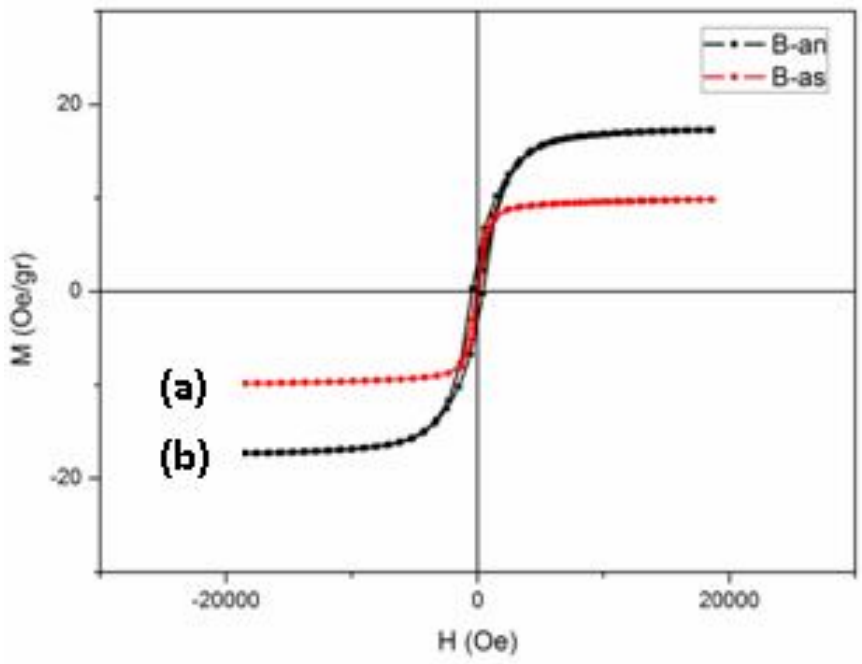

Fig. 6. Magnetic hysteresis loops of the (a) as-prepared and (b) annealed samples.

respectively.

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