



# Hydrothermal carbonization of carboxymethylcellulose: One-pot preparation of conductive carbon microspheres and water-soluble fluorescent carbon nanodots



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## HIGHLIGHTS

- Carboxymethylcellulose and urea were subjected to hydrothermal carbonization.
- Hydrothermal treatment of carboxymethylcellulose produced hydrochar and nano quantum dots.
- N-containing functional groups resulted in hydrochars with high electrical conductivity.
- Quantum dots can be used as photosensitizer in system of visible-light catalytic degradation.

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## ABSTRACT

Conductive carbon spheres (CSs) and water-soluble fluorescent carbon nano-dots (CNDs) were synthesized by the one-pot hydrothermal carbonization of carboxymethylcellulose (CMC) using urea as the nitrogen source. The CSs have diameters of 2–8  $\mu\text{m}$  and abundant nitrogen-containing functional groups. They contain N in two forms: (1) chemical N including amidogen and imido groups ( $-\text{NH}_2$ –/ $-\text{NH}-$ ), and (2) structural N including pyridine (N-6), pyrrolic/pyridone (N-5) and quaternary (N-Q) nitrogen. Activation at high temperature contributes to the formation of pyridine (N-6) and quaternary nitrogen (N-Q) with a graphite-like structure and higher stability. They are all conductive and  $\text{CS}_{0.2-900}$  was found to exhibit the highest electrical conductivity of 166 S/m. CNDs are monodispersed spheres with an average diameter of 32 nm and show abundant oxygen-containing groups on their surface. They have excitation- and emission-independent pH-sensitive properties. The use of CNDs as photosensitizer in a CNDs/ $\text{TiO}_2$  system for methylene blue and phenol degradation under visible light irradiation is attractive. The spectral response range of the system was thus expanded from UV region to include part of the visible light region.

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## 1. Introduction

Hydrothermal carbonization (HTC) is a novel, convenient and environmentally friendly way to convert biomass into higher value carbonaceous materials. It involves reactions in a closed system under mild temperatures (120–280 °C) and self-generated pressure. This avoids traditional harsh conditions such as strong acids, high temperatures, and long reaction times. Much work has been done using glucose, starch, cellulose, and lignocelluloses as biore-source precursors [1–3]. The resultant materials are nanostruc-

tured solid carbon microspheres with abundant functional groups on the surface. Therefore, they may be used in environmental and energy fields such as catalysis [4], adsorption [5], as supercapacitors [6] and as electrode materials [7]. HTC can also be used to tune product morphology, structural stability and surface functionality. To the best of our knowledge, both the properties and applications of direct biomass hydrothermal carbonization are simple and scalable.

Doping is an efficient method for the modification of carbon materials and many properties can be changed by changing the texture and the surface by manipulating the doping method and the sources. Most research into doping has focused on N-doping with synthesis being through nitrogen or oxygen rich precursors or by the modification of a carbon surface by introducing N-containing groups, followed by activation [6,8]. It has been reported

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that this modification of materials shows basic characteristics and that it is effective for the adsorption of acidic materials such as  $H_2S$ ,  $CO_2$ , and  $HCl$ . N-doping can influence the structural arrangement, surface functional groups, stabilities and thermal properties, which further expands the range of applications. The nitrogen source and the doping methods greatly influence the surface groups, the N content and the structure.

Several research groups have investigated, directly or indirectly, the reaction mechanisms of hydrothermal carbonization. A clear reaction pathway has still not been agreed upon, but many reports include chemical compositions, dehydrated intermediates, and the structure of the reaction products. Sevilla and Fuertes [9] used cellulose as a raw material and found that the process involved dehydration, polymerization, aromatization and carbonization. The final solid products consisted of lignin with condensed benzene rings and a large amount of oxygen-containing groups on the core-shell structure. Xiao et al. [2] found that in addition to solid residues (hydrochar), the liquid intermediate products that were extracted with ethyl acetate and analyzed by gas chromatography–mass spectrometry were mainly phenolic compounds and furan derivatives. This confirmed that dehydration and aromatization had occurred. Furthermore, water-soluble compounds in the aqueous solutions from HTC experiments contain a significant amount of sugar and lignin-derived compounds [10], indicating that the aqueous solutions may contain particles with structures and properties similar to that of hydrochar.

Most attention has been given to the solid products obtained to determine the desired structure and the reaction mechanism. The pale yellow liquid has always been regarded as waste and discarded. Research data about the properties and applications of solid carbon microspheres and liquid nano carbon dots is lacking. Our previous research confirmed that the liquid contains abundant carbon nanoparticles similar to quantum dots. They range from a few nanometers to hundreds of nanometers in size with oxygen-containing groups on their surface, and exhibit similar as well as different spectral properties compared with the obtained solid products because of the small size effect [11]. Compared with traditional fluorescent nanoparticles of semiconductor quantum dots [12] and metal nanoparticles [13], these carbon nanodots (CNDs) overcome disadvantages such as toxicity, high-cost, and undesirable oxidation. Additionally, they can be used in metal probes, imaging, optical sensors, catalysis and in energy fields [14–17].

We systematically studied the HTC of CMC with the addition of urea to understand the properties and applications of solid-liquid products that were obtained in the autoclave. Solid carbon spheres

with N-containing functional groups and their influence on electrical conductivity were investigated. The photoluminescent liquid products and the visible light catalytic activity of the CNDs/ $TiO_2$  system toward methylene blue (MB) and phenol degradation were also investigated.

## 2. Methods

### 2.1. Hydrothermal carbonization of CMC

In a typical experiment, CMC (1.5 g) and urea ( $X$  g;  $X = 0.1, 0.2, 0.4$ ) were dissolved in distilled water (40 ml) and ultrasonically agitated for 15 min. The solution was added to a stainless steel autoclave (55 ml volume). The autoclave was placed in a furnace at  $210^\circ C$  for 12 h, and then allowed to cool to room temperature. The black solid products were collected by centrifugation at 8000 rpm and washed with distilled water and pure ethanol until the solution was clear. Drying was done under vacuum at  $80^\circ C$  overnight and the product was designated  $CS_n$ , where  $n$  denotes the mass of added N. Samples without urea were designated CSs.

After obtaining the  $CS_{0.2}$  sample, the corresponding brown solution was collected by further centrifugation at 12,000 rpm for 20 min. The obtained light yellow solution containing the CNDs was subjected to dialysis (1000 Da molecular weight cut off) for about 48 h before further characterization. The sample obtained without the addition of urea was designated CNDs-0.

The synthetic strategy is shown in Fig. 1.

### 2.2. Activation of carbon microspheres under a $N_2$ atmosphere

The black solid  $CS_n$  and CSs samples were placed in an alumina combustion boat which then was placed in a calcination furnace. The sample was kept under a nitrogen atmosphere in the furnace and then heated to  $550^\circ C$ , and  $900^\circ C$  at a rate of  $5^\circ C\ min^{-1}$ . The residence time was 2 h after which the furnace was allowed to cool to room temperature. The obtained products were washed with boiling water to remove the excess urea decomposition products. The products after treatment are designated  $CS_n-T$  where  $T$  denotes the temperature of activation.

### 2.3. Preparation of the CNDs/ $TiO_2$

The CNDs/ $TiO_2$  composites were synthesized by the sol-gel method [11]. Tetrabutyl titanate (0.5 ml) was dissolved in ethanol

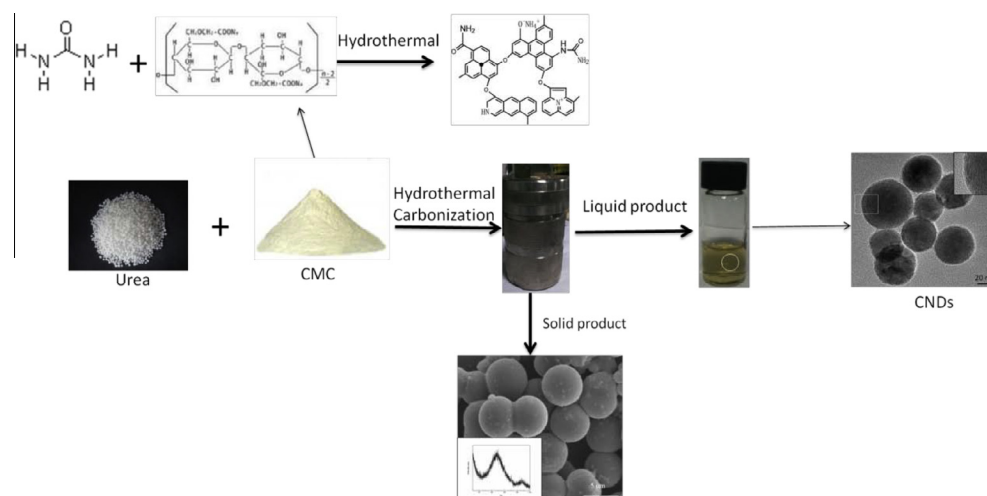


Fig. 1. Schematic showing the one-pot hydrothermal carbonization of CMC for N-doped carbon spheres and the CNDs.

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