Colloids and Surfaces A 549 (2018) 43–49

Contents lists available at ScienceDirect

Colloids and Surfaces A

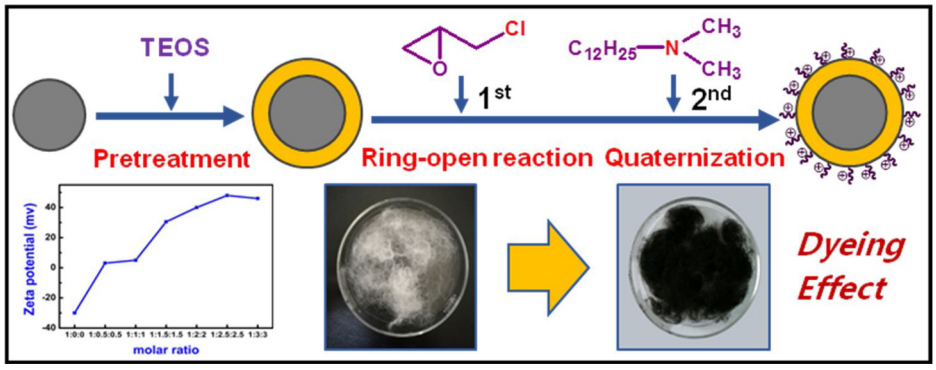
journal homepage: www.elsevier.com/locate/colsurfa

Synthesis and characterization of cationic carbon black pigment with quaternary ammonium groups and its dyeing properties for wool fabrics

Tingting Ma, Yaxing Cao, Hongling Chen*

College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Quaternization reaction
Carbon black nanoparticles
Cationic carbon black pigment
Dyeing
Wool

ABSTRACT

In this paper, the cationic carbon black pigment with quaternary ammonium groups was fabricated via the quaternization reaction of *N,N*-dimethyldodecylamine and epichlorohydrin-modified CB@SiO_2 core-shell structure composites. The CB@SiO_2 composites were prepared by stöber method using tetraethyl orthosilicate as precursor and carbon black (CB) nanoparticles as core. Scanning and transmission electron microscopic techniques (SEM & TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction method (XRD), thermogravimetric analysis (TGA), zeta potential and particle size distribution were employed to characterize the structure and properties of the cationic CB pigment as well as the intermediates. When the molar ratio of TEOS to epichlorohydrin to *N,N*-dimethyldodecylamine was 1:2.5:2.5, the zeta potential of the cationic CB pigment in aqueous dispersion reached the maximum +48 mv. The average diameter of the cationic CB pigment was *ca.* 45 nm with *ca.* 9 nm thickness of shell. Wool fabrics were dyed with the optimum cationic CB pigment through exhaust dyeing process. The L*a*b* values and the color appearance of dyed wool fabrics showed that the cationic CB-dyed wool fabrics had darker black and better fastness properties than the pristine CB-dyed wool fabrics.

1. Introduction

Black dyes and pigments occupy a pivotal position with the growing global demand in textile, cosmetic, paper and printing industries. In the field of textile, azo dyes, the main kind of synthetic colorants, are extensively used as black dyes because of their favorable characteristics, including high chemical stability, acceptable color strength and fastness, low biodegradability and simple application techniques [1,2].

* Corresponding author.
E-mail address: hlchen@njtech.edu.cn (H. Chen).

https://doi.org/10.1016/j.colsurfa.2018.04.005
Received 18 January 2018; Received in revised form 4 April 2018; Accepted 5 April 2018
Available online 06 April 2018
0927-7757/

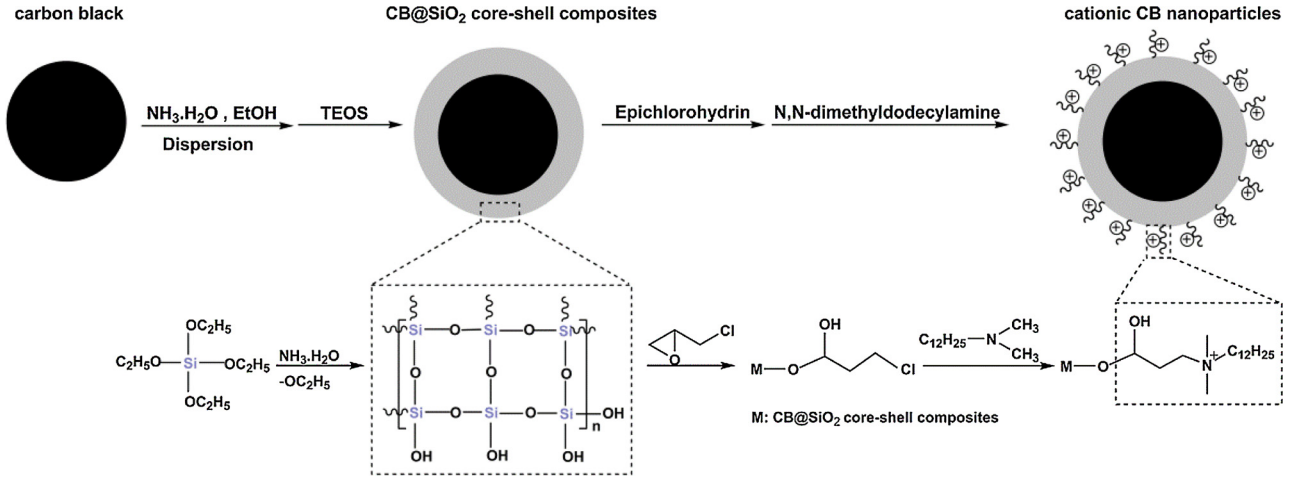


Fig. 1. Synthetic strategy and preparation process of cationic CB nanoparticles.

However, toxic and carcinogenic aromatic amines, such as aniline and its derivatives, are generated in the reductive-cleavage process of the azo linkage [3–5]. Therefore, eco-friendly black dyes or pigments have received extensive concern in order to substitutes for azo dyes.

Nano-sized carbon black (CB) is the most commonly black nanoparticles with great absorption, weather-resistance, excellent tinting and hiding power [6–9]. And the nano-structured CB with a primary particle size of 20 nm or larger had been authorized for use as a colorant in cosmetic products at a maximum concentration of 10% w/w according to the Cosmetics Regulation (EC) 1223/2009 in 2016 [10,11]. With the development of nanotechnologies, nano-sized CB has been applied in the textile industry [12,13], which can be a suitable alternative to azo dyes. Li et al. [14] reported that 8 nm CB nanoparticles dispersed by surfactant could diffuse towards the center of polyester and acrylic fibers at the temperature above their glass-transition temperatures in a thermal coloration process. And they [15] also showed that the self-dispersible CB nanoparticles with hydrophilic carboxylic groups achieved by nitric acid oxidation could dye cellulose, wool, acrylic and nylon fabrics through exhaust dyeing process without additional dispersing agent. Wang et al. [16] used CB aqueous dispersion to dye the cationic-modified cotton fabrics, and the results indicated that the dyeing exhaustion value of modified cotton was higher than the unmodified one due to the electrostatic attractions between CB nanoparticles and cationic cotton. However, the CB pigment for dyeing fabric in the previous researches carried few functional groups that could enhance the dyeability on the surface, which limited its application in the textile.

Quaternary ammonium compounds widely used as antibacterial agents, particularly those containing chains of 12–18 carbon atoms, carry positive charges in aqueous solution [17,18]. The compounds are predominantly attached to textiles by ionic interaction between the cationic quaternary ammonium groups and anion on the fiber surface [19,20]. Therefore, quaternary ammonium compounds can be directly exhausted in fibers under special conditions, such as polyester [21,22], cotton [23,24] and nylon [25,26]. Similarly, wool also can be treated with quaternary ammonium compounds for the carboxylic groups provided by the glutamyl and aspartyl residues [27]. Gao et al. [28] reported that the wool pretreated by peroxymonosulfate and sulfite could be rapidly and efficiently exhausted by cetylpyridinium chloride at room temperature and exhibited a strong antimicrobial ability. Besides, the dyes grafted with quaternary ammonium compounds could synthesize novel cationic dyes with simultaneous dyeing and antimicrobial ability [29]. In this case, the cationic CB pigment can be synthesized by linking the quaternary ammonium groups to the CB, which is beneficial for CB nanoparticles to apply in the dye field and reduce the pretreatment of fibers.

The purpose of this work was to prepare cationic CB pigment via endowing quaternary ammonium groups on the surface of CB nanoparticles. In order to enhance the CB chemical reactivity, the CB nanoparticles were pretreated to form core-shell structure composites with abundant hydroxyl groups by stöber method. And the application of the cationic CB pigment to the wool was further investigated in brief.

2. Experimental

2.1. Materials

Carbon black nanoparticles with average particle size of 24 nm were supplied by Nanjing Jayful novel Material Co., Ltd., China. Epichlorohydrin, and ammonia solution (25–28 wt.%) were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd., China. Ethanol was purchased from Wuxi Yasheng Chemical Co., Ltd., China. Tetraethyl orthosilicate (TEOS) and *N,N*-dimethyldodecylamine were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Sodium chloride was supplied by Nanjing Chemical Reagent Co., Ltd., China. All the chemicals were used without any further purification. Untreated wool fabrics were purchased from Heng Yuanxiang Group, China.

2.2. Preparation of CB@SiO_2 core-shell structure composites

CB@SiO_2 core-shell structure composites were synthesized by stöber method. 1 g CB was dispersed in 50 ml ethanol by ultrasonic treatment for 10 min. Then the mixture was transferred into a 100 ml flask and mixed with 3 ml ammonia solution under vigorous stirring at 50 °C for 1 h. Next 3 ml TEOS (2.8 g) was dissolved in 10 ml ethanol; and then the solution was added dropwise into the mixture above. The system was continuously stirred at 50 °C for 2 h. After that, the CB@SiO_2 core-shell structure suspension was obtained.

2.3. Preparation of cationic CB pigment

Cationic CB pigment was prepared by surface modification of the CB@SiO_2 composites with epichlorohydrin and *N,N*-dimethyldodecylamine. The schematic drawing for the preparation process was shown in Fig. 1. A certain amount of epichlorohydrin was added into CB@SiO_2 composites suspension mentioned above under continuously stirring and the system reacted at 50 °C for 2 h. Subsequently *N,N*-dimethyldodecylamine in equal mole with epichlorohydrin was added into the reaction mixture; the mixture continuously reacted for 2 h. After the end of reaction, the resultant suspension was centrifuged at 7000 rpm for 5 min and washed with ethanol and de-ionized water for several times respectively until the pH of supernatant liquor was