

Nanohybrids from Ion Exchange and Hydrothermal Reaction

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Two types of nanohybrid were synthesized by ion exchange, namely, polymer matrix (Dowex) containing nanocrystalline Fe_3O_4 and zinc ferrite particles, respectively, without or with post-ion exchange hydrothermal treatment. Upon ion exchange, nanocrystalline Fe_3O_4 occurs in Dowex matrix, instead of $\gamma\text{-Fe}_2\text{O}_3$ that was claimed by Ziolo et al [1], as confirmed using Raman, XRD and low temperature Mössbauer spectroscopy. For the nanohybrids containing nanocrystalline zinc ferrite, several synthesis parameters, including Zn/Fe ratio, hydrothermal temperature and time, and solution pH, were shown to strongly affect the formation of nanocrystalline ferrite particles, while the novel synthesis route allowed a lower temperature for formation of spinel ferrite than a number of other synthesis routes that were attempted for nanohybrids. A Zn/Fe ratio of as high as 1.5 was required for the aqueous nitrate solution during ion exchange, in order to obtain nanocrystalline ZnFe_2O_4 formed in Dowex, upon subsequent hydrothermal treatment at 150 °C.

Key words: Nanohybrids, hydrothermal treatment, ion exchange

1. INTRODUCTION

A number of novel magnetic and optical properties have been demonstrated by nanohybrids consisting of nanocrystalline magnetic particles dispersed in a suitable matrix of polymer, glass or ceramic [1-3]. The properties of these nanohybrids are affected by not only the nature of both the nanoparticles and matrix but also the configuration of their interfaces and the interactions between them. Various processing routes have been developed to incorporate nanophase magnetic particles into a matrix. For example, Bentivegna et al [4,5] attempted to study the magnetic and optical properties of a hybrid silica gel which was prepared by mixing an aqueous ferrofluid containing $\gamma\text{-Fe}_2\text{O}_3$ with a silica sol followed by gelation. Since the nanophase $\gamma\text{-Fe}_2\text{O}_3$ was not formed in situ, its concentration and distribution could not be controlled properly, resulting in an overall saturation magnetisation of as low as 0.38 emu/g. Yasumori et al [6] also introduced pre-synthesised Fe_3O_4 particles into a silica sol which was gelled at 60°C, resulting in a low Fe_3O_4 loading (5.58×10^{-3} mol%). In contrast, in-situ formation of magnetic nanoparticles in an appropriate matrix demonstrates several advantages, including a better control on particle growth and size distribution, increased loading of nanoparticles and hence improved magnetic properties. An excellent example was reported by Ziolo et al [1], who synthesized optically transparent magnetic nanohybrids using ion-exchange resin. In their experiment, the resin was ion-exchanged in solution containing Fe cations and then exposed to NaOH solution at 60 °C. Formation of the magnetic iron oxide nanoparticles could be further assisted by the addition of N_2H_4 or H_2O_2 . The nanoparticles thus obtained exhibited the required homogeneity in particle size and morphology. A saturation magnetization of as high as 46 emu/g was measured for the nanohybrid derived from ion exchange. Other in-situ processes, such as sol-gel, ion-implantation

and block-copolymer templating, have also been successfully used to synthesize magnetic nanohybrids [3,7,8]. In this study, in-situ ion exchange was employed to synthesize two types of nanohybrids. As detailed in the discussion below, the iron oxide phase formed in situ in resin matrix was confirmed to be Fe_3O_4 , rather than $\gamma\text{-Fe}_2\text{O}_3$ as claimed by Ziolo et al [1]. We also explored the feasibility of synthesizing Zn ferrite in resin matrix, where two cations (i.e., Zn^{2+} and Fe^{3+}) were involved by ion-exchange assisted by post hydrothermal treatment.

2. EXPERIMENTAL DETAILS

The starting chemicals employed in this study are commercially available iron (III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] of reagent grade with purity > 99% (Fisher Scientific); zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] of purity > 98% (Goodrich Chemical Enterprise); Dowex 50w-8(H) standard grade (Dow Chemical Company) and sodium hydroxide pellets (Merck) of 99% purity.

The nanohybrids containing Fe_3O_4 were prepared by following the experimental procedure described in reference [1], while the nanohybrid containing zinc ferrite were prepared by ion exchange between Dowex granules of size ranging from 0.39 to 1.00 mm and an aqueous solution of mixed zinc nitrate and iron nitrate at a range of Zn/Fe mole ratios, followed by hydrothermal treatment. The ion exchange involves sulfonated functional groups in Dowex that possess ability of attracting cations, such as Zn^{2+} and Fe^{3+} in the aqueous solution. It was carried out by keeping the aqueous solution at 40°C for one week, followed by thorough washing with deionized water to remove physisorbed Zn or Fe ions on the surface of the Dowex resin. The ion-exchanged resin was then placed in a Teflon-lined stainless steel autoclave cell filled with 15 ml 3M NaOH solution, which was heated in an oven at 150 °C for 10 hours. The hydrothermally treated nanohybrids were removed from the autoclave cell and washed thoroughly with deionized water and subsequently dried.

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The as-synthesized nanohybrids were characterized for phases present using a powder X-ray diffractometer (Cu K_{α} , Phillips PW1729 X-ray Diffractometer) and a Raman spectrometer (Renishaw 2000 micro-Raman system) employing an argon-ion laser source with an excitation wavelength of 514.5 nm. An ASA 7110S Congress LC-9A Mossbauer system (Austin Science Associate Inc., Austin, TX787455, USA) was employed for further phase confirmation in the nanohybrids. Particle characteristics of the zinc ferrite in Dowex matrix were studied using a transmission electron microscope (TEM) (JEOL-100CX), while their magnetic properties were measured using a vibrating sample magnetometer (VSM model, Oxford Instruments).

3. RESULTS AND DISCUSSION

3.1 Nanohybrids of Fe_3O_4 in Dowex

Nanohybrids containing Fe_3O_4 in the Dowex resin matrix was synthesized by ion exchange. Having carefully repeated the experimental procedure and reproduced the experimental results reported by Ziolo *et al* [1], followed by phase identification using various analytical techniques, we conclude that the nanocrystalline particles formed in the Dowex resin are Fe_3O_4 , instead of $\gamma-Fe_2O_3$ as claimed by Ziolo *et al*, on the basis of the following evidence and arguments.

According to Ziolo, the nanocrystalline iron oxide phase formed by ion-exchange in Dowex resin was identified as $\gamma-Fe_2O_3$ (maghemite) by both conventional and synchrotron energy-dispersive x-ray powder diffraction and Mössbauer spectroscopy. However, it is well known that phase analysis using XRD cannot effectively differentiate between $\gamma-Fe_2O_3$ and Fe_3O_4 , due to their similar cubic spinel structures [9-12]. This is especially so as far as the nanocrystalline particles are concerned, as a result of the considerable degree of peak broadening and therefore overlapping [10-12]. It is therefore difficult to identify whether the nanoparticles are $\gamma-Fe_2O_3$ or Fe_3O_4 . Similarly, the employment of synchrotron energy-dispersive X-ray powder diffraction does not help to differentiate between the two nanocrystalline phases. It is true that Mössbauer spectroscopy is useful as a complementary technique for phase identification in many Fe-containing compounds. In fact, the widely varying hyperfine fields resulting from their different magnetic ordering in conjunction with isomer shift δ and quadrupole interaction 2ϵ should be sufficient to distinguish between Fe_3O_4 and $\gamma-Fe_2O_3$ in bulk forms at room temperature. However when it comes to the nanoparticles, line broadening and superparamagnetic behaviour become major obstacles as a non-magnetic doublet dominates the RT spectrum. Low temperature measurement is therefore necessary for better phase identification. However, it is found that the 4K Mössbauer spectrum of the resin being treated through the preparative procedure twice cannot be fitted with only two magnetic sextets with hyperfine fields of 52.8 and 52.4T for $\gamma-Fe_2O_3$ [13]. The low temperature Mössbauer spectrum of Fe_3O_4 splits into additional discrete sextets, typically five, which make the fitting become very complicated. Clearly, the 4K Mössbauer spectrum does not support the claim that the nanocrystalline phase formed by ion-exchange in Dowex matrix is $\gamma-Fe_2O_3$.

In order to confirm the nature of the nanocrystalline phase formed in the Dowex polymer, the above mentioned resin was characterized using a Raman spectrometer, which has a much better resolution power than X-ray diffraction as far as the difference between Fe_3O_4 and $\gamma-Fe_2O_3$ is concerned [14,15]. In Figure 1, the Raman spectrum obtained for the sample is the one typical for Fe_3O_4 . Clearly, the peaks at wave numbers of 660, 530 and 300 cm^{-1} are indicative of Fe_3O_4 [14]. None of the characteristic features of $\gamma-Fe_2O_3$, such as those peaks at wave numbers of 1378 and 1570 cm^{-1} , are present in the spectrum. The Raman spectroscopic spectra were repeatedly measured at several different locations of the nanohybrid sample and the experimental results were almost identical to that in Figure 1. This clearly demonstrates that the nanocrystalline particles are Fe_3O_4 , instead of $\gamma-Fe_2O_3$. Apparently, part of the Fe^{3+} cations have been reduced to Fe^{2+} by the addition of N_2H_4 , forming Fe_3O_4 nanoparticles in the Dowex resin. The optical and magnetic properties measured by Ziolo *et al* [1] for the optically transparent magnetic nanohybrid can well be explained by the occurrence of Fe_3O_4 nanocrystalline particles.

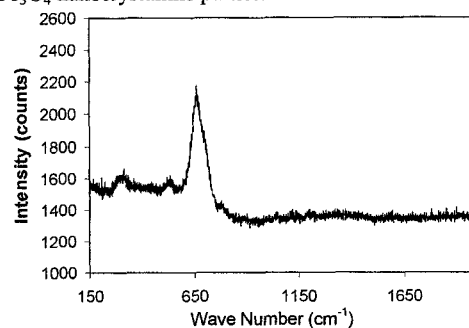


Fig.1 Raman spectrum of the nanohybrid containing iron oxide. The sample was treated through the preparative procedures twice.

3.2 Nanohybrid of $ZnFe_2O_4$ in Dowex

In order to investigate the feasibility of forming spinel ferrites containing more than one types of cation by ion exchange in the Dowex resin matrix, $ZnFe_2O_4$ was chosen in this study. The preparation was initially carried out by heating the Dowex granules in an alkaline solution in the ambient atmosphere after ion exchange, similar to the procedure for Fe_3O_4 mentioned above. However, it was observed that the ferrite phase thus obtained exhibited a very poor crystallinity, even when the temperature was raised to 100 °C. Obviously, the process did not lead to formation of a well crystallized zinc ferrite phase in the polymer matrix. As the temperature could not be increased further in the ambient atmosphere, the ion exchanged samples were subjected to hydrothermal treatment in order to promote crystallization of the ferrite phase. There occurred a notable improvement in the crystallinity with the sample hydrothermally treated at 150 °C, as confirmed by the sharpened XRD diffraction peaks. The hydrothermal process allowed for a much lower formation temperature for spinel zinc ferrite as compared to 1180°C for obtaining a single phase $ZnFe_2O_4$ in the conventional

ceramic synthesis [16] and 600°C in the sol-gel process [17].

Figure 2 is a bright field TEM micrograph, together with the associated selected area diffraction (SAD) pattern for the nanohybrid hydrothermally treated at 150 °C for 10 hours, showing the morphology and size distribution of zinc ferrite nanoparticles in Dowex matrix. It clearly demonstrates that the zinc ferrite particles occur as more or less spherical nanoparticles, which are uniformly dispersed in the polymer matrix. The particle sizes measured fall in the size range of 4 to 10 nm, which is consistent with the average crystallite size of ~6.4 nm calculated from the FWHM in XRD trace using the Scherrer equation. The well-defined diffraction rings in SAD pattern in Figure 2 demonstrates the nanocrystallinity of these zinc ferrite particles. Values of d spacing derived from the SAD pattern further confirmed the existence of the spinel zinc ferrite phase.

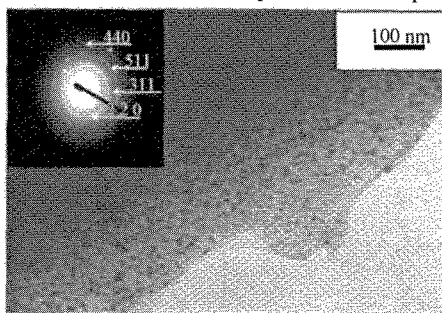


Fig.2 TEM micrograph of the nanohybrid containing zinc ferrite hydrothermally treated at 150 °C with the SAD pattern.

Zn/Fe ratios in the nanohybrid were different from those in the starting nitrate solutions, indicating that the ion-exchange of Fe^{3+} in Dowex resin occurred at a much faster rate than that of Zn^{2+} . This was confirmed by elemental analyses of the resulting nanohybrids. The phases present in the nanohybrids derived from mixed nitrate solutions of different Zn/Fe mole ratios were examined by XRD and the experimental results are illustrated in Figure 3. They were synthesized from Zn/Fe mole ratios of 0, 0.5, 1.0 and 1.5, respectively, while pH of the NaOH solution was kept at 14, hydrothermal temperature at 150 °C and duration for 10 hours. The nanohybrid derived from the nitrate solution of Zn/Fe ratio of 0 (i.e. where no zinc cation was presented) exhibits an amorphous morphology in XRD trace, suggesting that no detectable nanocrystalline phases were resulted. With increasing Zn/Fe ratio from 0.5 to 1.5, there is a gradual increase in the crystallinity of ferrite phase, as demonstrated by the increasing sharpness in major XRD peaks. These XRD patterns are clearly indicative of spinel zinc ferrite phase being the predominant phase and that there is no other transitional phase being involved in the formation process of nanocrystalline zinc ferrite at high Zn/Fe ratios. This suggests that a higher Zn^{2+} ion concentration in the nitrate solution of ion exchange favors the formation of zinc ferrite nanoparticles in Dowex. Apparently, an excess Zn/Fe ratio is required in order to obtain the required nanocrystallinity and stoichiometry for ZnFe_2O_4 nanoparticles, which is accounted for by the

difference in ion-exchange rate between Zn^{2+} and Fe^{3+} in association with their difference in both size and charge together with the selectivity of Dowex resin [18,19]. Furthermore, in a strong alkaline condition, Zn^{2+} can form complex ion of $\text{Zn}(\text{OH})_4^{2-}$, leading to depletion of Zn^{2+} from Dowex [19]. Although $\text{Fe}(\text{OH})_6^{4-}$ can also occur in strong NaOH solution, they serve as the nucleation sites for formation of zinc ferrite in Dowex [1]. Elemental analysis confirmed that the Zn/Fe ratios in the sample after hydrothermal treatment were increased with increasing Zn/Fe ratio in the ion-exchange solution. A Zn/Fe ratio of 1.5 in the solution was found to result in the formation of a composition of $\text{Zn}_{0.89}\text{Fe}_{2.39}\text{O}_4$.

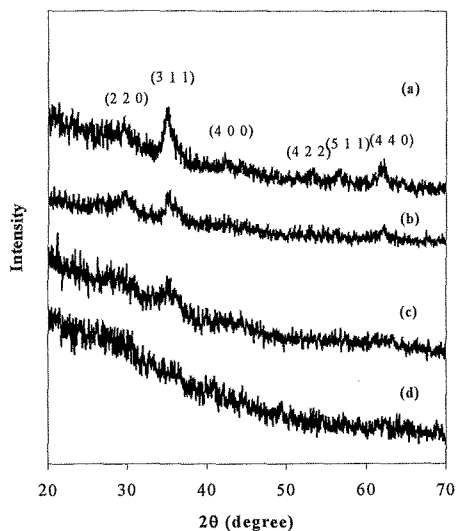


Fig.3 XRD traces for the nanohybrids containing zinc ferrite nanoparticles derived from mixed nitrate solutions of Zn/Fe mole ratios of (a) 1.5, (b) 1.0, (c) 0.5 and (d) 0.0, respectively.

To study the possible effects of pH of the aqueous phase during hydrothermal treatment on formation of nanocrystalline zinc ferrite phase in Dowex, pH of the aqueous phase was lowered progressively from pH14 to pH10. It was shown that a single zinc ferrite phase of nanocrystallinity was established at pH14 (Figure 3). However, lowering in pH adversely affected formation of zinc ferrite nanoparticles in Dowex. At pH 10 for example, no detectable crystalline phases were established. The nanohybrid derived from pH 13 consisted of nanocrystalline zinc ferrite particles, however together with $\alpha\text{-Fe}_2\text{O}_3$ as an impurity phase. Phases present in the nanohybrids derived from pH14, pH13 and pH10 are also supported by their magnetization behaviors. Figure 4 plots the magnetization as a function of applied magnetic field up to 3 Tesla for the nanohybrids derived from pH14, pH13 and pH10, respectively. The sample derived from pH 14 exhibits a magnetic moment of 1.52 emu/g at an applied field of 3 Tesla at room temperature, compared to 0.82 emu/g for the nanohybrid synthesized at pH 13 with the present of $\alpha\text{-Fe}_2\text{O}_3$. Their magnetization increases rapidly at low field, followed by a more or less linear rise with no saturation at 3 Tesla. The much enhanced magnetic moment for the sample synthesized at pH14 is

attributed to the well established crystallinity of spinel structure for the nanocrystalline zinc ferrite particles, as indicated by FWHM of (311) peak, which is 1.31° , compared to 1.68° for the sample derived from pH13. It is known that cation distribution in nanocrystalline zinc ferrite particles can be significantly different from that of their bulk counterparts [3, 19]. Partial cation inversion occurring in zinc ferrite nanoparticles can generate strong *A-B* interactions, leading to an unusually high magnetization and a ferrimagnetic behavior [8]. The unsaturated magnetization at high field is a result of superparamagnetism. It can be also due to the possible existence of a spin canted surface layer, which can give rise to high magnetic anisotropy as commonly observed in ultrafine ferrite particles [6-7]. The magnetic moment at 3 T calculated for single phase zinc ferrite, based on the 8.46% weight loading of zinc ferrite in Dowex, is 17.97 emu/g for the nanohybrids synthesized at pH 14. This value is comparable with the results measured for zinc ferrite nanoparticles [20]. However, it is not saturated and is very much dependent on the sizes of zinc ferrite nanoparticles. As expected, the nanohybrid synthesized at pH 10 shows no hysteresis loop upon application of a magnetic field, where the magnetization increases linearly with increasing magnetic field, apparently due to the lack of any crystalline magnetic phase occurring in Dowex.

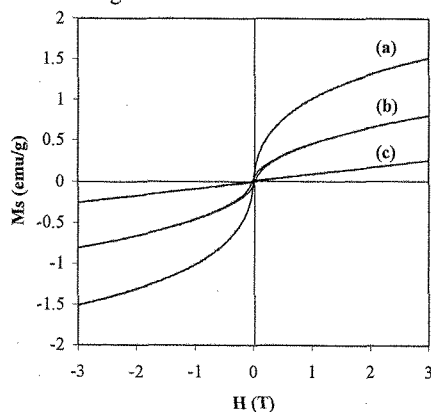


Fig.4 Magnetization curve for the hydrothermally treated nanohybrids derived from pH of (a) 14, (b) 13 and (c) 10, respectively.

4. CONCLUSION

Two types of nanohybrids containing Fe_3O_4 and zinc ferrite nanoparticles in polymer matrix (Dowex), respectively, have been successfully synthesized via ion exchange, without or with hydrothermal treatment. In the case of iron oxide, the nanoparticles formed in Dowex matrix were shown to be Fe_3O_4 , instead of $\gamma\text{-Fe}_2\text{O}_3$ as claimed by Ziolo et al in their paper published in Science [1]. This was confirmed using Raman, XRD and low temperature Mössbauer spectroscopy. In the case of the nanohybrids containing zinc ferrites, post hydrothermal treatment after ion exchange was employed to promote the crystallization of zinc ferrite nanoparticles, which were strongly affected by several synthesis parameters. A Zn/Fe ratio of as high as 1.5 was required in order to obtain nanocrystalline ZnFe_2O_4 particles by hydrothermal treatment at 150°C . A strong alkaline (pH14) condition was also necessary for

formation of a well established zinc ferrite phase. The magnetic properties of the nanohybrids thus synthesized are strongly dependent on the nanocrystalline phase formed in Dowex matrix at different pH values, where the nanohybrid synthesized at pH14 containing zinc ferrite as the only nanocrystalline phase exhibits a magnetic moment of 1.52 emu/g at 3 Tesla, compared to 0.82 emu/g for the nanohybrid synthesized at pH13 with the present of $\alpha\text{-Fe}_2\text{O}_3$.

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