

Preparation, microstructure and electrorheological property of nano-sized TiO₂ particle materials doped with metal oxides

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Abstract New nano-sized TiO₂ electrorheological (ER) materials doped with different metal (M = Na, Zr, Ce, Al, Ca, Zn) oxides have been prepared. Relationships between the composition, microstructure, conductivity, dielectric property and ER effect of these materials have been studied. The results show that doping Na₂O, ZrO₂, Al₂O₃ or CeO₂ can enhance the ER performance of the TiO₂ material, whereas, doping CaO or ZnO would decrease the ER activity of the material. The shear stress (τ_E) of the suspension (25 wt%) of Na-doped TiO₂ in dimethyl silicone oil reaches 1.6 kPa at the electric field strength $E = 4.2$ kV/mm and shear rate $\dot{\gamma} = 300$ s⁻¹, and its τ_r value of 54.6 ($\tau_r = \tau_E/\tau_0$, where τ_0 is the shear stress at no electric field) is seven times higher than that of pure TiO₂ suspension. This high τ_r value is very advantageous to the use. The dielectric loss tangent ($\tan\delta$) plays a dominant role in influencing the ER performance of a particle material, and the effect of the surface area (pore volume, especially) and grain size should be taken into account.

Introduction

Electrorheological (ER) fluid is a special type of suspension, in which the dispersed particles would be polarized and attracted to each other to form a chain structure, which would make an ER fluid increase its viscosity under an applied electric field; however, the viscosity change of an ER fluid is reversible upon removal of the applied electric field [1, 2]. Because of their reversible and quick response to external electric fields, ER fluids have attracted much interest for their applications in various mechanical devices, such as clutches, valves, damping devices, etc. [3–5]. However, ER fluids have not been widely utilized because their ER effect is not strong enough to meet the requirements of most of these applications. The mechanism of the ER effect has been intensively discussed in many articles in an effort to obtain better ER materials. Hao [6] has proposed a dielectric loss model, and indicated that both ER and non-ER particles could be polarized under an electric field, and in this process, the particle dielectric constant is dominant. After the particle polarization, the ER particles could re-orientate along the electric field direction and build fibrillated bridges between two electrodes, determined by the particle dielectric loss; the non-ER particles, however, are incapable of doing so. This is probably because the ER particles, which have a large dielectric loss tangent, could generate a large amount of bounded surface charge. Hao and his co-workers [7] have demonstrated that interfacial polarization, rather than other types of polarization, would contribute to the ER effect of the materials. The material, which has a large dielectric loss, could give a large interfacial polarization once it is dispersed into a liquid, namely, a large dielectric loss is required for a good ER material.

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Table 1 Composition and characteristic of samples 1–7

Sample No.	Composition	Surface area (m ² /g)	Pore volume (cm ³ /g)	Grain size (nm)	κ (s/m)	ϵ	$\tan\delta$
1	TiO ₂ + Na ₂ O	37.692	0.1370	14	9.75×10^{-05}	677	2.59
2	TiO ₂ + ZrO ₂	50.017	0.08240	11	1.60×10^{-07}	24.2	0.119
3	TiO ₂ + Al ₂ O ₃	61.268	0.09469	8	1.87×10^{-07}	19.4	0.074
4	TiO ₂ + CeO ₂	38.172	0.08013	11	8.60×10^{-08}	21.2	0.073
5	TiO ₂ + CaO	34.069	0.08743	16	9.07×10^{-08}	25.1	0.065
6	TiO ₂ + ZnO	3.568	0.007165	14	5.61×10^{-09}	13.7	0.0074
7	TiO ₂	5.409	0.02838	16	5.39×10^{-08}	13.5	0.072

It is well known that the microstructure, surface properties, and composition of the particles, which would influence the physical and chemical natures of a material, are essential to the dielectric and polarization properties of the material. Therefore, it is possible to modify a material's dielectric and polarization properties by adjusting the synthetic procedure such that an ER material having a desired microstructure and composition can be produced.

ER materials doped with metal oxide have been prepared and studied [8–14], showing that doping La₂O₃, CeO₂ or Cr₂O₃ in TiO₂ can enhance ER performance of TiO₂ particle material. Zhao and Yin [11] have attributed the ER effect improvement of doped TiO₂ to the modification of its dielectric and conduction properties, particularly the increase of dielectric loss and conductivity that come with doping rare earth elements, and the lattice distortion and defects may be responsible for the modification of the dielectric and conduction properties of TiO₂. Wu et al. [15] have investigated the ER properties of Sr and Ba-doped TiO₂ materials. However, up until now, no clear connection has been established between the ER activity of a material and its microstructure. Therefore, in order to gain a better understanding of the ER mechanism, and obtain suitable ER materials, it is critical to investigate the effect of composition and microstructure on the ER performance of a particle material.

Experimental

TiO₂ materials doped with different metal oxides have been synthesized by sol–gel methods. First, to add the ethanol solution of the metal nitrate (M = Zr, Ce, Al, Ca, Zn) or acetate (M = Na) into ethanol solutions containing tetrabutyl titanate with a M/Ti molar ratio of 0.1. After the transparent gels were formed at room temperature, they were then dried at 85–90 °C, and finally roasted for 8 h at 550 °C. Samples 1–6 were thus obtained. Pure TiO₂ material (sample 7) was prepared

by a procedure similar to the one mentioned above. The compositions of these samples are listed in Table 1.

All particle materials, after water removal, were mixed with dimethyl silicone oil under stirring and ultrasonically dispersing for 5 min to produce all the ER suspensions (25 wt%). The shear stresses and apparent viscosities of the ER suspensions were determined in electric fields (dc field) of different strengths (E) and at a shear rate ($\dot{\gamma}$) range of 0–300 s⁻¹ and 25 °C on a German Rotary Viscometer (Type HAAKE CV20).

Results and discussion

Figure 1 shows that the shear stresses of all samples are comparable without an electric field. However, the TiO₂ materials doped with different metal oxides exhibit various ER behaviors in an electric field. Comparing to pure TiO₂ (sample 7), the shear stresses of samples 1, 2, 3, 4 (doped with Na, Zr, Al, Ce, respectively) are higher, and that of samples 5 and 6

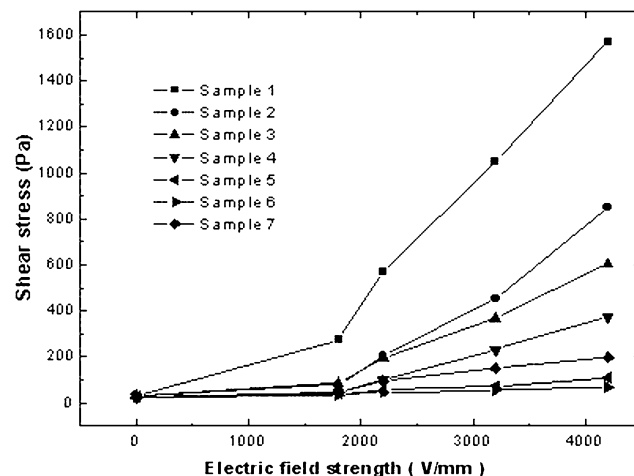


Fig. 1 Electric field strength dependence of shear stress for suspensions of samples 1–7 at $\dot{\gamma} = 300 \text{ s}^{-1}$

(doped with Ca, Zn, respectively) are lower. The suspension of sample 1 shows the highest shear stresses at $E > 0$ among these seven materials. These results indicate that doping Na_2O , ZrO_2 , Al_2O_3 or CeO_2 in the TiO_2 material can enhance the ER activity of the material, whereas, doping CaO or ZnO would weaken its ER activity, and doping Na_2O proves to be the most effective in improving the ER property of the TiO_2 material. The shear stress (τ_E) of sample 1 reaches 1.6 kPa at $E = 4.2$ kV/mm and $\gamma = 300$ s⁻¹, and its τ_r value of 54.6 ($\tau_r = \tau_E/\tau_0$, where τ_0 is the shear stress at no electric field) is seven times higher than that of pure TiO_2 suspension. In addition, the ER activity of sample 2 (doped with ZrO_2) is stronger than that of sample 3 (doped with Al_2O_3), and that of sample 4 (doped CeO_2) is weaker than that of sample 3. The difference between these materials in their ER performance can be ascribed to the difference in their conductivity, dielectric property and microstructure, which includes the surface area, pore volume and grain size of the particle material.

Figure 2 illustrates the X-ray diffraction (XRD) patterns of all materials that are obtained by roasting at 550 °C. It shows that the pure and doped TiO_2 particles only exhibit anatase phase (body-centered tetragonal crystal system and space group I41/amd, JCPDS No. 21-1272), and no independent phase from a doped metal oxide can be observed indicating that the metal oxide has entered into the TiO_2 crystal lattice. However, when compared to pure TiO_2 material (see Table 1), the average grain size of the particles decreases and the surface area and pore volume of the material increase with a metal oxide doping, except for doping ZnO or CaO , which can be a result of Ti^{4+}

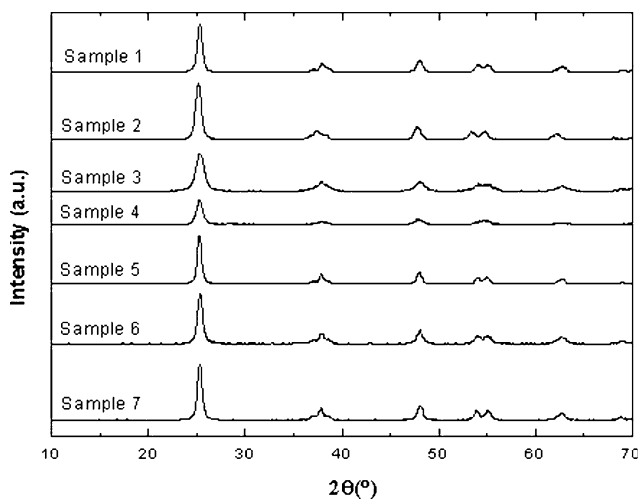


Fig. 2 XRD patterns of samples 1–7 (roasting temperature 550 °C)

ions substituted by metal ions causing lattice distortions and defects. Metal oxide doping is well known to not only cause lattice distortion, but also induce changes in the number of oxygen atom defects [16], both leading to the changes in the conductivity and dielectric property, and consequently inducing the change in the ER property of a material. Therefore, the change in the microstructure should be an important factor in influencing the ER property of the TiO_2 material.

Hao, Kawai and Ikazaki [7] have suggested that a large interfacial polarization would facilitate the particle to attain a large amount of charges on the surface, then lead to the turn of the particle along the direction of an electric field to form a fibrillation structure. At the same time, they indicated that if the particle surface charge density is d , its surface area is S , and the particle is uniform, then one single particle bounds charge $q_s = Sd = k_1E$, where E is the electric field strength, k_1 is a constant, $k_1 = S\epsilon_s/4\pi$, and ϵ_s is the static dielectric constant. Using this equation, one can estimate the critical (minimum) electric field strength required to drive a particle to turn. Therefore, the magnitude of the q_s value should be related to the ER effect. According to the equation, q_s would increase with the surface area S when both ϵ_s and E are kept constant. The surface area and pore volume of the particle materials, measured on an ASAP 2010 Accelerated Surface Area & Porosimetry made by the US Micromeritics Company, are listed in Table 1. Comparing samples 1–6 with sample 7, their surface area and pore volume are larger than those of sample 7, except for sample 6. Based on the observed ER performance mentioned above, we can speculate that larger surface area and pore volume are advantageous for enhancing the ER activity of a material. However, the ER activity of sample 5 is weaker than that of sample 7, although its surface area and pore volume are larger than those of sample 7. This result should be attributed to its dielectric loss tangent ($\tan\delta$) being lower than that of sample 7 (see Table 1). That is to say, $\tan\delta$ is the more dominant factor, when compared to surface area and pore volume, in influencing the ER effect of a particle material.

The surface area of a particle material is related to its average grain sizes. The average grain sizes of the particle materials are estimated by applying the XRD line broadening analysis using the Scherrer formula [17], revealing the values ranging from 8 to 16 nm (see Table 1), thus the materials belong to nano-sized particle materials, and doping metal oxide, except for CaO , results in the decline of the grain sizes of TiO_2 materials. The TEM micrographs of the material

powders, determined on a JEM-200 CX electron microscope, indicate that the grain size (<10 nm) (Fig. 3b) of sample 3 (Al-doped TiO₂) is the least, that (ca. 20–30 nm) (Fig. 3c) of sample 7 (pure TiO₂) is the largest, that of sample 5 (Ca-doped TiO₂) is similar to sample 7, the TEM micrographs of samples 1, 2, 4 and 6 are approximative in the grain sizes exhibiting a

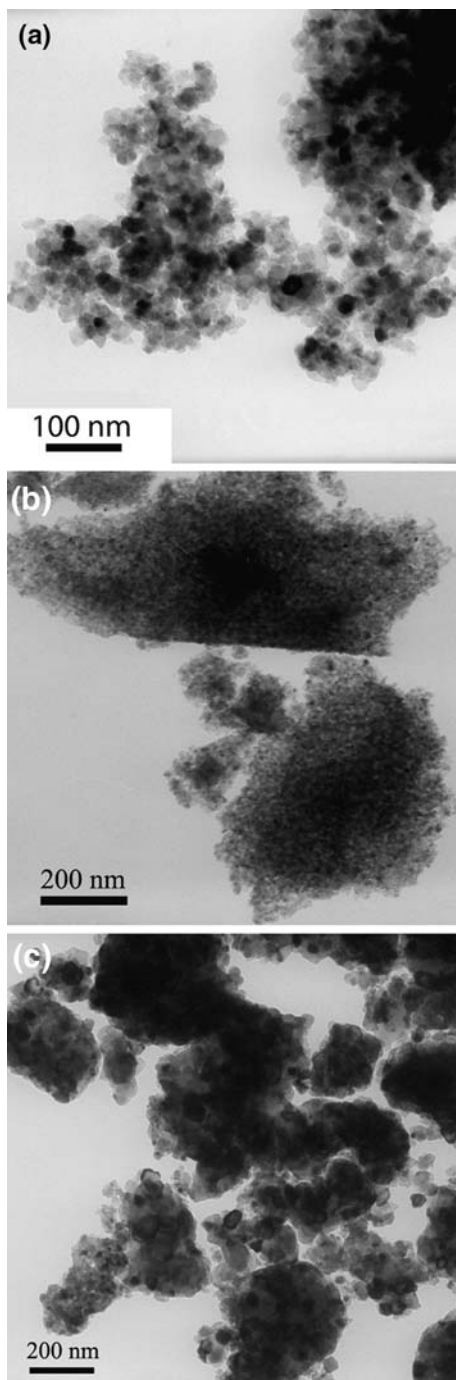


Fig. 3 The TEM micrographs of the powders of samples 1 (a), 3 (b) and 7 (c)

range of 10–20 nm, among these materials. Namely, in comparing the magnitude of the grain sizes between the particle materials, the result of TEM micrographs is consistent with that estimated by applying the XRD line broadening analysis. Therefore, the TEM micrographs of the powders of samples 1, 3 and 7 are chosen as representatives (see Fig. 3a, b, c, respectively).

Comparing the surface area and pore volume between samples 1–4, we can see that the surface area of the Zr, Al and Ce-doped materials is the larger than that of the Na-doped material, but their ER activity is lower than that of the Na-doped material. Such a phenomenon could be explained as follows: the value of the surface area given in Table 1 is the total area containing both the surface area of the grain and that of the pores in the grain; therefore, not only the smaller grain size, but also the larger pore volume, can enlarge the surface area of the particle material. The larger grain size of sample 1 makes its surface area smaller. It is well known that the Brownian motion tends to compete with particle fibrillation [5], as a result, larger grain size should be more beneficial in enhancing the ER performance of nano-sized particle materials; however, larger grain size would cause a decrease in the surface area of the particles, which may lead to lower ER activity, as mentioned above; therefore, larger pore volume (the surface area of the pore, essentially) would be required for a nano-sized particle material. The Na-doped material, which has the best ER performance, has the largest pore volume. Consequently, between surface area and pore volume, the later should be the more dominant factor in influencing the ER effect of a nano-sized particle material. Nonetheless, the larger grain size of sample 1 can also play a very important role contributing to its higher ER activity. In other words, the co-action of larger grain size and larger pore volume is critical for improving the ER property of a nano-sized particle material.

To compare the conductive and dielectric property of these materials, the dried powder (0.3 g) was dry-pressed at 6 MPa for 5 min to pellets of 8 × 2 mm in diameter and thickness, the capacitance (*C*), conductivity (κ) and dielectric loss tangent ($\tan\delta$) of the pellets were obtained on a HP4274A Multi-frequency LCR Meter at room temperature. The dielectric constant (ϵ) of the materials were derived from the measured *C* according to the conventional relation, $\epsilon = C(4\pi d)/S$, where *d* and *S* are the thickness and area of the pellet, respectively. The results (see Table 1) at 1 kHz indicate that the Na-doped material, the ER activity of which is the highest, exhibits the largest values of κ , ϵ and $\tan\delta$. Based on the ER effect mentioned above, the ER activities of these materials

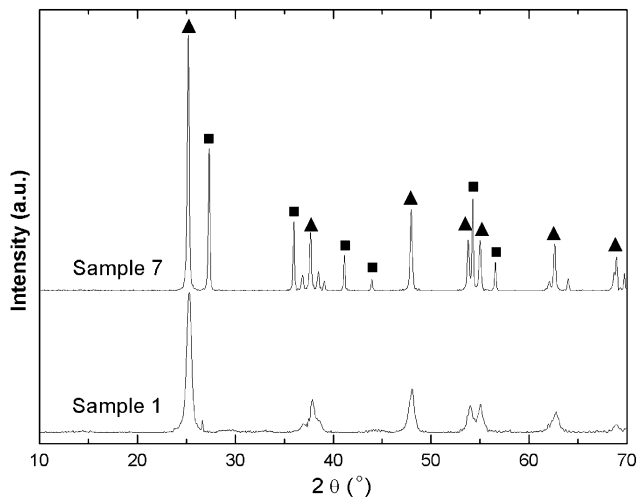


Fig. 4 XRD patterns of samples 1 and 7 (roasting temperature 570 °C) (▲ anatase titania, ■ rutile titania)

are found to decrease with decreasing $\tan\delta$ values. The ER activity of sample 3 (doped with Al_2O_3) is lower than that of sample 2 (doped with ZrO_2), even though its κ value is larger than that of sample 2, this can be a result of its smaller $\tan\delta$ and very small grain size. Doping CaO (sample 5) weakens the ER activity of the TiO_2 material, despite that the values of κ and ε of the material are larger, because doping CaO decreases the $\tan\delta$ of the TiO_2 material. The ER activity of the Zn-doped material is the lowest, its surface area, pore volume, κ and $\tan\delta$ all are the smallest, only the ε is slightly larger than that of pure TiO_2 material, among all materials. Hence, the experimental results on the electrorheological and dielectric properties of these materials show that $\tan\delta$ has a stronger impact on the ER effect of the material, and the above correlation found between $\tan\delta$ and the ER effect is consistent with the conclusion deduced by Hao et al. [7].

In addition, in previous investigation [18], we have found that anatase titania has better ER activity than rutile titania, and the ER activity of the material would lower with increasing rutile titania, when the TiO_2 is the substrate of an ER material. In order to know the stability of the materials in their crystal structure, the materials, which have been roasted at 550 °C as described above, are baked for 2 h at 570 °C, and then the crystal structures of samples 1 and 7 are studied. Their XRD patterns (see Fig. 4) have shown that: there are both anatase titania and rutile titania (the tetragonal crystal system and space group $P4_2/mnm$, JCPDS No. 21-1276) in the pure TiO_2 material (sample 7), however, there is only anatase titania in the

Na-doped material (sample 1). This result indicates that doping Na_2O not only can heighten ER activity of the TiO_2 material, but also can heighten its phase transformation temperature. The properties of the TiO_2 material doped with Na_2O in the ER effect and phase transformation temperature is very advantageous in the preparation and the use as an ER material.

Conclusion

The κ , ε , $\tan\delta$, surface area, pore volume and grain size are important factors in influencing the ER performance of a nano-sized particle material, and the impact of $\tan\delta$ is predominant. However, the effect of the surface area (the pore volume, especially) and grain size should also be taken into account; a small surface area or a very small grain size can be detrimental to the ER effect of nano-sized particle materials when different nano-sized materials have the same crystal structure type and similar particle compositions.

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