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Low-temperature plasma preparation and application of carbon black nanoparticles

J.J. Yuan [a], R.Y. Hong [a,b,c,*], Y.Q. Wang [c], W.G. Feng [d]

[a] College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, SIP, Suzhou 215123, China
[b] College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, China
[c] Jiangsu Provincial Key Laboratory of Environmental Materials and Engineering, Yangzhou University, Yangzhou 225002, China
[d] Suzhou Nanocomp Inc., Suzhou New District, Suzhou 215011, China

HIGHLIGHTS

- We use a novel plasma method for the preparation of high-quality carbon black (CB).
- The method is environmentally benign and economic.
- CB nanoparticles are successfully modified by polyvinylpyrrolidone.
- The modified CB is used as a pigment for the preparation of water-based ink-jet ink.
- Physical and printing properties of the ink are comparable with the commercial one.

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ABSTRACT

A new route is presented for the production of carbon black (CB) in which the propane is cracked into CB and hydrogen using electric energy from a low-current, high-voltage plasma discharge. The spherical CB produced by this process possessed a narrow size distribution, an average diameter of 50 nm and a high oil absorption number (OAN) of 136 mL/100 g. The prepared CB nanoparticles were first hydroxymethylated with a formaldehyde solution and subsequently oxidized using concentrated nitric acid to introduce hydroxyl and carboxyl acid groups onto the CB surface. These hydrophilic groups were beneficial for breaking up the large CB particles into smaller particles, and they significantly improved the dispersity of the CB nanoparticles in aqueous media. The modified CB was then coated by polyvinylpyrrolidone (PVP), in which the carbonyl oxygens acted as proton acceptors to form hydrogen bonds with the carboxyl acid groups. Finally, the PVP-coated CB was dispersed in an aqueous solution and was formulated into a pigmented ink-jet ink. The physical and printing properties of the prepared ink were demonstrated to be comparable with the commercial ink.

1. Introduction

Recently, carbon materials have attracted considerable attention due to their superior physical and chemical properties. Carbon black (CB) is one of the most popular raw chemical materials that now plays an important role not only as a reinforcing filler for tires and other rubber goods but also as a pigment for printing inks, coatings, plastics, and a variety of other applications [1,2].

The manufacture of carbon blacks (CBs) mainly includes furnace, thermal, channel, and acetylene blacks. Furnace blacks are produced by the partial combustion of hydrocarbons in a furnace. Channel blacks (a very small fraction of the market) are manufactured by the impingement of natural gas flames on channel irons. Thermal blacks are produced by the thermal decomposition of natural gas, while acetylene black, a special type of thermal black, is produced by the exothermal decomposition of acetylene [3]. From a chemical viewpoint, CB manufacturing processes can be classified into two categories: incomplete combustion and thermal decomposition of hydrocarbons, which depend on either the absence or presence of oxygen [4]. The predominant method for the production of CB is the furnace process, which possesses certain disadvantages, including its low yields, its large amounts of

* Corresponding author at: College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, SIP, Suzhou 215123, China. Tel./fax: +86 512 6588 2057.
E-mail address: rhong@suda.edu.cn (R.Y. Hong).

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polluting emissions and its limited reaction temperature [5]. Two growth mechanisms are employed to explain the particle formation mechanism of this type of CB. One is the radial growth mechanism [6], in which many aromatic species nucleate, grow, join face to face, and finally form the elementary CB particles. These particles make contact with each other within a very short time, which induces the formation of the aggregates that are responsible for the texture at the macroscopic level. The other mechanism [7] postulates that the polyaromatic species (PAHs that result from the polycondensation and polyaromatisation reactions involving the secondary species formed) produced by the thermal cracking of gaseous hydrocarbons gather into liquid hydrocarbon droplets, whose carbonisation within the gas phase induces the formation of carbon nanoparticles with a somewhat concentric texture (e.g., furnace-type CB). The two growth processes are not exclusive and may both occur simultaneously. An environmentally benign plasma process for the preparation of CB has also been proposed. The principle of the plasma method is the direct cracking of hydrocarbons in the absence of oxygen by means of an external electric energy supply [8]. Compared to the furnace process, it has the following three main advantages: (1) the products are two valuable industrial raw materials: carbon black and hydrogen, (2) the method is environmentally benign and is free of pollutants, (3) the conversion rate of the raw material is high, as it can theoretically reach 100% [9].

Different plasma technologies used in chemical and material engineering can be generally distinguished into two main types: thermal plasma and non-thermal plasma (or called low-temperature plasma). Thermal plasma processes are generally operating under high currents conditions (largely higher than 1 A), which is characterized by thermodynamic equilibrium, i.e., all the species (neutral, ions, electrons) have the same temperature (energy). While non-thermal plasma processes are generally operating under low currents conditions (lower than 1 A). The different species are not under thermodynamic equilibrium and the temperature of heavy particles (neutrals, ions) can be much lower than that of the electrons. The temperature of electrons can reach 10000–100000 K (1–10 eV) while the gas temperature can remain as low as room temperature [10]. Based upon mechanisms of which plasma is generated, pressure applied and the electrode geometry, the non-thermal plasmas comprise very different types including glow discharge, corona discharge, silent discharge or dielectric-barrier discharge (DBD), microwave discharge and radio frequency (RF) discharge [11]. Among the different types of non-thermal plasmas, microwave discharge and gliding arc discharge attract great attention. The former operates at very high frequencies, e.g. 2.45 GHz in the range of microwaves, with which only light electrons can follow the oscillations of the electric field. Therefore, this discharge is far from local thermodynamic equilibrium and can be operated in a wide pressure range [12,13]. Experimental investigations through this method have been performed for the preparation of carbon materials, e.g. the synthesis of small carbon nanoparticles [14] nanocrystalline diamond film [15,16] and graphene sheets [17]. The latter is a combination of high power equilibrium arc discharge and better selectivity of non-thermal plasmas, which has been reported to be used for reforming application, e.g. the reform of methane [18,19], propane [20] cyclohexane, heptane, toluene, gasoline (SP95), diesel oil. The particle formation mechanism can be summarized as the following three different stages: (1) nucleation, which corresponds to the transformation of a molecular system to a particulate system, (2) aggregation due to collisions of nanometer-sized particles (results of the nucleation process) to form 0–50 nm spherical particles, (3) agglomeration of the previous spherical particles into chains up to about 1 mm in length. In the present investigation, gliding arc discharge is employed for the synthesis of carbon black nanoparticles with propane as the feedstock.

CB has been widely used as a black pigment in the ink, paint and ink-jet industries due to its broad spectral absorption [21,22]. In most applications, the performance of CB is determined to a large extent by its surface and interfacial properties [23], which are difficult to control. Aqueous media in the above areas have attracted more attention for their decreased pollution, lower price and better quality than traditional organic solvents. However, the self-aggregation of CB particles in aqueous media greatly limits their utility. Only when the CB is well dispersed in aqueous suspensions can the excellent properties of the ink products be obtained. However, the manufacturing process of CB is limited with regard to the extent of contact with oxygen, and, for this reason, the products are less oxidized and non-polar [24]. Thus, the prepared CBs are hydrophobic and prone to agglomerate, leading to a poor dispersion in aqueous solutions. Consequently, surface modification is frequently used for CB to achieve better performances in aqueous suspensions [25–27].

Among the different surface modification approaches for CB, oxidation treatments have particular relevance because the introduction of oxygen functional groups onto the surface of CB not only provides desired qualities (e.g., enhanced adhesion and hydrophilicity) to the material [28–30], but they also enable additional functionalization strategies to be performed using such groups as anchoring sites [31]. Acidic oxidation methods have been widely reported as effective approaches to purify and functionalize the CB surfaces, and nitric acid has been the most frequently utilized agent for the oxidation of CBs. Oxygen-containing functional groups (OH and COOH) can be introduced onto the CB surfaces through this procedure [32]. Hydroxymethyl groups ($-CH_2OH$) can be introduced onto the CB surface by treating the CB with formaldehyde solution under alkaline conditions prior to oxidation by nitric acid [33], thus increasing the affinity of CB for water and facilitating the attack of nitric acid against the surface of CB. The polar groups –OH, $-CH_2OH$ and –COOH greatly improve the dispersion of CB in water and the compatibility between CB nanoparticles and polymer matrices [34,35].

The most widely used substances for the stabilization of nanoparticles are polymers and ligands, especially natural or synthetic polymers that possess an affinity toward them and that are soluble in suitable solvents [36,37]. Such substances can also control the reduction and the aggregation of the nanoparticles in solution. Polyvinylpyrrolidone (PVP) is a hydrophilic, biocompatible and non-antigenic polymer [38], and it is non-toxic to organisms. Additionally, PVP is very soluble in water and can form an aqueous solution with excellent wetting properties.

Using PVP as a protective layer, we managed to obtain a stable suspension of CB in aqueous media. The dispersity enhancement of the PVP-coated CB nanoparticles was due to the hydrogen bond interactions between PVP and the modified CB nanoparticles in which the carbonyl oxygens acted as proton acceptors to form hydrogen bonds with the carboxyl acid groups. [34,39,40].

In this study, CB nanoparticles were synthesized using a low-current, high-voltage AC plasma discharge process at atmospheric pressure. The effects of the current and the argon and propane flow rate on the morphology of the CB nanoparticles were investigated. Spherical CB products obtained under optimal preparation conditions were first treated with formaldehyde solution and nitric acid and then coated by PVP via a simple phase separation method. The effects of the surface treatment on the stability of the CB in aqueous media were investigated. Furthermore, we obtained a type of black pigmented ink-jet ink with the addition of solvents, surfactants and other additives. The physical and printing properties of the prepared ink were also evaluated.