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# Preparation and properties of red inorganic hollow nanospheres for electrophoretic display



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# ABSTRACT

An effective approach had been developed for the preparation of Fe-doped TiO<sub>2</sub> red hollow nanospheres *via* template method using PMMA-BA copolymers as the core template by a two-step hydrolysis process. The nanospheres were rarely displayed fragmentation and exhibited hollow structures with uniform size and shape. Then, the multicomponent Fe/Co/Al-doped TiO<sub>2</sub> hollow nanospheres were produced with Co and Al as tinting metal ions so as to endow them with higher color saturation and brightness. The average diameter of the hollow spheres coated with a layer of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was approximately 300 nm and the thickness of the layer was roughly 50 nm. The electrophoretic mobility and zeta potential of two kinds of hollow particles were about  $-1.0 \times 10^{-5}$  cm<sup>2</sup> v<sup>-1</sup> s<sup>-1</sup> and -100 mV, respectively. Finally, the electrophoretic inks prototype device was successfully assembled using dispersion of the obtained red hollow nanospheres in a mixed dielectric solvent with TiO<sub>2</sub> white particles as contrast. Under an applied bias voltage of 30 V, the response time of the simple EPD device was 1121 ms and the max contrast was 3.173, which had shown great potential for practical application in a vivid chromatic electrophoretic display.

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#### 1. Introduction

Electrophoretic display (EPD) was a reflective digital display [1], which was often considered to be suitable for reading because of its stable image, wide viewing angle, good contrast ratio and low power consumption [2–7]. Currently, one of the most common challenges for electrophoretic display techniques was the achievement of full-color e-paper [8]. Even though the RGB tricolor was achieved through the placement of a color filter array on the electrophoretic film, the color filter not only limited the brightness to less than a third of the incident light, it also sacrificed the saturation of the colors [9–11]. On the other hand, the control of electrophoresis rate [12–14] and a pixel composed of tricolor ink particles [15,16] were two promising approaches to achieve chromatic EPD. Hence, the preparation of tricolor electrophoretic particles, and the corresponding electronic ink with vivid color as well as good electrophoretic responses [17] were necessary and irreplaceable.

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http://dx.doi.org/10.1016/j.apsusc.2014.08.121 0169-4332/© 2014 Elsevier B.V. All rights reserved. Recently, as one of three primary colors, the red ink particles were commonly prepared employing the red pigments as a colorant. Kim et al. [18] and Lee et al. [19] encapsulated with copolymer using dispersion polymerization in the presence of red colored organic pigment. Guo et al. [20–22] presented a type of red encapsulated electronic ink prepared by in situ polymerization and pigment scarlet powders were modified with polyethylene to have superior affinity for tetrachloroethylene. However, organic pigments, as solid aggregates of colored molecules, also had the weakness in heat and solvent resistance, UV shielding properties and regular morphology. These might result in a reduced life time and lower contrast in the EPD.

The iron oxide red, as an inorganic pigment, seemed to be a suitable alternative to organic pigments due to its superior abilities in color properties, light stability and heat resistance [23]. Kang et al. [24] utilized inorganic pigments as electrophoretic particles, the surface of inorganic pigments were modified by the dispersion polymerization of MMA and EGDMA. The weakness in high density as colored electrophoretic particles limited their practical application, resulted in severe sedimentation and a slow response speed in dielectric media, and polymer coating on the pigments or polymer–pigment hybrid decreased the reflex light brightness and saturation. Hollow nanostructures could effectively overcome the disadvantages, prevent the nanoparticles from agglomeration

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500°C **PVP** FeCl<sub>3</sub>.6H<sub>2</sub>O 2h TBOT refluxing 600℃ 2h Red Hollow РММА-ВА PMMA-BA/TiO<sub>2</sub>/Fe(OH)<sub>3</sub> PMMA-BA/TiO, Particle **Core-shell Particle Hybrid Particle** Copolymer TiO<sub>2</sub> PMMA-BA Fe(OH)<sub>2</sub>  $\alpha$ -Fe<sub>2</sub>O<sub>2</sub>

Scheme 1. Preparation of red inorganic hollow nanoparticles.



Fig. 1. XRD of  $TiO_2$  hollow particles (a), Fe-doped  $TiO_2$  red hollow particles (b) and Fe/Co/Al-doped  $TiO_2$  red hollow particles (c).

and improve the stability of the particles in the electrophoretic dispersion because of its characteristics, such as a regular spherical structure, high surface-to-volume ratio, low coefficients of thermal expansion and a low refractive index [25,26]. Therefore, the preparation of inorganic pigment-based hollow particles offered some distinct advantages to fabricate full-color electrophoretic display which was uncommonly study.

In this paper, a general and facile method was developed to prepare inorganic pigment red hollow particles (Scheme 1) and the hollow particles were employed for electrophoretic display for the first time. The Fe-doped TiO<sub>2</sub> red hollow particles had been prepared through boiling hydrolysis process, in which PMMA-BA at TiO<sub>2</sub> core-shell nanoparticles were synthesized by a mixed-solvent method, and then mixed with metal oxide in the solution, followed by calcination in the atmosphere. Based on this method, multi-component Fe/Co/Al-doped TiO<sub>2</sub> red hollow particles with better brightness and saturation were also successfully prepared. Furthermore, the electrophoretic performance of the prepared hollow particles was evaluated by fabrication of red/white EPD prototype.

#### 2. Experimental

## 2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), titanium butyrate (TBT) and polyvinylpyrrolidone (PVP) were purchased from Guangfu Chemical Regent Company (Tianjin, China). 2,2'-Azobis(2-amidinopropane) hydrochloride (AIBA) was provided by Dupont Company (China). FeCl<sub>3</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, absolute ethanol, ammonia solution (28% by weight) were all supplied by the Tianjin Jiangtian Reagent Company (China). Isopar-L was purchased from Huishuo Chemical Co., Ltd. (Shanghai, China). TiO<sub>2</sub> was obtained from China New Materials Technology Co., Ltd.

#### 2.2. Synthesis of copolymer core

The cationic copolymer core was prepared *via* emulsifier-free emulsion polymerization, using the cationic initiator AIBA. Typically, after gentle stirring, MMA, BA, PVP, as well as 120.0 g of H<sub>2</sub>O were mixed into a 250 ml three-necked flask with a nitrogen gas inlet. After AIBA was added, the mixture was heated to 80 °C and was stirred for 12 h. The resulting copolymer template was recovered by centrifugation and washed with deionized water.

## 2.3. Preparation of copolymer core coated with titania

The coating reaction was processed in ethanol by hydrolyzing TBT in the presence of cationic copolymer spheres. 1.0 g copolymer was dispersed in 60 ml absolute ethanol and then 20 ml ethanol containing 0.5 g TBT was added rapidly. After 4 h, the particles were collected by centrifugation and washed several times with ethanol. Then the suspension of core-shell particles was freeze-dried.

#### 2.4. Preparation of red hollow particles

The monodisperse Fe-doped TiO<sub>2</sub> red hollow particles were prepared by using the process of boiling hydrolysis and the requisite metal salt was FeCl<sub>3</sub>·6H<sub>2</sub>O. The core–shell particles were dispersed in ethanol, and added to a certain amount of FeCl<sub>3</sub> solution of sulfuric acid. The dispersion was stirred at 60 °C for 30 min and then refluxed for 2 h. A uniform thin layer of Fe(OH)<sub>3</sub> was deposited on the surface of PMMA-BA/TiO<sub>2</sub> core–shell particles. The obtained product was dried at 60 °C for 8 h. Then the particles were placed in a muffle furnace and annealed at 500 °C for 2 h with a heating rate of 5 °C/min, then up to 600 °C for 2 h with a heating rate of 2 °C/min consequently.

The multicomponent Fe/Co/Al-doped TiO<sub>2</sub> red hollow particles were prepared through the same method. The requisite metal salts were FeCl<sub>3</sub>· $6H_2O$ , Co(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ , Al(NO<sub>3</sub>)<sub>3</sub>· $9H_2O$  and Fe:Co:Al molar ratio was 6:4:1.

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