Eutectic crystallized FePd nanoparticles for liquid metal magnet

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Eutectic crystallized FePd nanoparticles for liquid metal magnet

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Abstract

Magnetically hard nanoparticles have been widely explored in colloidal solution synthesis while high temperature induced phase transformation is indispensable to achieve its high magnetocrystalline anisotropy. However, long-standing challenge of magnetic nanoparticles is the inaccessibility of the size-controlled growth without the sintering induced agglomeration. Here, we report a universal one-pot eutectic reaction scheme of magnetically hard FePd nanoparticles on which the crystallization conditions are critical for its magnetic performance. We demonstrate the stoichiometry between transition metal and eutectic salt and sintering temperature can play an important role in the magnetic coercivity of FePd nanoparticles. In addition, gallium liquid metal is employed as the conductivity filler for the formation of magnetorheological fluid after mixing with metallic FePd nanoparticles. The liquid composite shows a high metallic and thermal conductivity as unconventional cooling metallic ferrofluid conductor, and we further demonstrate its potential application in sensors, conductors and thermal interfaces.

Magnetic nanoparticles are of intense interests due to their potential applications in permanent magnets, information technology and biomedical engineering.[1-3] The nanoparticle nature offers major advantages due to its size and surface properties, and therefore much attention has been explored in the controlled synthesis of magnetic nanoparticles with pronounced magnetic properties.[4] In this context, magnetically hard nanoparticles are particularly critical to cover a broad spectrum of industrial applications, such as data storage, nanomagnets, and ferrofluid.[5] The energy density and stability of magnetic particles depends on the dimension of the particles.[6] In almost all uses, the colloidal solution synthesis of magnetic nanoparticles represents one of the most studied approach while it is indispensable to activate its magnetically hard properties through the application of high temperature sintering induced phase transformation.[7-9] However, a long-standing challenge of maintaining nanosized magnetic hard particles is the inaccessibility of sintering-induced phase transformed hard nanoparticles without the agglomeration.[10]

A eutectic reaction, known as liquid phase transformation, is based on a solid-state eutectic composition with low melting point to minimize energy consumption, making a low-cost manufacturing process.[11-14] Such thermodynamic solidification shows a common structure of alternate lamellae. An understanding of microstructure formation is essential to explore the potential of eutectic reaction for magnetic nanoparticle formation.[15, 16] For magnetically hard iron palladium (FePd), the nanoparticles of face-centered cubic (fcc) phase can be conventionally obtained through colloidal hot-injection approach by using relatively low boiling point organic solvents, while the phase transition of FePd nanoparticles from fcc to face-centered tetragonal (fct) is always accompanied by high temperature sintering to exhibit high magnetocrystalline anisotropy.[17, 18] Here, we report the eutectic crystallization approach to one-pot grow magnetically hard FePd nanoparticles by using the eutectic composition salt (KCl-LiCl) as high temperature reaction solvent medium, in which the as-synthesized FePd nanoparticles exhibit the hard magnetism dictated by the reaction conditions, such as the composition ratios, reaction temperature and stoichiometry of Fe and Pd elements (The details are discussed in supporting information). The traditional magnetic fluid materials consist of magnetic nanoparticles, organic/aqueous solvent component, and the surfactants for the improved stability and dispersion. However, a long-standing limitation of such system is the low operation temperature of solvent/organic additives, and electric insulating nature to limit its broad applications.[19, 20] In order to overcome these challenges, the liquid magnetic metal, doping magnetic particles into liquid metal, is considered as a new approach to develop electrically and thermal conductive

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magnetic fluid system. Hence, we demonstrate the liquid metallic magnet by mixing the as-synthesized FePd nanoparticles with liquid metal gallium filler for the formation of magnetorheological fluid. The liquid composite shows a high metallic and thermal conductivity as unconventional cooling metallic ferrofluid conductor, promising potential applications in sensors, conductors and thermal interfaces.[21]

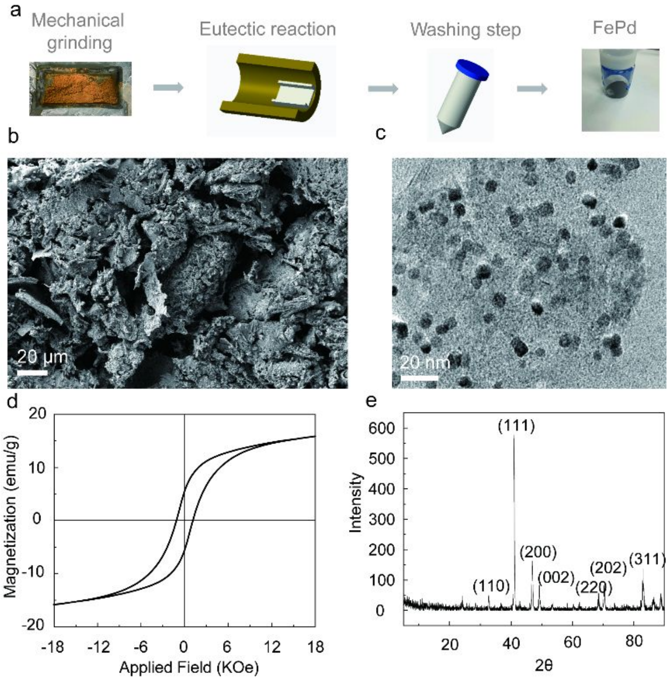

Figure 1. (a) Eutectic salt melt synthesis and crystallization of FePd powder; (b) The SEM image of FePd powder; (c)The TEM image of FePd; (d) Magnetic hysteresis loops of FePd powder; (e) The XRD pattern of FePd powder.

Eutectic salt reaction, a powder metallurgical method, involves the molten salt as the solvent medium to prepare the metallic FePd magnetic nanoparticles. Molten salt (KCl-LiCl, in this study) can enhance the rates of solid-state reactions, in which the amount of salt is typically a few percent of the total weight to control the characteristics (size, shape, etc.) of magnetic FePd nanoparticles (Figure 1a). Flake-shaped FePd nanostructures consisting of nanoparticle building blocks are obtained in one-step eutectic reaction, where this unique flake-shaped FePd could be a result of the lamellar structure formed during the solidification of the eutectic salts. Figure 1b and 1c show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of as-synthesized FePd nanoparticles, confirming the layered assembly structure consisting of FePd nanoparticles. Figure 1c presents the TEM image of the FePd nanoparticles with an average diameter of 11 nm. Meanwhile, according to Fig. 1c, magnetic hysteresis loop of as-synthesized FePd nanoparticles shows the coercivity of 1,800 Oe. In addition, X-ray diffraction (XRD) (Fig. 1e) suggests the formation of the fct-FePd phase after eutectic solidification, while (202) and (002) planes signal the fct phase of FePd nanoparticles.[14, 22]

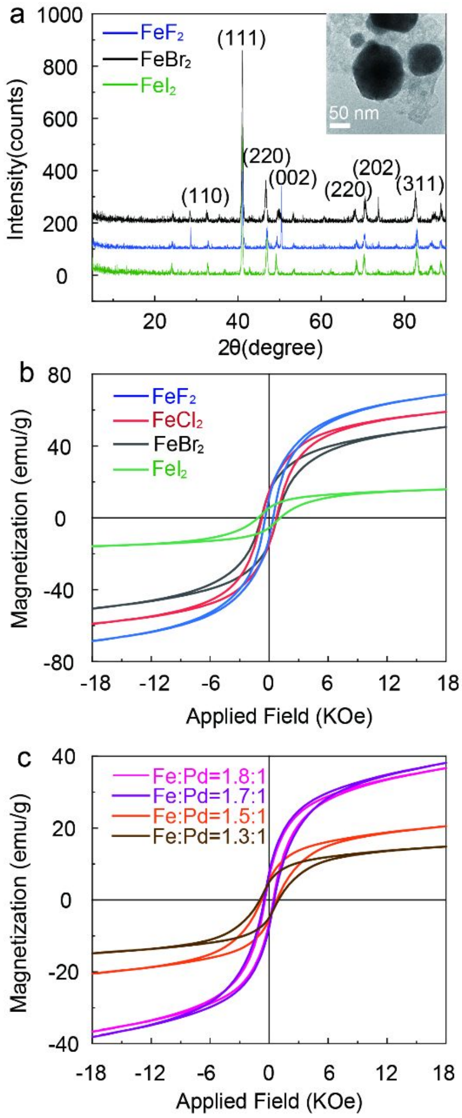

Figure 2. (a) XRD patterns of FePd with different halide precursors (the inset image is the TEM image of FePd with FeI_2 precursor); (b) Magnetic hysteresis loops of FePd with different precursors; (c) Magnetic hysteresis loops of FePd with different ratios of precursor.

The chemical precursor, such as iron halide compounds, plays an important role in controlling the stoichiometry of FePd nanoparticles during the eutectic crystallization reaction. The decomposition of iron halides is based on the concept of hard-soft acid-base application, while the basic degree of halogen elements gradually decreases from the iodine to fluorine anions. When the difference of basic degree between two elements is slight, the bonding between iron cation and halide anion is strong and not readily decomposed. Meanwhile, the more basic degree increases, the softer Lewis base presents. The bonding between Fe^{2+} and I^- is relatively weak, leading to a readily decomposed FeI_2 under the same eutectic reaction conditions. Figure 2a shows the XRD spectra of as-synthesized FePd nanoparticles by using the different halide precursors, which evidences the stoichiometry of FePd by using the FeI_2 precursor. The TEM image of FePd by using FeI_2 precursor is shown in the upper right in Fig 2a, the TEM image of FePd with other halide precursors presents in Fig. S2-4. Figure 2b illustrates the magnetization hysteresis (M-H) loops of as-synthesized FePd nanoparticles prepared by different halide precursors under the same ratio between Fe and Pd precursors. The M-H loop suggests the optimum coercivity of FePd nanoparticles synthesized from the FeI_2 precursor, confirming the role of stoichiometry on magnetic performance of FePd. We further demonstrate the stoichiometry role of FePd nanoparticles on its magnetic performance by controlling the ratios between Fe and Pd precursors (Fig. 2c). According to the Fig. 2c, the stoichiometry of Fe:Pd plays an important role in its magnetization and coercivity of FePd nanoparticles. A higher composition of Fe element leads to a high magnetization, while the stoichiometry of FePd results in an optimum coercivity. The eutectic salt melt and crystallization method is shown to be an efficient and single-step method to prepare the FePd with an average diameter of 11 nm, which presents a coercivity of 3,000 Oe and a magnetization of 17 emu/g. The eutectic reaction provides a new one-pot synthetic pathway to control the growth of magnetically hard FePd phase, in which its stoichiometry can be controlled by the input precursor ratio or reaction conditions.[23]

Liquid metal magnet is an emerging application of colloidal magnetic nanoparticles. The conventional ferrofluid is made of magnetic nanoparticles and organic solvent, in which its electrically insulating nature and volatile organic solvent limits its broad applications. Liquid gallium shows both high electrical and thermal conductivity at room temperature. The cooling effect of liquid gallium is well-known for emerging thermal interfaces, while the control of liquid feature can be a challenging task. The as-synthesized FePd nanoparticle filler can be mechanically mixed with liquid Ga matrix for the formation of magnetorheological fluid with a permanent-magnet-like characteristic. It is worth noting that the fluidity of FePd-Ga can be controlled by the concentration of FePd nanoparticle loading due to the potential interfacial surface bonding between Fe and Ga matrix. Figure 3a shows the M-H loop of liquid magnetic FePd-Ga composite with 4 wt% concentration of FePd nanoparticles, suggesting the magnetic nature of liquid magnet inherited from the FePd nanoparticles. The uniform distribution of FePd nanoparticles in the liquid composite can be resolved from the SEM (Fig. S5a) and its energy dispersive X-Ray spectroscopy mapping images (Fig. S5b). Figure 3c shows the current-voltage (I-V) curves of FePd-Ga composites. The electrical conductivity of liquid composite can be influenced by the temperature and magnetic field. At room temperature (298 K), the conductivity is $6.88*10^5$ Sm^{-1} regardless of the presence of the magnetic field, when the temperature rises to323 K, the value of conductivity of metallic liquid composite decreases to 2.61 $*10^5$ Sm^{-1}. However, with the application of magnetic field, the conductivity could increase to $2.95*10^5$ Sm^{-1}, suggesting magnetic field effects in metallic magnetic conductor. It is worth mentioning that the positive effect of the application of magnetic field suggests the potential alignment of FePd nanoparticles in the liquid composite contributing to its improved conductivity. In addition, the rapid cooling effect of liquid metal composite can be obtained by Infrared (IR) camera, presented in Fig. 3d and Fig. S6. Sequential snapshots shows the variation of temperature of the cooling location with respect to the time. Under the application of magnetic field, the droplet of FePd-Ga composite is swiftly pulled along the channel following the magnetic flux direction, suggesting its magnetic fluid nature for cooling applications. The heat flux for FePd-Ga composite could reach 475 W/m^2 based on steady thermal simulation (Fig. S6d), indicating the efficient cooling potentials (Fig. S6e).

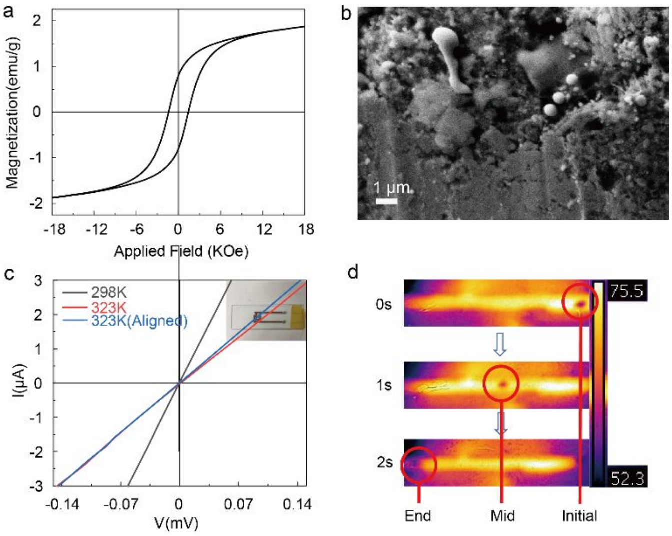

Figure 3. (a) Magnetic hysteresis loop of Ga-doped FePd, (b) SEM image of Ga-doped FePd, (c) IV-curve for Ga-doped FePd, (d) IR-camera images for fluid cooling effect of Ga-doped FePd.

In conclusion, we report a new eutectic solidification strategy to synthesize magnetically hard FePd nanoparticles with an average diameter of 11 nm, which can be further mechanically mixed with liquid metal Ga for the formation of liquid metal magnet with electrical and thermal conductivity. Eutectic salt melt method effectively prevents the sintering induced aggregation of magnetic nanoparticles during the phase transformation process. Meanwhile, eutectic method also simplifies the procedure of production and reduces the energy consumption for a potential scalable manufacturing method of magnetic nanoparticles. The liquid metal magnet of FePd-Ga composites exhibits a metallic conductivity and rapid cooling effect controlled by external magnetic field. The findings presented here provide a new arena of liquid metal magnet for liquid conductor and thermal interface applications.

Conflicts of interest

There are no conflicts to declare.

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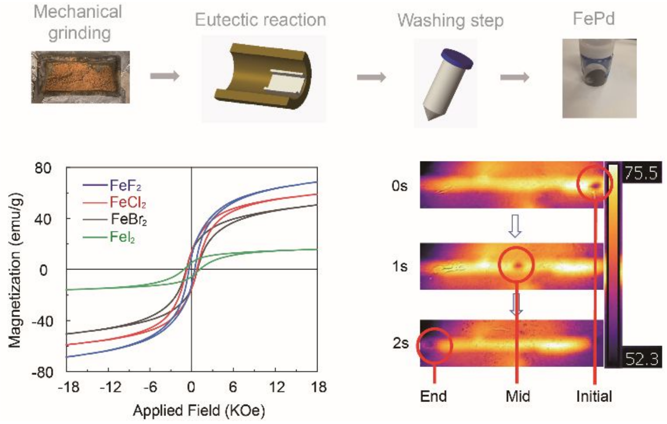

Liquid metal magnet achieved by eutectic grown FePd nanoparticles in liquid metal gallium medium.