



## Carbon sphere as a black pigment for an electronic paper

Kang Uk Lee<sup>a</sup>, Kyung Ju Park<sup>a</sup>, Oh Joong Kwon<sup>b,\*</sup>, Jae Jeong Kim<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Biological Engineering, Institute of Chemical Process, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul 151-742, Republic of Korea

<sup>b</sup> Department of Energy and Chemical Engineering, University of Incheon, 12-1 Songdo-dong, Yeonsu-Gu, Incheon 406-772, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 15 June 2012

Received in revised form

25 August 2012

Accepted 7 September 2012

Available online 17 September 2012

#### Keywords:

Carbon sphere

Electronic paper

Grafting polymerization

Charge control agent

Zeta potential

Mobility

### ABSTRACT

Carbon black, a black material popular for use in electronic paper, could limit the performance of the electronic paper due to its non-uniform structure. Carbon spheres, with spherical shape and relatively narrow size distribution, are expected to overcome this limitation and substitute for carbon black in the electronic paper. Carbon spheres were synthesized through a hydrothermal reaction using glucose as a raw material. By controlling reaction time and glucose concentration, appropriate non-agglomerated carbon spheres with an average diameter of 202.26 ( $\pm 26.15$ ) nm were fabricated. To increase their dispersibility in dielectric fluid, *p*-(2-ethylhexyl acrylate) was grafted onto the surface of the carbon spheres. Then, acid and base charge control agents were mixed with the carbon spheres to produce a pigment with higher mobility in the dielectric fluid. The optimized combination of pigment, charge control agent and solvent reveals reasonably fast switching time of about 540 ms.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Electronic paper (ePaper) is distinguished from liquid crystal displays (LCD) in appearance, operation mechanism and energy consumption. ePaper resembles regular paper, with high black/white contrast and a wide range viewing angle, because it uses reflective light. The utilization of reflective light in ePaper also has advantages of low power consumption. Furthermore, some unavoidable disadvantages in other displays such as eye fatigue and heat loss can be avoided in ePaper because of its operational principle using reflective light [1]. For these reasons, ePaper has been intensively researched as an alternative display.

ePaper is generally composed of two electrodes and a suspension colloid inserted between them [2]. The suspension colloid contains black and white pigments that disperse in dielectric fluid to form a monochromic image. When an electric field is applied to the suspension colloid, oppositely charged black and white pigments migrate to the respective electrodes by electrostatic force, and images can be realized based on this movement. In addition, the image is sustained by restricting the agglomeration and the

sedimentation of pigment, which is attributed to the repulsion between pigments and the density matching between pigment and dielectric fluid. The repulsive force between the pigments in the dielectric fluid more strongly depends on steric repulsion than electrostatic repulsion, because the stabilization of charged pigments in non-polar solvent needs longer separation distance compared to that in polar solvent [3]. Thus, polymer compounds are usually coated onto the pigment in the interest of imposing steric hindrance and thus securing sufficient distance between the pigments [4–9]. Even though the effect of electrostatic repulsion is negligible with respect to keeping the pigment stable, surface charges of pigments are recommended to be as high as possible. This is because the switching time required for changing one image to another depends on the surface charge of the pigment [1]. Therefore, the addition of charge control agent is commonly used to control the surface charge of pigments to have high absolute value in each dielectric fluid [10,11].

Various kinds of materials have been employed to be used as a black and a white pigment. As the black pigment, carbon black is the most commonly used owing to its good electrical properties, remarkable blackness and availability [12]. However, carbon black has an inherent cluster structure similar to a bunch of grapes. Irregular shape and non-uniform size make it hard to control the properties of the black pigment. Accordingly, the use of carbon black imposes a limit in the performance of ePaper, and it is thus highly demanded that the carbon black should be substituted with

\* Corresponding author. Tel.: +82 2 880 8863; fax: +82 2 888 1604.

\*\* Corresponding author. Tel.: +82 32 835 8414; fax: +82 32 835 8423.

E-mail addresses: [ojkwon@incheon.ac.kr](mailto:ojkwon@incheon.ac.kr) (O.J. Kwon), [jjkimm@snu.ac.kr](mailto:jjkimm@snu.ac.kr) (J.J. Kim).

different, spherical black pigment. Hollow black TiO particles [8], carbon–iron oxide microspheres [13], cadmium sulfo-selenide, iron oxide and nigrosines [14] have been introduced as substitutes for the carbon black. Carbon spheres are one of the probable candidates for substitute pigments, and have spherical shape and chemical and electrical properties similar to carbon black. However, there is no related study on applying carbon spheres as black pigment in ePaper.

In this paper, carbon spheres were prepared through a hydrothermal synthesis method [15], and the effects of hydrocarbon concentration and reaction time were investigated in order to control the size and the shape of the pigments. The synthesized carbon spheres were coated with *p*-(2-ethylhexyl acrylate), which has branch molecular structure, to exploit the advantageous effect of steric repulsion [16,17]. The suspension stability of the carbon spheres coated with polymer was tested in TCE, and the surface charge of pigment was modified by adsorbing a charge control agent. The combination of carbon spheres, dielectric fluid and charge control agent was optimized.

## 2. Experimental

### 2.1. Materials

Glucose, 2-ethylhexyl acrylate (EHA), hydrogen chloride (HCl), 4-vinylaniline, sodium nitride, azobisisobutyronitrile (AIBN), cyclohexane, tetrachloroethylene (TCE), ethanol, acetone, tetrahydrofuran (THF) were provided from Sigma–Aldrich.

### 2.2. Carbon sphere synthesis

1.0–2.5 M glucose was dispersed in deionized (D.I.) water as a carbon precursor, and the solution was put into an autoclave reactor. Then, the autoclave reactor was heated to 160 °C for several hours. After finishing the synthesis, the reactor was cooled down to room temperature. Products were centrifuged, and the precipitated pigments were rinsed with ethanol and D.I. water.

### 2.3. Grafting polymerization

Step1: Synthesized carbon spheres, 0.2 ml hydrogen chloride and 0.10 g of 4-vinylaniline employed for molecular grafting were dispersed in D.I. water through stirring. The temperature of the solution was raised up to 40 °C. 0.174 g of sodium nitride dissolved in D.I. water was injected for 10 min for electrochemical reduction of diazonium salts [16]. The solution was agitated for additional 16 h. The product was centrifuged and rinsed with acetone. The rinsing was repeated for several times and the rinsed products were dried in vacuum oven at 60 °C for 1 day.

Step2: The product prepared in step 1 was dispersed in toluene, and EHA was added as a monomer. The solvent was purged with nitrogen gas in a round bottom flask for 20 min. Then, AIBN was added for initiating the polymerization reaction. The solution was heated up to 70 °C and the temperature was maintained for 1 h. The product was rinsed with acetone and THF several times. The obtained compounds were dried in a vacuum oven.

## 3. Results and discussion

### 3.1. Preparation of carbon spheres

The raw material employed for the synthesis of carbon spheres was glucose. Glucose concentration and reaction time were varied to obtain suitable carbon spheres for ePaper by manipulating the size of nanoparticle. Reaction conditions for the synthesis of carbon

spheres are listed in Table 1. From these reactions, the carbon spheres with size distribution between 100 nm and 400 nm were formed, except one condition (160 °C, 1.5 M glucose conc., 2 h), which produced polymeric compounds.

It is known that the hydrothermal reaction of glucose follows the LaMer model [18]. According to the model, the concentration of polymers including aromatic compounds and polysaccharides increases at the initial stage of the reaction. The polymer is the base material for forming spherical carbon. After reaching some critical concentration of the polymer compounds, nucleation occurs and the polymer compounds grow radially to form a carbon sphere. Fig. 1 exhibits the variation of carbon shape according to the reaction time at the same glucose concentration of 1.5 M. When the reaction progressed for 2 h, a small amount of particles with irregular shape and tangled polymers was observed, as shown in Fig. 1(a). However, over 4 h of reaction time, spherical particles finally appeared, and the average diameter of the particle increased from 148.84 nm to 202.26 nm after 8 h. Even though particle nucleation might occur before 2 h, a longer time is required for particles to grow and for the formation of spherical shapes consuming the polymer compounds.

In addition, it is ascertained that the glucose concentration affected the particle size and structure when the reaction was conducted for the same time, as shown in Fig. 2. The size of carbon spheres increased according to the glucose concentration. Since high concentration of glucose accelerated the chance of polymerization, polymer concentration reached the critical concentration for nucleation more quickly. However, the polymer-rich condition brought more severe accretion between particles and broadened the size distribution of the pigments. Thus, the carbon spheres produced at 1.5 M glucose concentration with 8 h reaction time were appropriate to be applied to ePaper due to high production yield and non-agglomerated state. Furthermore, the carbon spheres obtained at this condition had 202.26 (±26.15) nm of average particle size small enough to substitute for the carbon black in size. Thus, these carbon spheres were employed as core black material for the next step.

### 3.2. Surface modification of carbon sphere

The surface of the carbon spheres was manipulated carefully to impose dispersion stability on the carbon spheres and to improve mobility. The dispersion stability based on the steric repulsion could be obtained through polymer coating, and the improvement of mobility could be also achieved by the addition of charge control agent.

#### 3.2.1. Grafting polymerization on the carbon sphere

The hydrophilic surface of the carbon spheres fabricated by a hydrothermal reaction makes it impossible for the carbon spheres to have good dispersion in organic solution. Thus, the hydrophilic surface of the carbon spheres should be modified to hydrophobic because most of the dielectric fluids are organic

**Table 1**  
Reaction conditions for carbon sphere preparation.

Reaction temperature (°C)	Glucose conc. (M)	Reaction time (h)	Product	Avg. particle diameter (nm)
160	1.0	8	Carbon sphere	102.06 (±24.94)
160	1.5	2	Polymer	Non detectable
160	1.5	4	Carbon sphere	148.84 (±40.70)
160	1.5	8	Carbon sphere	202.26 (±26.15)
160	2.0	8	Carbon sphere	333.45 (±49.26)
160	2.5	8	Carbon sphere	435.40 (±57.01)

Download English Version:

<https://daneshyari.com/en/article/1786505>

Download Persian Version:

<https://daneshyari.com/article/1786505>

[Daneshyari.com](https://daneshyari.com)