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Research Article

Clarification of the Magnetocapacitance Mechanism for Fe_3O_4-PDMS Nanocomposites

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We mainly focused on the magnetocapacitance effect of Fe_3O_4-PDMS nanocomposites. We also proposed the preparation method and measured microstructures, magnetic properties, and magnetocapacitance value of the nanocomposites. The magnetocapacitance measurement results show that the nanocomposites have magnetocapacitance property, the magnetocapacitance with magnetic field depends on the magnetic property, and the value at the same magnetic field is increasing with the volume fraction of Fe_3O_4 nanoparticles. The magnetocapacitance model is proposed to explain this phenomenon by analyzing the magnetic interaction between particles and the viscoelasticity of PDMS. We also calculated the theoretical capacitance value of all samples using the magnetization of nanoparticles and mechanical parameters of PDMS. From the theoretical values, it is concluded that the model we proposed can well explain the magnetocapacitance effect of Fe_3O_4-PDMS nanocomposites.

1. Introduction

Materials with magnetocapacitance effect are promising for advanced applications in magnetic field sensors, data storage, and microwave communication devices [1–3]. Currently, main attention has been paid to the magnetocapacitance composites with magnetoelectric coupling, which consist of piezoelectric phase and piezomagnetic or magnetostrictive phase, such as CFMO-PBT, CFO-KNN, and Terfenol-D-PZT [4–9]. Recently, magnetocapacitance nanocomposites without magnetoelectric coupling composed of magnetic nanoparticles and polymer have also been reported [10, 11]. However, most of the studies on the composite have focused on the magnetocapacitance effect at radio frequencies [12] and the variation of magnetocapacitance with magnetic field at lower frequency electric field and the mechanism of magnetocapacitance effect are rarely discussed. Further, this magnetocapacitance effect is very significant for designing magnetic field sensors and actuators with novel mechanism.

Fe_3O_4 nanoparticles have wide applications because of their good electrical and magnetic characteristics, such as drug delivery and magnetic resonance imaging (MRI) [13, 14]. There are also plenty of studies on synthesis and properties of the particles in recent papers [15–17]. Polydimethylsiloxane (PDMS) is mainly used in microfluidic devices due to its biocompatibility and easy fabrication [18, 19]. Recently, researchers also have reported conducting property of the composites with PDMS and silver or carbon nanoparticles [20–22].

In this study, we investigated the magnetocapacitance effect of Fe_3O_4 nanoparticles-PDMS composite at lower frequency (200 kHz). Firstly, the composite preparation method is introduced, and samples with different volume fraction of nanoparticles are prepared. Then. the variation of the composite magnetocapacitance dependence of magnetic field is studied. Finally, the model of composite magnetocapacitance effect is also analyzed.

Table 1: Experimental compositions and volume fractions of nanoparticles.

Sample number	Fe_3O_4 particle size (nm)	Particle content (vol%)
1	200	20
2	200	17
3	200	13
4	200	9
5	200	5
6 (Pure PDMS)	—	—

2. Experimental Section

In this experiment, Fe_3O_4 particles (200 nm, 99%) were used (Beijing DK Nanotechnology, china). Sylgard 184 Silicone from (Dow Corning, MI, USA) was chosen as PDMS polymer matrix. All materials were used as received.

The preparation procedure of Fe_3O_4-PDMS nanocomposite was as follows. First, Fe_3O_4 particles were weighted and mixed with alcohol, and then the suspension was sonicated for about 10 min. Amount of PDMS was added to the suspension. After a stirring of about 15 min, the mixture was dried at 100°C for 1 h in a vacuum for evaporating all alcohol. The curing agent was added with the ratio of 10 : 1 of PDMS to curing agent and stirred for 10 min. The prepolymer mixture was dropped into a square module with a size of 15 mm × 15 mm × 1.5 mm, degassed at ambient temperature under vacuum for 30 min to remove any air bubbles, and then cured for 2 h at 90°C in air atmosphere. After curing, the nanocomposite film was peeled off from the module. The detail experimental compositions are shown in Table 1.

Microstructures of the prepared samples were examined by scanning electron microscope (SEM, Quanta 250 FEG). Magnetic properties of particles and nanocomposites were investigated using superconducting quantum interference device (SQUID, MPMS-XL-7) magnetometry. Elastic modulus of PDMS was measured by dynamic thermomechanical analysis (DMA, SDTA861e) at ambient temperature. In order to determine the magnetocapacitance properties of the nanocomposite, the film samples were fabricated to be parallel plate capacitor with copper electrode and shielding shell. The magnetic field dependence of the capacitance was measured in the magnetic field range of −10 Gs to 10 Gs at the frequency of 200 kHz using an Agilent high-precision LCR meter (HP4284A). The magnetic field was applied by electromagnet (EMP3, East Changing Technologies). The scheme of the experimental setup is depicted in Figure 1.

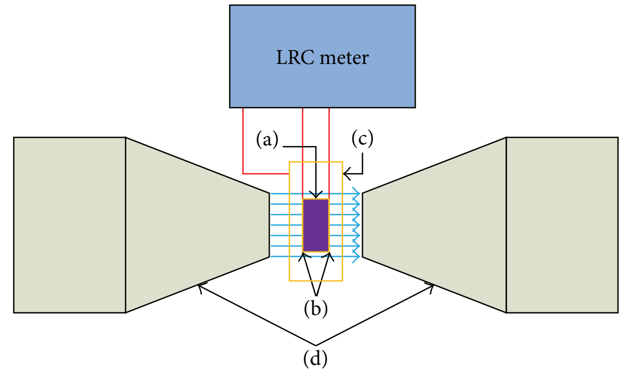

Figure 1: The scheme of the experimental setup: (a) nanocomposite; (b) Cu electrode; (c) Cu shielding shell; (d) electromagnet.

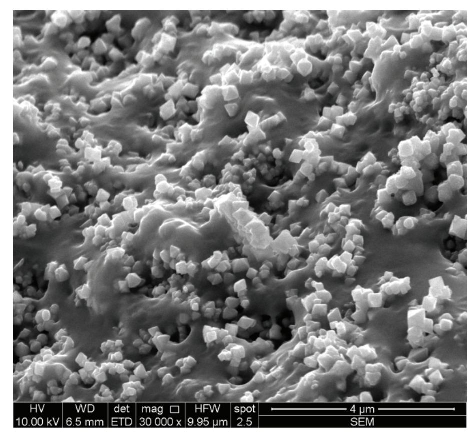

Figure 2: Scanning electron microscope (SEM) photographs of sample number 1.

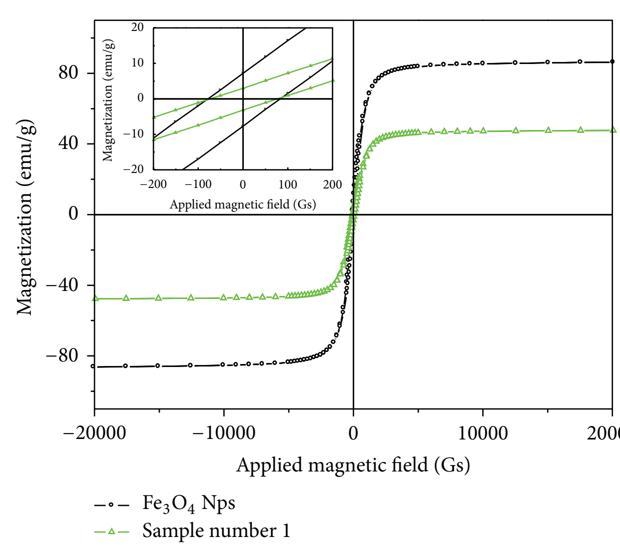

Figure 3: Variation of magnetization with applied magnetic field for 200 nm Fe_3O_4 nanoparticles (Nps) and sample number 1 at ambient temperature.

3. Results and Discussion

3.1. The Characterizations of Fe_3O_4 Particles and Fe_3O_4-PDMS Nanocomposites. The SEM micrographs of sample number 1 are shown in Figure 2. The particles are equally distributed in the composite materials with the average size of 200 nm. Figure 3 shows magnetization at the room temperature as a

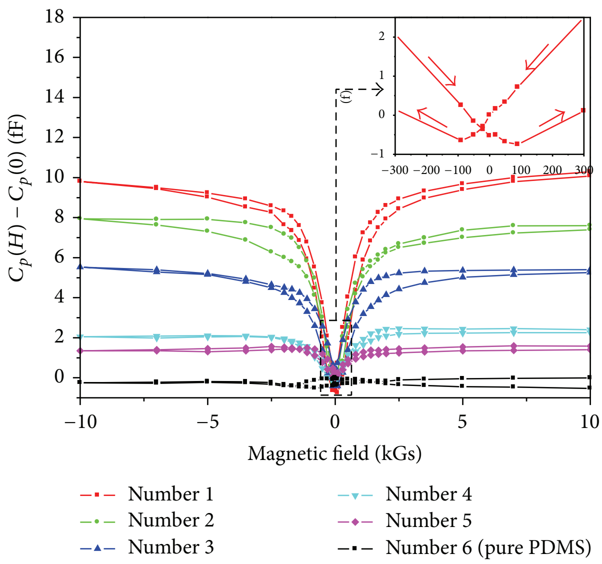

FIGURE 4: Variation of magnetocapacitance with applied magnetic field for all samples. Inset: an amplification of the curve for sample number 1.

function of applied magnetic field for 200 nm Fe_3O_4 nanoparticles and sample number 1. There is hysteresis present for Nps and nanocomposites with the same coercivity of 90 Oe, which is consistent with ferrimagnetic behavior. When the magnetic field exceeds 2 kGs, their magnetization would be saturated. However, the magnetic permeability and the saturation magnetization of the nanocomposites are smaller than that of the particles, because there is nonmagnetic material in the nanocomposites. Therefore, we can conclude that the magnetic properties of magnetocapacitance nanocomposites depend on the magnetic properties of magnetic nanoparticles in the nanocomposites.

3.2. Magnetocapacitance Properties of the Fe_3O_4-PDMS Nanocomposites. For analyzing the magnetocapacitance effect of nanocomposite, we have measured the magnetic field dependences of the capacitance of all samples at the frequency of 200 kHz. During the measurements, the magnetic field and the electric field are parallel. At one measurement, the magnetic field starts at 10 kGs and gradually decreases to −10 kGs (defined as decreasing cycle) and then gradually increases to 10 kGs back (defined as increasing cycle).

Figure 4 shows the variation of difference capacitance with applied magnetic field. The magnetocapacitance (MC) effect is defined as [Cp(H) − Cp(0)], where Cp(H) and Cp(0) are the capacitance at magnetic field H and zero field. Here, magnetocapacitance was found to increase with increasing the magnetic field for all samples, which illustrates that Fe_3O_4-PDMS nanocomposites have magnetocapacitance property. The sample with higher volume fraction of nanoparticles has bigger magnetocapacitance, and the magnetocapacitance effect was not observed in the sample of pure PDMS. When the magnetic field exceeds 2 kGs, the magnetocapacitance of all samples would be saturated. It can be seen from the inset of Figure 4 that the magnetocapacitance of the composite did not reach the minimum at zero field, but the magnetocapacitance minimum is at −90 Gs when the magnetic field decreases from 10 kGs to −10 kGs and is also at 90 Gs when the magnetic field increases from −10 kGs to 10 kGs. It can be seen that the magnetocapacitance effect for nanocomposite with magnetic field is similar to that for nanoparticles.

3.3. The Magnetocapacitance Effect Mechanism of Fe_3O_4-PDMS Nanocomposite. The capacitance dependence of the magnetic field is mainly induced by the magnetostriction effect of Fe_3O_4-PDMS nanocomposite. We assumed that the particles are completely equally distributed in the composites. When the magnetic field is applied to the composites, the arrangement of particles and the attraction between particles are directed along magnetic field vector. Because of the similarity between the magnetic nanoparticles and the magnetic dipole, the strength of the magnetic attraction force is given by

$$F = -\frac{3\mu_0 m^2}{2\pi r^4}, \qquad m = \frac{4}{3}\pi a^3 B. \tag{1}$$

Here, r is the distance between the two particles dipole, a is the radius of the particle, B is the magnetic induction of the particle, and μ_0 is the permeability of vacuum.

Due to the viscoelasticity of PDMS which is the matrix of the nanocomposite, the motion of particles in the composites induced by applied magnetic field depends on elastic force, viscous force of PDMS, and the attraction force between two adjacent particles. The viscoelasticity of PDMS can be depicted as Kelvin model which contains parallel spring and damper. The particles are supposed as spherical. According to Stokes Law, the motion of dipoles with magnetic field can be described as follows:

$$m_p \frac{d^2 r}{dt^2} + 6\pi\eta a \frac{dr}{dt} + \pi a^2 E \frac{r-\delta}{\delta} = -\frac{8\pi\mu_0 a^6 B^2}{3r^4}, \tag{2}$$

in which m_p, η, E, δ, and r are the mass of one particle, the viscosity of PDMS, the elasticity modulus of PDMS, the mean mutual distance between the two adjacent particles at zero field, and the distance between the two neighboring particles with applying magnetic field in the direction of magnetic field, respectively.

If the particles are completely equally distributed in the composites, the mean mutual distance between the two adjacent particles at zero field is given by

$$\delta = \sqrt[3]{\frac{Lld_0}{n}} = \sqrt[3]{\frac{4\pi}{3\Phi}}a, \qquad n = \frac{Lld_0\Phi}{(4/3)\pi a^3}, \tag{3}$$

in which L is the length of the sample, l is the width of the sample, d_0 is the thickness of the sample at zero field, Φ is the volume fraction of the nanoparticles, and n is the number of particles in the sample.

The distance r can be defined as

$$r = \delta + \Delta, \tag{4}$$

in which Δ is the distance variation between particles induced by applied magnetic field.

Therefore, (2) can be rewritten as follows by substituting (4) for r in (2):

$$m_p \frac{d^2\Delta}{dt^2} + 6\pi\eta a \frac{d\Delta}{dt} + \pi a^2 E \frac{\Delta}{\delta} = -\frac{8\pi\mu_0 a^6 B^2}{3(\delta + \Delta)^4}. \tag{5}$$

It is known that $m_p \approx 2.09 \times 10^{-17}$ kg and the first term of (5) becomes negligible with respect to the others. For simplifying (5), we use Taylor expansion method to rewrite the right part of the equation. The variation distance Δ is small enough to make the higher order Taylor expansion terms be also negligible. Accordingly, (5) becomes

$$6\pi\eta a \frac{d\Delta}{dt} + \pi a^2 E \frac{\Delta}{\delta} \approx -\frac{8\pi\mu_0 a^6 B^2}{3} \left(\frac{1}{\delta^4} - \frac{4}{\delta^5}\Delta\right). \tag{6}$$

If a stable compressive stress is applied, the variation of the strain with time for PDMS has the creep property and Δ is given by

$$\Delta = 0 \quad (t = 0;\ B \neq 0). \tag{7}$$

Using the initial condition (7), the solution of (6) becomes

$$\Delta = \frac{8\mu_0 a^4 B^2 \delta}{32\mu_0 a^4 B^2 - 3E\delta^4} \left(1 - e^{((32\mu_0 a^5 B^2 - 3aE\delta^4)/18\eta\delta^5)t}\right). \tag{8}$$

The number of each chained particle directed along the magnetic field on the sample thickness can be calculated by

$$n_d = \frac{d_0}{\delta}. \tag{9}$$

When $t \neq 0$, $B \neq 0$, the thickness of the sample d can be approximated as

$$d = (n_d - 1)(\delta + \Delta) \cong d_0 \left(1 + \frac{\Delta}{\delta}\right) \quad \text{for } n_d \gg 1. \tag{10}$$

On the other hand, the capacitance of the sample is

$$C = \varepsilon_0 \varepsilon_r \frac{Ll}{d} = \varepsilon_0 \varepsilon_r \frac{Ll}{d_0} \left(\frac{\delta}{\delta + \Delta}\right), \tag{11}$$

where ε_0 is the dielectrical permittivity of the vacuum and ε_r is the relative permittivity of sample.

When the magnetization of the particles is zero, the capacity of the sample is

$$C_0 = \varepsilon_0 \varepsilon_r \frac{Ll}{d_0}. \tag{12}$$

Equation (13) describing the variation of the capacitance of the sample with the magnetization of particles and time of magnetic field can be obtained by substituting (8) and (11) into (12), as follows:

$$\begin{aligned} C &= C_0 \left(\frac{\delta}{\delta + \Delta}\right) \\ &= C_0 \left(\left(32\mu_0 B^2 - 3E\left(\frac{4\pi}{3\Phi}\right)^{4/3} \right) \right. \\ &\quad \times \left(40\mu_0 B^2 - 3E\left(\frac{4\pi}{3\Phi}\right)^{4/3} \right. \\ &\quad \left.\left. - 8\mu_0 B^2 e^{((32\mu_0 B^2 - 3E(4\pi/3\Phi)^{4/3})/18\eta(4\pi/3\Phi)^{5/3})t} \right)^{-1} \right). \end{aligned} \tag{13}$$

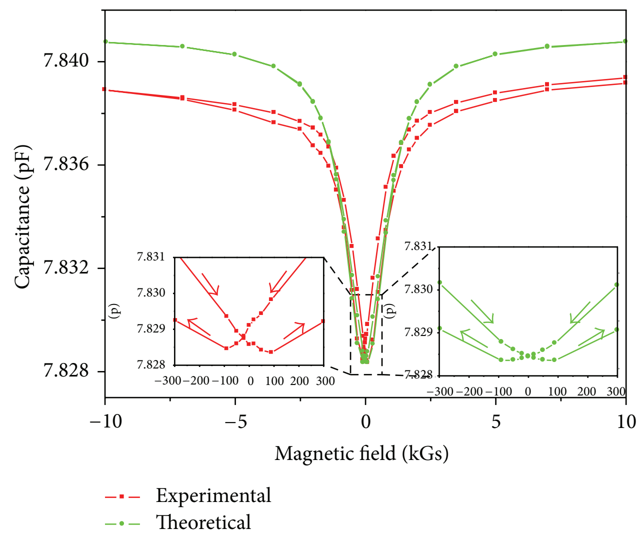

Figure 5: Variation of experimental and theoretical capacitance with magnetic field for sample number 1. Left inset: an amplification of experimental data. Right inset: an amplification of theoretical data.

Therefore, we can conclude from (13) that the magneto-capacitance variation of nanocomposites with magnetic field depends on the elastic module and the viscosity of PDMS; it also depends on the magnetic property and the volume fraction of nanoparticles.

We can know that elastic modulus of PDMS is 6.72 Mpa and viscosity is 5.09×10^3 Pa·s by using DMA. We can also obtain the magnetic induction B of nanoparticles at different magnetic field from the hysteresis loop of nanoparticles in Figure 3. Accordingly, we can calculate the capacitance of the samples with different volume fraction of nanoparticles at $t = 10$ s by using (13). Figure 5 shows the variation of experimental and calculated capacitance value with magnetic field for sample number 1. Figure 6 shows the variation of calculated magnetocapacitance with applied magnetic field for samples with various volume fractions. It is clear from these figures that the variation of experimental and calculated capacitance value with magnetic field has the same characteristic and the deviation between the experimental

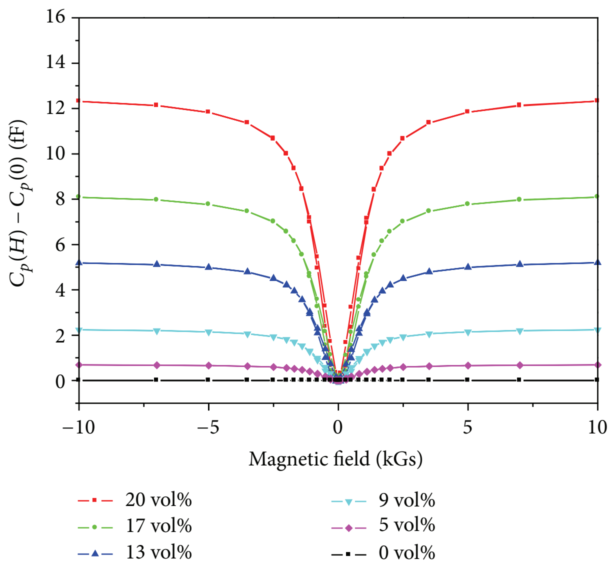

FIGURE 6: Variation of calculated magnetocapacitance with applied magnetic field for samples with various volume fraction.

and calculated capacitance value is smaller, which is caused by the unknown measurement errors. In conclusion, the proposed model can describe the magnetocapacitance effect of Fe_3O_4-PDMS nanocomposites well.

4. Conclusions

In this paper, Fe_3O_4-PDMS nanocomposites are prepared. The morphology characteristics, magnetic property, and magnetocapacitance effect are investigated. By analyzing the viscoelasticity of PDMS and the magnetic interaction between particles, the magnetocapacitance model of nanocomposites is also proposed. The particles are equally distributed in the composite materials with the average size of 200 nm. The magnetic properties of nanocomposites depend on the magnetic properties of nanoparticles. The magnetocapacitance effects of nanocomposites are observed. The velocity, hysteresis, and saturation value of the variation of the magnetocapacitance with applied magnetic field depend on the magnetic property and the volume fraction of Fe_3O_4 nanoparticles. The magnetocapacitance model shows that the variation of magnetocapacitance also depends on the elastic module and the viscosity of PDMS. By comparing the calculated value with experimental value, we demonstrate that the model can well explain the magnetocapacitance effect in Fe_3O_4-PDMS nanocomposites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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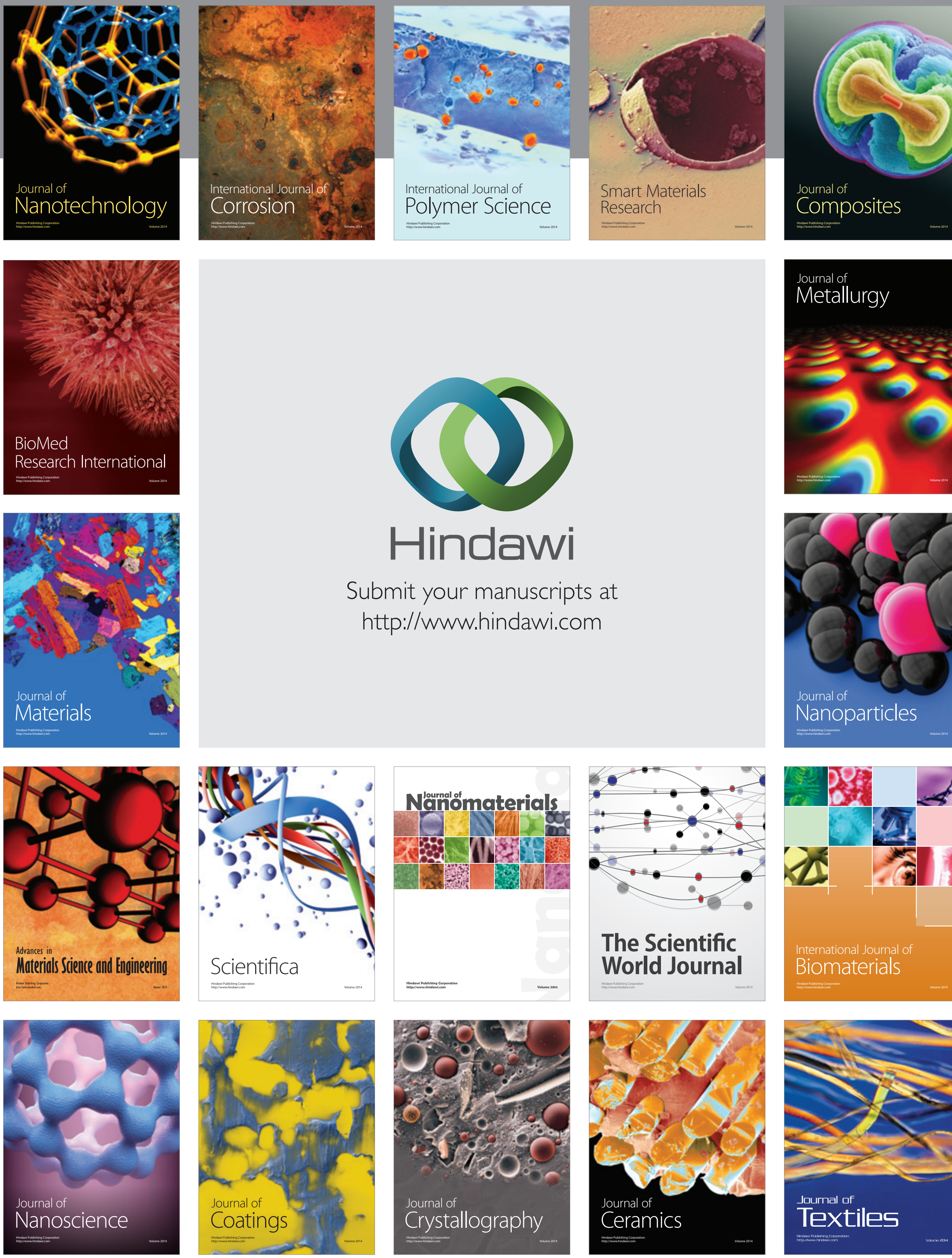
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