Synthesis and electrorheological effect of Cr doped TiO_2 nanorods with nanocavities in silicone oil suspensions

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Abstract. Titanium dioxide (TiO_2) nanorods with nanocavities doped with chromium (Cr) were synthesized by hydrothermal method. The morphology of prepared nanorods was determined by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX). The electrorheological (ER) behaviour of suspensions based on TiO_2 was investigated under the steady shear, and the yield stress was chosen as a suitable tool for a comparison of ER performance. Some optimum in level of Cr doping of TiO_2 was found.

1. Introduction

In principle, the semi-conducting particles dispersed in non-conducting liquid can be reversibly organised into the chain-like or columnar structures after the application of an external electric field. This electrorheological (ER) phenomenon which sets in the order of milliseconds is reflected in a dramatic change of the rheological properties and thus attracts considerable attention in both academic and technical fields since the pioneer study was presented by Winslow in 1947 [1–4].

For preparation of ER fluids, various materials including organic, inorganic or composite were employed [5–14]. Among them, suspensions based on titanium oxide (TiO_2) seem to be very promising mainly because of a relatively high ER performance. TiO_2 nanotubes were synthesized by hydrothermal synthesis in alkali solution and their ER properties in silicone oil suspensions were measured [15]. The ER behaviour of sea-urchin-like hierarchical doped with chromium (Cr) was also investigated [16]. TiO_2 particles coated with polyaniline and polypyrrole were synthesized and effect of coating on ER response was studied [17, 18]. In another study [19], positive influence of rare earth doping of TiO_2 particles on ER performance was pointed out. ER effect of TiO_2 particles doped with different elements was compared. Suspensions of TiO_2 particles doped with aluminium showed a shear modulus (G_0, $G_0^2 = G'^2 + G''^2$) of hundreds of kilopascals at electric field strengths $E = 3.0$ kV mm^{-1} [20].

In the present study, TiO_2 nanorods doped with Cr were synthesized as a novel material for ER fluids. Cr was doped into the particle structure, nanocavities, and oxidized at the surface by the annealing process.

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2. Experimental

2.1. Chemicals

For the preparation of the ER particles, TiO_2, P25 powder, sodium hydroxide (NaOH), hydrochloric acid (HCl) and hydrated chromium chloride ($CrCl_6.6H_2O$) were employed. All chemicals were used as received without any further purification.

2.2. Synthesis of Cr doped TiO_2 nanorods with nanocavities

The synthesis was carried out according to literature [21] with some modification. TiO_2 (0.75 g) was dissolved in 10 M NaOH (70 mL) and placed into 100 mL Teflon autoclave. A given amount of $CrCl_6.6H_2O$ was added during the mixing (for 5 min). The mixture was heated for 48 h at 180°C. Product was washed with HCl and distilled water to pH $\approx$ 7. Finally, TiO_2 nanoparticles were dried in an oven and annealed for 1 h at 650°C.

2.3. Structure characterization

The morphology of synthesized nanoparticles was characterized by scanning electron microscopy (SEM) VEGA II LMU (Tescan, Czech Republic) and transition electron microscopy (TEM) JEOL 1200 (JEOL, Japan). Elemental analysis was done by energy dispersive X-ray spectroscopy (EDX) using SEM VEGA II LMU (Tescan, Czech Republic).

2.4. Preparation of ER fluids and rheological measurements

ER fluids (5 wt.%) were prepared by mixing of Cr doped TiO_2 nanoparticles with corresponding amount of silicone oil (Fluid 200, Dow Corning, UK; viscosity $\eta = 100$ mPa s, density $\rho = 0.965$ g cm^{-3}). Rheological parameters were measured by means of a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) equipped with coaxial cylinders (14 mm and 15.4 mm in diameter) modified for ER measurements. The ER cell was connected to the DC high-voltage source TREK 668B (TREK, USA) providing the electric field strengths in the range of 0 – 3 kV mm^{-1}.

ER fluids were sonicated for 60 s before measurements. The built-up particulate structure (in the presence of electric field) was always destroyed by shearing at the shear rate 40 s^{-1} for 60 s in the absence of electric field. The temperature during all experiments was kept at 25 °C.

2.5. Dielectric measurements

Dielectric properties (the relative permittivity and the dielectric loss factor) of 5 wt. % suspensions were monitored using Impedance Material Analyzer Agilent 4294-A (Agilent, Japan) in frequency range of 50 Hz – 1 MHz.

3. Results and discussion

The morphologies of synthesized nanorods are presented in figure 1. SEM analysis shows rod-like structure and size of TiO_2 nanoparticles (figure 1a). The presence of small cavities in the surface of the nanorods was confirmed by TEM (figure 1b). According to literature [22], these cavities can be in the size of tens of nanometres (10 – 20 nm) in diameter with different structures – circular, hexagonal or rectangular.

The quantitative analysis of the TiO_2 nanorods performed by EDX confirmed the presence of Cr by two characteristic peaks at 5.40 and 5.95 keV (figure 2). These peaks result from energy emitted by the excited electrons during their return to the original level (stable state). The amount of energy depends on the difference between the energy levels inside the atoms.

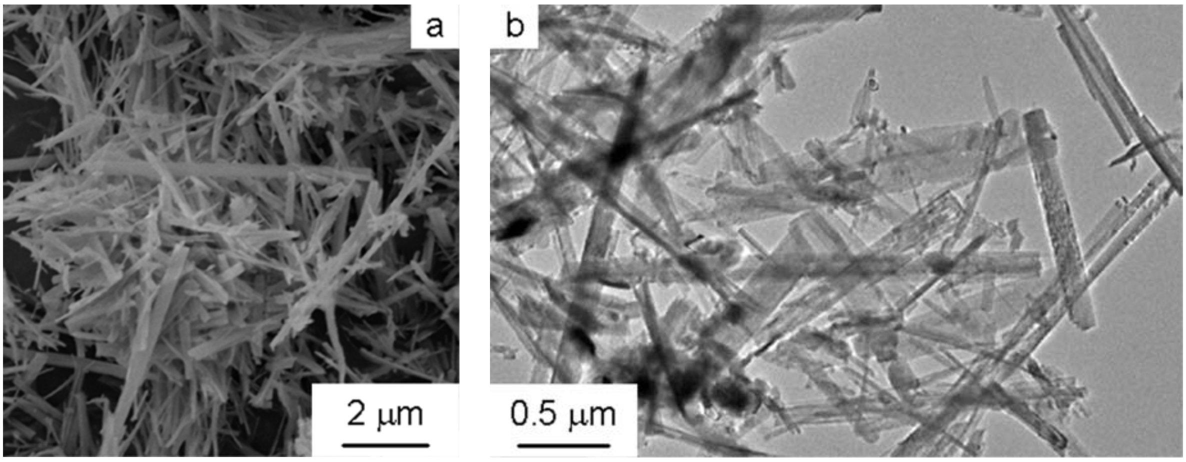

Figure 1. SEM image (a) of TiO_2 nanorods and TEM image (b) of 0.7 mol % Cr doped TiO_2 nanorods.

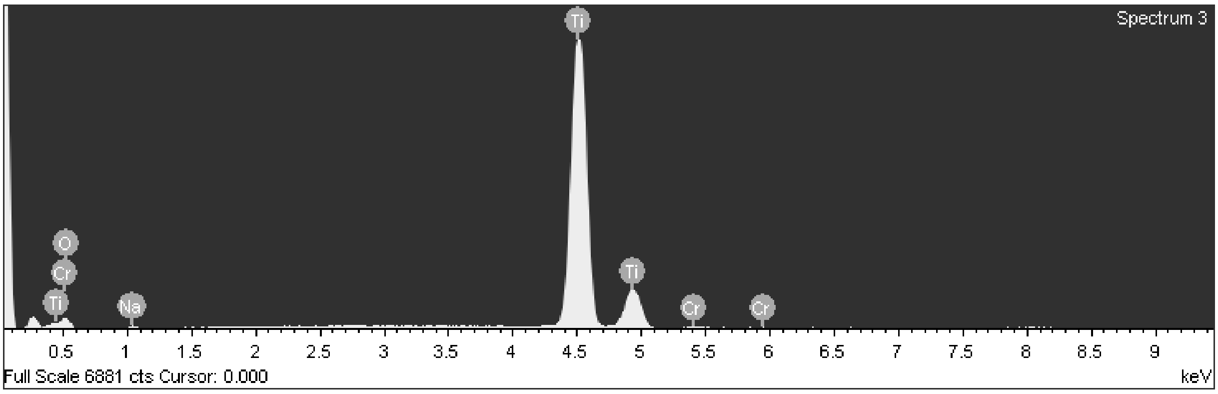

Figure 2. EDX analysis of 0.7 mol % Cr doped TiO_2 nanorods.

The stability of developed ER structures is moderated by reorganization and destruction of chain-like structures given by the competition between the electrostatic and the hydrodynamic interactions. The electrostatic interactions are responsible for the reorganization of polarized particles and hinder the flow, while the hydrodynamic interactions tend to destroy ER structures and promote flow.

Flow curves (the shear stress and the shear viscosity *vs*. the shear rate) of suspension (5 wt.%) prepared by dispersing TiO_2 nanorods doped with 0.7 mol% Cr in silicone oil are plotted in figure 3. In the absence of the electric field, suspension behaved almost as a Newtonian fluid. When the electric field was applied, the rheological behaviour dramatically changed as a result of particle chaining, especially at low shear rates. Higher intensity of the electric field was reflected in higher shear stress and higher viscosity corresponding to the stiffer ER structure. This suspension exhibited the strongest ER effect as will be discussed further.

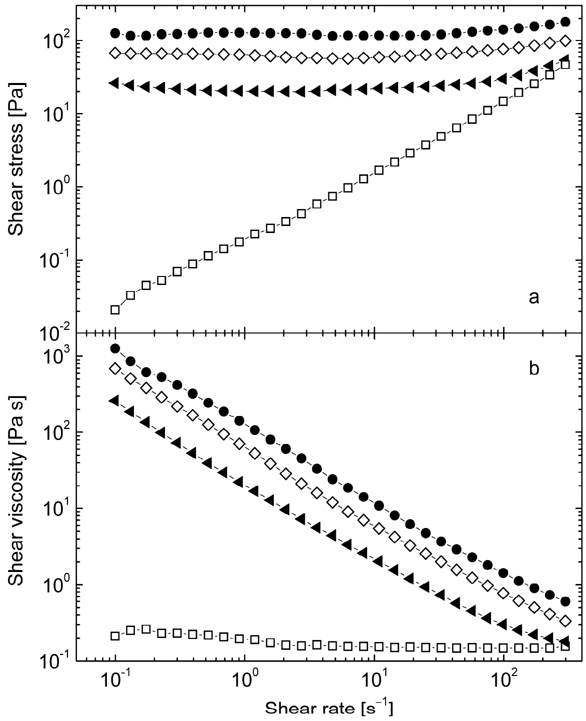

Figure 3. The shear stress (a) and the shear viscosity (b) *vs.* the shear rate dependence for 5 wt. % suspension of TiO_2 nanorods doped 0.7 mol % Cr in silicone at electric field strengths: (□) 0, (◀) 1, (◇) 2, and (●) 3 kV mm^{-1}.

Figure 4 shows the dependence of the yield stress of suspensions on Cr content (0 – 5 mol %) in doped TiO_2 nanorods at electric field strength 3 kV mm^{-1}. Evidently, very low content of Cr (0.7 mol %) in TiO_2 nanorods strongly supports ER effect and the maximal yield stress (130 Pa at 3 kV mm^{-1}) for 5 wt. % suspensions was observed. On the other hand, higher ratio Cr/TiO_2 results in a reduction of the yield stress because of increased conductivity of the TiO_2 nanorods doped to higher levels. As a consequence, the current density passing through ER suspensions increases and seems to be responsible for destroying of chain-like structure and thus significantly lower ER performance.

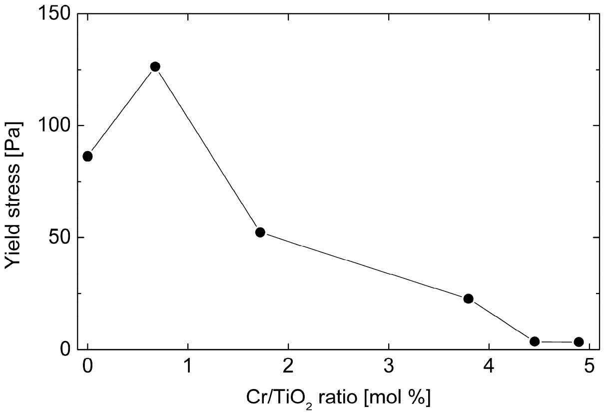

Figure 4. The yield stress of silicone oil suspensions (5 wt.%) *vs.* Cr content in doped TiO_2 nanorods at electric field strength 3 kV mm^{-1}.

The dielectric parameters of TiO_2 nanorods based suspensions were evaluated in the frequency range $10^2 – 10^6$ Hz. The relative permittivity and dielectric loss factor of the suspension with the highest ER effect are shown as an example in figure 5.

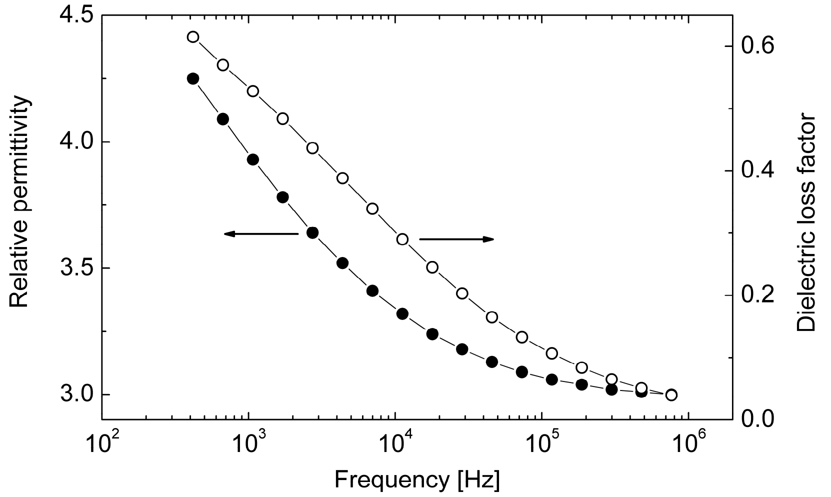

Figure 5. Dependence of the relative permittivity (●) and the dielectric loss factor (○) on the frequency for suspension of TiO_2 nanoparticle doped with 0.7 mol% Cr in silicone oil.

To obtain the ER effect, high polarizability (proposed as maximal difference in the relative permittivity approaching to zero and infinite frequency) as well as proper relaxation time (a reciprocal value of maximal frequency of dielectric loss factor) are necessary. Interfacial polarization showing relaxation maxima in the frequency range $10^2 – 10^5$ Hz was accepted as responsible for suitable ER activity [23].

4. Conclusions

TiO_2 nanorods doped with Cr in nanocavities were synthesized by solvothermal method for preparation of novel ER fluids. The influence of Cr amount on ER performance was investigated and optimum doping of TiO_2 nanorods with 0.7 mol % Cr was found. Higher or lower doping level resulted in low ER performance. Rather dilute suspension (5 wt. %) of TiO_2 nanorods doped with 0.7 mol% Cr in silicone oil showed interestingly large ER effect providing yield stress over 120 Pa.

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