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Preparation of the carbon sphere coated with iron oxide and its application for electronic paper

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ABSTRACT

Carbon sphere is a candidate for black pigment in electronic paper (ePaper) due to the fast and reliable response time based on narrow size distribution and spherical shape. However, its dark brown color, which reduces the contrast ratio between black and white pigments, needs to be manipulated. To overcome the poor blackness of the carbon sphere, iron oxide nanoparticles that have high blackness were coated on its surface. From a reflectance analysis, the increase of blackness was verified and was then optimized by controlling iron salts concentration. After fabricating the carbon sphere coated with iron oxide nanoparticle, 2-ethylhexyl acrylate (EHA, monomer) was grafted on the carbon sphere to match the density of that of tetrachloroethylene (TCE) for high dispersibility as well as bistability. This approach enables us to make the carbon sphere with narrow size distribution, high blackness, high dispersibility and bistability. A monochrome operation was successfully conducted with high contrast ratio and fast response time of 128.5 ms.

1. Introduction

Recently, the carbon sphere has been highlighted in various research fields because of its simple applicability. Similar to most carbon products, the carbon sphere is chemically inert and has high mechanical strength, good electrical conductivity, and a high surface area [1]. Furthermore, their intrinsic properties can be easily controlled by changing the production condition [2] or modifying the surface of the carbon sphere [3]. Owing to these merits, the carbon sphere has been applied to a catalyst support [4], an electrode material [5], an absorbent for water purification [6] and a pigment in an electronic paper (ePaper) [7].

In ePaper, the carbon black has been used as a popular black pigment because of low reflectivity and easy accessibility [8]. However, the broad size distribution caused by the non-uniform structure makes it difficult for the carbon black to have a reliable response time. Accordingly, it is difficult to ensure the pigment has a dependable dynamic characteristic using the carbon black. Thus, various approaches have been introduced to overcome the issue [9]. As a candidate, the carbon sphere is considered an alternative to carbon black due to its narrow size distribution and spherical shape [10]. Moreover, abundant functional groups on the surface of the carbon sphere facilitate the control of zeta potential and the density through surface modification. The zeta potential should be controlled for reliable and fast migration of the pigment by assigning uniform and high absolute surface charge onto the pigment, and the density needs to be modified during pigment preparation because the realized image could be sustained when the pigment density was matched with that of dielectric fluid. Thus, the carbon sphere, where zeta potential and density can be easily controlled, is promising as a pigment for ePaper. However, using the carbon sphere as the black pigment also has a disadvantage. The carbon sphere takes on a brown color. Intrinsically, the level of blackness of carbon sphere is insufficient for its use as a black pigment, as it decreases the contrast ratio between the carbon sphere and white pigments. To overcome the low blackness of carbon sphere, the color of carbon sphere should be manipulated.

One way to manipulate the color of carbon sphere is to attach nanoparticles to the surface. Depending on the type of nanoparticles, it could improve the blackness of the carbon sphere. Various metal oxide nanoparticles can be easily obtained and have their own color. Among them, Fe_3O_4 (magnetite) takes on a black color which could compensate the blackness of the carbon sphere [11]. Accordingly, Fe_3O_4 is a promising candidate to be investigated to increase the blackness of the carbon sphere.

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In this work, an iron oxide nanoparticle was introduced to provide the carbon spheres with a black color. The iron oxide nanoparticles were prepared through a co-precipitation of $FeCl_2$ and $FeCl_3$ [12], and the adsorption of iron oxide nanoparticles on the carbon sphere was controlled and optimized to give the carbon sphere a high blackness. In using the carbon sphere modified with iron oxide, the surface of the composite was grafted by polymerized 2-ethylhexyl acrylate (p-EHA) to match the density of the composite with that of TCE. Finally, the blackness and dynamic characteristic of the polymerized composite (CS/FEO/EHA) were investigated through a reflectance analysis and an electrophoretic migration test, respectively.

2. Experimental

2.1. Synthesis of carbon sphere

1.5 M (27 g) glucose solution was prepared as a carbon source, and a 100 ml capacity autoclave reactor was filled with the solution. The reactor was sealed and positioned in an oven heated to 160 °C. After 8 h reaction time, the reactor was transferred to the outside and cooled promptly at low temperature to suppress additional particle growth which could widen the size distribution [2].

2.2. Surface treatment of the carbon sphere

0.8 g of carbon sphere was dispersed in 200 ml of D.I. water, and 1.74 ml of 0.1 M 3-mercaptopropionic acid was added to the solution. The solution was sonicated for 2 h. After the sonication, the solution was centrifuged and supernatant fluid was drained. The solid product was rinsed with acetone, ethanol and D.I. water several times.

2.3. Iron oxide formation on the carbon sphere

2 mM of $FeCl_3 \cdot 6H_2O$, 1 mM of $FeCl_2 \cdot 4H_2O$ and 0.05 g of pretreated carbon sphere were dispersed in 10 ml D.I. water. The solution was purged with nitrogen for 30 min while stirring. 8 ml of 1 M TMAH (tetramethyl ammonium hydroxide) was added dropwise at the rate of 0.4 ml/min. After the addition of TMAH, the solution was further stirred for 12 min and centrifuged. The products were rinsed with D.I. water several times and redispersed in D.I. water for filtration [12]. To eliminate the homogeneously formed iron oxide, the dispersed solution was sonicated for 2 h then filtered using 200 nm pore size filter. The filtered particle was dried in a vacuum oven for 6 h.

2.4. Grafting polymerization

Grafting step: the carbon sphere coated with iron oxide, 0.2 ml hydrogen chloride and 0.10 g of 4-vinylaniline was dispersed in D.I. water for the grafting of polymer onto the composite pigment. The temperature of the solution was increased to 40 °C, and 0.174 g of sodium nitride dissolved in D.I. water was added for 10 min for the electrochemical reduction of diazonium salts. The solution was agitated for an additional 16 h. The product was centrifuged and rinsed with acetone several times. The rinsed products were dried in a vacuum oven for one day.

Polymerization step: the grafted composite pigment was dispersed in toluene, and 2-ethylhexyl acrylate was added as a monomer. The solution was purged with nitrogen for 20 min while stirring. Subsequently, 0.106 g of 2-2′-azoisobutyronitrile (AIBN) was added to initiate the polymerization at 70 °C. After the reaction was finished, acetone was added to eliminate the residual reactant,

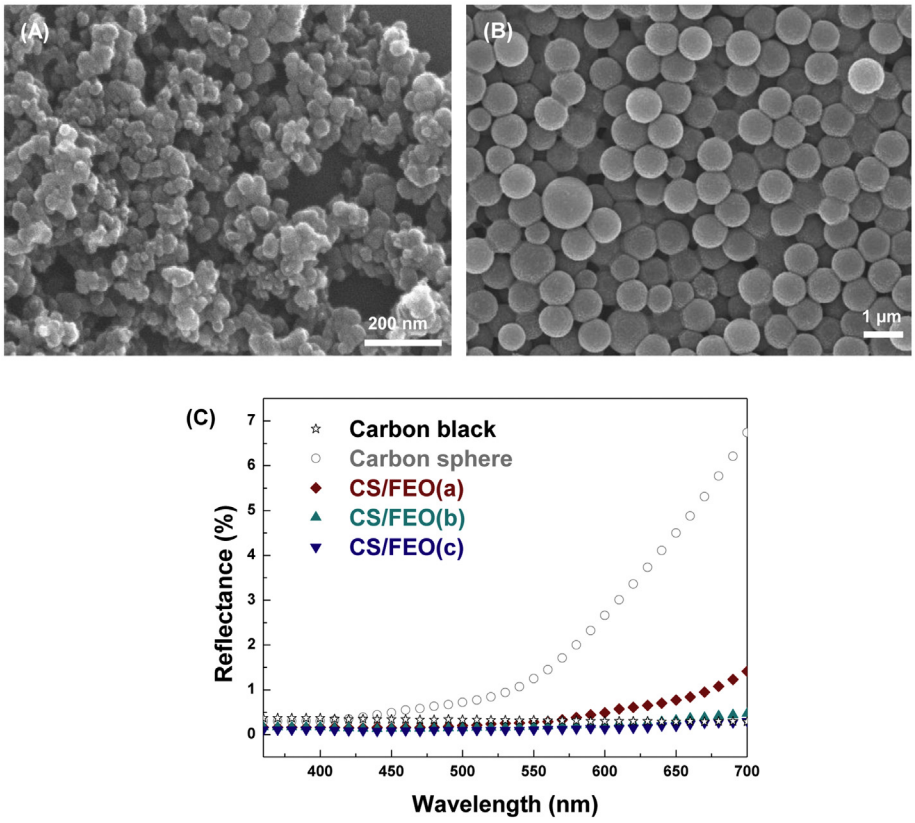

Fig. 1. FE-SEM images of (A) carbon black and (B) as-prepared carbon sphere, and (C) reflectance spectrum of the carbon black, the carbon sphere and CS/FEO composites made with (a) 2 mM $FeCl_3 \cdot 6H_2O$/1 mM $FeCl_2 \cdot 4H_2O$, (b) 1.5 mM $FeCl_3 \cdot 6H_2O$/0.75 mM $FeCl_2 \cdot 4H_2O$ and (c) 1 mM $FeCl_3 \cdot 6H_2O$/0.5 mM $FeCl_2 \cdot 4H_2O$ of iron salts concentration.