Preparation and characterization of nano silver immobilized hydrochar derived from hydrothermal carbonization of tobacco stem

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Abstract
In this present study, silver nanoparticles (AgNPs) immobilized hydrochar was prepared through a facile one-pot co-hydrothermal carbonization of tobacco stem and silver nitrate. The effect of concentration of silver precursor, hydrothermal temperature and reaction time on the chemical compositions, structural property, combustion performance, as well as gaseous products release behavior of the resultant AgNPs immobilized hydrochar were evaluated. The co-hydrothermal treatment decreased the volatile matter while increased the ash content of hydrochar. Single-phase AgNPs were successfully generated and evenly immobilized onto the hydrochar during the hydrothermal process. The immobilized AgNPs played a notable catalytic role during the char combustion stage, thereby decreased the ignition temperature, burnout temperature and maximum rate temperature for char combustion. Meanwhile, TG-FTIR analysis suggested that the emission amount of harmful gas CO during hydrochar combustion was reduced due to the catalytic effect of AgNPs. This phenomenon may indicate the appropriate amount of nanoparticles immobilization could enhance the combustion behavior of hydrochar fuel.

1. Introduction

Research on hydrothermal carbonization (HTC) was assumed to start from 1913 by Bergius who first described the hydrothermal transformation of biomass into coal-like materials [1]. As an eco-friendly and cost-effective approach, HTC technique has attracted much attention due to its moderate reaction temperatures in autoclave with self-generated pressure. In recently years, many efforts have been devoted to the HTC of various biomass in order to produce functional hydrochar materials that exhibited a wide variety of applications in adsorption, catalyst support and solid fuel [2–6]. For example, rice bran biomass was hydrothermally carbonized to produce carbon microspheres that could be used as a nanoparticle catalyst support [7]. Raveendran et al prepared luminescent carbon dots from mint leaves through a simple hydrothermal treatment to detect Fe(III) and ascorbic acid [8]. In addition, many biomass such as bamboo, wood sawdust, wheat straw [9], and corn cob residues [10] etc have been subjected to hydrothermal treatment to generate hydrochar with favorable fuel properties.

Previous studies have demonstrated that HTC is a promising thermochemical conversion technology for upgrading the fuel properties and realizing energy utilization of biomass. It is generally believed that a series of devolatilization, intramolecular condensation, dehydration and decarboxylation reactions would occur during the HTC of biomass, resulting in the formation of lignite-like materials with decreased oxygen and hydrogen contents and enhanced energy density [11]. The product quality of resulted hydrochar was influenced by several parameters including the hydrothermal temperature, residence time, and feedwater characteristics. High
reaction temperature and long residence time is normally favored for the decomposition of lignocellulosic component and condensation [12], leading to the production of hydrochar with higher heating value (HHV). Moreover, several recent studies on HTC conversion of biomass have focused on the introduction of additional acid/alkali or metal ions catalyst which could enhance the cleavage of hydrogen bonds and facilitate the hydrolysis of lignocellulose [13], and ultimately affect quality of hydrothermal products. For instance, Lynam et al have reported that the addition of acetic acid or Ca salts could increase the HHV of the hydrochar product [14, 15]. Our previous study found that graphene oxide also promoted the nucleation and carbonization of soluble carbohydrates and even played a catalytic role during the hydrochar combustion process [16].

Actually, it is known that abundant functional groups, e.g., hydroxyl and carboxyl groups, are present on the surface of hydrochar. These groups are expected to interact with the additional catalysts, especially for the metal ions, during the catalyst-assisted co-hydrothermal process. The reduction ability of these functional groups under HTC condition would contribute to the formation of corresponding metal nanoparticles. This phenomenon has been confirmed in recent study by Gai et al, who prepared iron nanoparticles supported hydrochar through a facile one-pot HTC of lignocellulosic matrix and iron(III) nitrate [4]. Sun et al also reported a one-pot synthesis of cobalt nanoparticles supported hydrochar achieved by co-HTC of mixtures of rice bran biomass and cobalt source [7]. These reported hydrochar-supported metal nanoparticles that prepared by HTC method exhibited great potential in heterogeneous catalysis. While to the best of our knowledge, the effect of generated nanoparticles on the fuel properties and especially the combustion process of hydrochar has seldom been studied.

In the present study, a facile one-pot HTC process of tobacco stem (TS) biomass and metal precursor was conducted for the production of silver nanoparticles (AgNPs) immobilized hydrochar solid fuel. TS is an abundant biomass resource generated by domestic cigarette manufacturing enterprises, which is otherwise treated as waste [17]. In fact, TS is rich in cellulose, hemicellulose and lignin, and composed of polysaccharide, pectin and phenolic compounds. And thus, HTC is an effective way to realize the reasonable utilization of this untapped resource for energy or functional material production. During the co-HTC process, AgNPs were expected to be synthesized and in situ immobilized onto the hydrochar matrix. The objective of this study is to employ TS and silver precursor as raw materials to prepare hydrochar through co-HTC method, and meanwhile to characterize the hydrochar produced under different conditions in the respective of fuel property, physicochemical structural characteristics and combustion behavior.

2. Materials and methods

2.1. Materials

TS was obtained from a tobacco-threshing factory (Xuchang, Henan Province in China). The samples were washed with tap water to remove surface dust, dried naturally and crushed for 30 s using ultrafine pulverizer. Subsequently, the TS powder was stored in a sealed bag before further use. Silver nitrate (AgNO₃) was obtained from Sinopharm Chemical Regent Co., Ltd (Shanghai, China).

2.2. Synthesis of AgNPs immobilized hydrochar

The AgNPs immobilized hydrochar was prepared through a co-hydrothermal treatment of TS and AgNO₃ according to our previous procedure in a 100-ml Teflon-lined autoclave [16]. In a typical experiment, 4 g of TS powder was dispersed with 60 ml deionized water in the autoclave. And then, 1 ml of AgNO₃ solution (the concentration was 10, 50 and 100 mM, respectively) was added and stirred continuously to form a homogeneous suspension. After that, the autoclave was securely sealed and placed into an electrical furnace with desired temperature (180 °C, 210 °C, and 240 °C) and maintained for a specific reaction time (1 h, 3 h, and 6 h). Meanwhile, HTC of TS without the addition of AgNO₃ was conducted under 210 °C for 3 h as control experiment (the hydrochar product was denoted as HTC-210–3). When the reaction was finished, the autoclave was removed from furnace and cooled down under tap water. The resulting AgNPs immobilized hydrochar was recovered by vacuum filtration, washed with distilled water and dried at 105 °C overnight. The hydrochar product was denoted as Agₘ₀@HTC-X-Y, where M represents the molar concentration of silver precursor, X and Y represent the hydrothermal temperature and residence time, respectively.

2.3. Sample characterization

Ultimate analysis of raw TS and the corresponding hydrochar were carried out with an Elementar Vario EL cube CHNS analyzer. Proximate analysis of TS and the AgNPs immobilized hydrochar was measured to determine the contents of moisture (M), volatile matter (VM), fixed carbon (FC) and ash (A) by using thermogravimetric method [18]. The surface morphological features of the samples were observed by using a JEOL-6010LA Scanning electron microscope (SEM) coupled with energy-dispersive x-ray spectroscopy (EDX). X-ray
condensation, and aromatization processes, resulting in the formation of brown 

During the HTC process, TS was expected to undergo several reactions, including the dehydration, 

3.1. Chemical compositions analysis

3. Results and discussion

2.4. Combustion behavior analysis

Combustion behavior of the TS and nanoparticles supported HTC samples were investigated using the thermogravimetric analyzer (Discovery TGA, TA Instruments). For the combustion experiment, approximately 10 mg sample was loaded into a platinum crucible and conducted in the temperature range of 40 °C to 800 °C with a heating rate of 20 K min⁻¹. The furnace atmosphere was simulated air (V_{\text{N}_2} = 80\%, V_{\text{O}_2} = 20\%) with a flow rate 40 ml min⁻¹. The key combustion characteristic parameters, such as ignition temperature (T_i), maximum combustion rate temperature (T_{\text{max}}), maximum combustion rate temperature (T_{\text{mean}}), and burnout temperature (T_b) were determined from the TG and DTG (first order derivative of TG curve) profiles according to previous study [19]. Comprehensive combustibility index s index was applied to evaluate the combustion characteristics of tobacco stem, hydrochar and pellets, and was calculated from the following equation:[20]

\[ S = \frac{\text{DTG}_{\text{max}} \times \text{DTG}_{\text{mean}}}{T_i^2 \times T_b} \]

where \text{DTG}_{\text{max}} and \text{DTG}_{\text{mean}} represent the maximum and average rates of weight loss (wt%/min), respectively. Moreover, the combustion process of HTC–210–3 and Ag_{50}@HTC–210–3 samples were monitored by a TG instrument (NETZSCH TG 209F3) coupled with an FTIR spectrometer (Nicolet 8700, Thermo Electron, America). The sample loading amount, furnace atmosphere and heating rate were consistent with the above TG combustion experiment. The volatiles released during the combustion process were analyzed online using the FTIR spectrometer recorded from 400–4000 cm⁻¹. The spectra were recorded at a resolution of 2 cm⁻¹ and the data were processed using the OMNIC software (Thermo Electron, America).

Table 1 shows the proximate analysis of raw TS and the AgNPs immobilized hydrochar samples. The fixed carbon of raw TS was 12.37\%, and it increased to 18.39\% after the HTC under 210 °C for 3 h. The volatile matter of all the AgNPs loaded hydrochar samples was lower than that of HTC–210–3, and it was significantly decreased with the increase of AgNPs amount. This indicated that the addition of AgNO₃ may promote the hydrolysis of cellulose in TS by acting as a catalyst in subcritical water [23], which was similar to the effect of iron in the HTC of fallen leaves. Moreover, under the same addition amount of AgNO₃, the volatile matter gradually decreased with hydrothermal treatment intensity, while the fixed carbon exhibited the opposite trend. This result suggested that higher temperature and longer reaction time promoted the decomposition of TS and facilitated the aromatization reaction to produce hydrochars. The ash content of AgNPs loaded hydrochar was generally higher than that of HTC–210–3 due to the introduction of different amounts of inorganic nanomaterials.

**Table 1.** Elemental analysis of TS and the HTC-210–3 hydrochar.

| Sample       | N (wt%) | C (wt%) | H (wt%) | S (wt%) | O (wt%) | O/C | H/C  |
|--------------|---------|---------|---------|---------|---------|-----|------|
| Raw TS       | 1.62    | 40.94   | 5.97    | 0.52    | 44.62   | 0.82| 1.75 |
| HTC-210–3    | 0.86    | 55.74   | 5.05    | 0.21    | 33.16   | 0.45| 1.09 |

diffraction (XRD) analysis was conducted on D/max 2500 XRD spectrometer (Rigaku, Japan) with a Cu Ka x-ray source. Fourier transform infrared spectroscopy (FTIR) analysis of the TS and hydrochar was performed using Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) in the range 400–4000 cm⁻¹ with a pure KBr pellet as background. X-ray photoelectron spectra (XPS) of the HTC-210–3 and Ag_{50}@HTC-210–3 were recorded by the Thermo ESCALAB 250 spectrometer with an Al Kα source (hv = 1486.6 eV). The C1s spectra of the samples were deconvoluted into three components using the XPSPeak software.

2.3. X-ray diffraction analysis

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3. Results and discussion

3.1. Chemical compositions analysis

During the HTC process, TS was expected to undergo several reactions, including the dehydration, condensation, and aromatization processes, resulting in the formation of brown/black colored hydrochar product. Elemental composition analysis (table 1) shows that carbon content increased from 40.94\% to 55.74\%, accompanied by a decrease in hydrogen and oxygen contents during the HTC process. Meanwhile, a decreased nitrogen and sulphur content was also observed. These results illustrated the occurrence of dehydration, decarboxylation and condensation reactions, which resulted in the declined O/C and H/C ratio and partial carbonization of TS biomass. The fuel property of TS was also expected to be enhanced after the HTC treatment. Moreover, the abundant functional groups of hydrochar, intermediate products of reactions and the soluble constituents of TS were reported to have some metal ions chelation and reduction capacity, which could reduce Ag⁺ into Ag⁰ and lead to the formation of AgNPs in situ during the HTC process [21, 22].

Table 2 shows the proximate analysis of raw TS and the AgNPs immobilized hydrochar samples. The fixed carbon of raw TS was 12.37\%, and it increased to 18.39\% after the HTC under 210 °C for 3 h. The volatile matter of all the AgNPs loaded hydrochar samples was lower than that of HTC–210–3, and it was significantly decreased with the increase of AgNPs amount. This indicated that the addition of AgNO₃ may promote the hydrolysis of cellulose in TS by acting as a catalyst in subcritical water [23], which was similar to the effect of iron in the HTC of fallen leaves. Moreover, under the same addition amount of AgNO₃, the volatile matter gradually decreased with hydrothermal treatment intensity, while the fixed carbon exhibited the opposite trend. This result suggested that higher temperature and longer reaction time promoted the decomposition of TS and facilitated the aromatization reaction to produce hydrochars. The ash content of AgNPs loaded hydrochar was generally higher than that of HTC–210–3 due to the introduction of different amounts of inorganic nanomaterials.
3.2. Structural properties of the AgNPs immobilized hydrochar

The SEM images in figure 1 show the micromorphology of raw TS, HTC-210–3 and AgNPs immobilized hydrochars that produced at different hydrothermal reaction conditions. As displayed in figure 1(a), the raw TS exhibits a relatively smooth fibrous surface which is the typical architectural feature of lignocellulosic biomass. After the hydrothermal treatment, surface of the hydrochars became irregular and rougher due to decomposition of the cellulosic components in biomass. Meanwhile, the hydrochars were decorated with several carbonaceous microspheres which may be formed by the decomposition and the subsequent aromatization, nucleation of the carbohydrates in lignocellulosic biomass during the HTC process. The as-synthesized AgNPs can be hardly seen under the SEM observation, probably because of their small sizes. Furthermore, elemental composition of representative Ag50@HTC-210–3 sample was examined by EDX (figure 2(a)). The appearance of Ag element (3.0 keV) evidenced that AgNPs were immobilized on the surface of hydrochars [24]. The C, O and Ca elements were also detected on the surface of TS hydrochars. EDX elemental mapping analysis (figure 2(b)) of Ag50@HTC-210–3 further confirmed that AgNPs were evenly distributed on the hydrochar support.

| Sample          | M     | VM    | FC    | Ash  |
|-----------------|-------|-------|-------|------|
| Raw TS          | 5.64  | 75.66 | 12.37 | 6.33 |
| HTC-210–3       | 3.32  | 73.31 | 18.39 | 4.98 |
| Ag10@HTC-210–3 | 2.30  | 72.46 | 16.97 | 8.27 |
| Ag50@HTC-210–3 | 1.85  | 58.23 | 18.82 | 21.10|
| Ag100@HTC-210–3| 1.53  | 46.66 | 19.07 | 32.74|
| Ag10@HTC-180–3 | 2.45  | 60.36 | 13.30 | 23.88|
| Ag50@HTC-240–3 | 1.60  | 51.64 | 22.27 | 24.49|
| Ag10@HTC-210–1 | 3.89  | 62.43 | 8.88  | 24.80|
| Ag50@HTC-210–6 | 1.86  | 54.71 | 21.12 | 22.31|

Table 2. Proximate analysis of TS and the produced AgNPs loaded hydrochar.

Figure 1. SEM images of TS and the hydrochar samples produced under different conditions. (a) raw TS; (b) HTC-210–3; (c) Ag10@HTC-210–3; (d) Ag50@HTC-210–3; (e) Ag50@HTC-210–3; (f) Ag50@HTC-240–3; (h) Ag50@HTC-210–1; (i) Ag50@HTC-210–6.
XRD analysis was conducted to further confirm the presence of single-phase AgNPs on the hydrochars. As shown in Figure 3, the HTC-210–3 sample exhibits two characteristic peaks of cellulose at 2θ = 14.8° and 22.3°, indicating the cellulosic structure of TR was partially preserved under this hydrothermal condition [25]. All the other samples exhibit similar diffraction patterns with five characteristic diffraction peaks at 2θ of 38.1°, 44.3°, 64.6°, 77.4°, and 81.6°, which could be attributed to the (111), (200), (220), (311), and (222) crystal fcc crystalline silver, respectively [26, 27]. The detailed morphology and size distribution of the formed AgNPs supported on the hydrochar (Ag50@HTC-210–3) was characterized by TEM measurement. As shown in Figure 4(a), approximately spherical nanoparticles with several aggregates are generated. The corresponding size distribution histogram is shown in Figure 4(b), which indicates that the sizes of the synthesized AgNPs were mainly in the range of 20–70 nm, with the mean diameter of 46.9 nm. Frankly speaking, the particle size of AgNPs is not large at such a relatively high solution temperature. This may benefit from the stabilization function of hydrochar support and the capping effect of soluble components from TS, which inhibit the aggregation and growth of AgNPs.

FTIR analysis was conducted to investigate the surface structural changes in the TS biomass during the HTC and formation of AgNPs process. Figure 5 compares the FTIR spectra of raw TS, hydrochar and AgNPs immobilized hydrochars produced at different HTC conditions. The wide absorption band around 3430 cm\(^{-1}\) of TS is attributed to the stretching vibration of –OH [28, 29]. A narrowing of the OH vibration band was observed for HTC-210–3, due to the dehydration reaction during HTC treatment. The absorbance band at 1640 cm\(^{-1}\) with a shoulder at 1740 cm\(^{-1}\) is associated with the C=O stretching vibration of carboxylic group [30]. The disappearance of the band at 1740 cm\(^{-1}\), as well as narrowing the band at 1640 cm\(^{-1}\) for hydrochar suggested the occurrence of decarboxylation reaction [31]. The bands at 1415 cm\(^{-1}\) and 1310 cm\(^{-1}\) could be respectively ascribed to C=C stretching of aromatic group and breathing vibrations of syringyl units of biomass [32]. In addition, a broad band at around 1065 cm\(^{-1}\), which corresponded to C–O–C stretching vibrations in cellulose,
decreased and split into several bands during the HTC treatment. These observations can be attributed to the disruption of hemicellulose/cellulose and lignocellulosic components. As for the AgNPs immobilized hydrochar samples, a decrease in the intensity of bands at 3430 cm$^{-1}$ and 1640 cm$^{-1}$ is observed, which may imply that $\text{-OH}$ and $\text{C=O}$ were involved in the reduction of Ag$^+$ and formation of AgNPs during HTC.

XPS measurement was also performed to further analyze the surface chemical state of the typical hydrochar samples. As shown in figure 6(a), the whole XPS survey scan spectrum of the hydrochars exhibits the presence of C 1 s, N 1 s, and O 1 s signals. Meanwhile, the Ag 3d core level signal is observed for the Ag$_{50}$@HTC-210–3 sample. The Ag 3d core-level spectrum shown in figure 6(b) exhibits two peaks centered at 367.8 and 373.8 eV, which corresponded to Ag 3d$^5$/2 and Ag 3d$^3$/2, respectively \cite{33}. The splitting of the 3d doublet of Ag is 6.0 eV, indicating the formation of metallic AgNPs on the hydrochar matrix. The curve-fitted high-resolution C 1 s XPS spectra of HTC-210–3 and Ag$_{50}$@HTC-210–3 samples are presented in figures 6(c) and (d). The peak located at 284.4 eV, 286.1 eV are attributed to the aliphatic/aromatic carbon (C–C, C–Hx, and C=–C) and C–O groups, respectively. The peak of carboxyl group (C=–O) appears at 288.1 eV for HTC-210–3, which is shifted to lower binding energy (287.8 eV) after the formation of AgNPs on the surface of hydrochar. In addition, the relative content of carboxyl group was calculated to decrease from 6.0% to 2.5%. These results may imply that C=–O of the hydrochar was responsible for the generation and stabilization of AgNPs.

3.3. Combustion behavior analysis

The combustion behaviors of the raw TS, HTC-210–3 and AgNPs immobilized hydrochars produced at different conditions were determined through thermogravimetric analysis. TG and DTG profiles of the samples’ combustion processes are presented in figure 7, and a notable difference in the combustion behaviors of raw TS can be observed after the HTC treatment. The main combustion process can be divided into three stages, that is...
Figure 6. Whole survey scan (a), Ag 3d core-level (b) and C 1s curve-fitting XPS spectrum of HTC-210–3 and Ag50@HTC-210–3.

Figure 7. TG and DTG curves of raw TS and hydrochars produced under different conditions.
As for the AgNPs immobilized hydrochars generated under 210 °C for 3 h, the temperature intervals in zone 2 further narrowed and shifted to lower temperature, and the corresponding weight loss was continued to decrease when compared with HTC-210–3. Meanwhile, the temperature intervals in zone 3 was also shifted to lower temperature. And this trend of change became more and more significant with the increase amount of AgNPs loading. These results may imply that the immobilized AgNPs played a catalytic role during the devolatilization and char combustion process by acting as catalysts. Moreover, the effect of HTC temperature and time on the combustion behavior of AgNPs immobilized hydrochars were also investigated. As can be seen from figures 7(c), (d) and tabel 3, there was gradual decrease of weight loss and an obviously narrowed temperature interval in zone 2 with increasing operation temperature and time. For instance, the weight loss decreased to 18.70% and the intervals shifted to 155 °C when the HTC temperature increased to 240 °C. As for the zone 3 that corresponded to the combustion of char, in contrast, an opposite trend was observed, the weight loss was increased along with a widened temperature interval compared with that of raw TS. These results suggested that increased HTC intensity could facilitate the decomposition and carbonization of lignocellulosic structure in TS during the HTC process.

As for the AgNPs immobilized hydrochars, a higher fixed carbon content, consistent with the above proximate analysis [35]. Table 3 lists the temperature intervals of the three combustion stages and the corresponding weight loss at each stage. There exists an obvious difference in the combustion behavior as for the raw and its corresponding HTC product (HTC-210–3). Specifically, the weight loss in zone 1 decreased from 5.56% to 2.98%, indicating an increased hydrophobicity of hydrochar. The temperature intervals of zone 2 that corresponded to the devolatilization and combustion stage narrowed and shifted to a lower temperature, accompanied by a decrease in the weight loss from 53.05% to 42.43% after HTC treatment. However, in zone 3, an opposite trend was observed, the weight loss was increased along with a widened temperature interval compared with that of raw TS. These results were ascribed to the decomposition and carbonization of lignocellulosic structure in TS during the HTC process.

The characteristic combustion parameters (including \( T_i \), \( T_m \), \( T_b \), S, and residues) of TS and hydrochar samples are summarized in table 4. Ignition temperature \( T_i \) of TS increased from 218.2 °C to 310.2 °C after the hydrothermal treatment under 210 °C for 3 h, which may be related to the decrease of volatile matters. An obvious increase in \( T_i \) was observed for zone 2 and 3, and the burnout temperature \( T_b \) also increased from 558.3 °C to 575.4 °C, which can be associated with the destruction of lignocellulosic component and the increase of fixed carbon, respectively [16]. All the AgNPs immobilized hydrochar samples exhibit slightly lower \( T_i \) than that of HTC-210–3. Meanwhile, the \( T_m \) of zone 3 decreased significantly compared with HTC-210–3. It is reported the \( T_m \) is inversely proportional to the reactivity of the fuel [36], and thus these results demonstrate that the AgNPs immobilized hydrochar samples possess more reactivity. In addition, the increased maximum weight loss rate of zone 3 also suggested a higher reactivity during the char combustion process. A profound decrease in \( T_b \) was also observed after the immobilization of AgNPs, also indicating an enhanced oxidative reactivity of the samples [37]. These phenomena could be ascribed the immobilized AgNPs on the hydrochars, which played significant catalytic effect on the combustion of char. The catalytic activity may be related to the concentration of silver precursor. For instance, the Ag10@HTC-210–3 sample exhibits the highest comprehensive combustibility index (2.08 × 10⁻⁶ min⁻¹ °C⁻¹). It is usually considered that combustibility index S is an indicator to stand for the combustion reactivity of fuel during the whole combustion process and a higher value of S reflects better combustion performance. Thus, the immobilization of small amount of AgNPs may beneficial for the hydrochar fuel. While the detailed mechanism needs to be further studied.

### Table 3. Weight loss at different temperature intervals during combustion of TS and hydrochar samples.

| Sample       | Zone 1 Temperature intervals | Zone 1 Weight loss (%) | Zone 2 Temperature intervals | Zone 2 Weight loss (%) | Zone 3 Temperature intervals | Zone 3 Weight loss (%) |
|--------------|-------------------------------|------------------------|-------------------------------|------------------------|-------------------------------|------------------------|
| Raw TS       | 40–120                        | 5.56                   | 120–400                       | 53.05                  | 400–570                       | 28.16                  |
| HTC-210–3    | 40–155                        | 2.98                   | 155–390                       | 42.43                  | 390–584                       | 44.70                  |
| Ag10@HTC-210–3 | 40–155               | 2.18                   | 155–380                       | 39.78                  | 380–533                       | 44.06                  |
| Ag50@HTC-210–3 | 40–155              | 2.13                   | 155–365                       | 28.99                  | 365–516                       | 43.59                  |
| Ag50@HTC-210–3 | 40–155              | 1.69                   | 155–348                       | 21.03                  | 348–496                       | 41.41                  |
| Ag50@HTC-180–3 | 40–155              | 1.98                   | 155–372                       | 35.91                  | 372–510                       | 34.41                  |
| Ag10@HTC-240–3 | 40–155              | 1.50                   | 155–347                       | 18.70                  | 347–520                       | 51.96                  |
| Ag10@HTC-210–1 | 40–155              | 3.22                   | 155–386                       | 43.88                  | 386–510                       | 24.24                  |
| Ag10@HTC-210–6 | 40–155              | 1.66                   | 155–360                       | 25.31                  | 360–520                       | 47.05                  |
Table 4. Characteristic combustion parameters of the raw TS and hydrochars produced under different conditions.

| Sample          | $T_i$ (°C) | $T_m$ (°C) | $T_b$ (°C) | DTG$_{\text{max}}$ (%) | DTG$_{\text{mean}}$ (%) | $S$ ($10^{-6} \times \text{min}^{-2} \times \degree \text{C}^{-1}$) | Residues (%) |
|-----------------|------------|------------|------------|------------------------|-------------------------|-------------------------------------------------|--------------|
| Raw TS          | 218.2      | 305.9      | 481.4      | 7.3                    | 5.6                     | 558.3                                           | 4.61         |
| HTC-210–3       | 310.2      | 336.5      | 503.4      | 15.8                   | 7.1                     | 575.4                                           | 5.56         |
| Ag$_{10}$@HTC-210–3 | 307.4     | 338.2      | 445.6      | 15.2                   | 12.5                    | 520.5                                           | 6.73         |
| Ag$_{10}$@HTC-210–3 | 301.8     | 337.1      | 436.8      | 11.8                   | 9.2                     | 510.9                                           | 6.11         |
| Ag$_{100}$@HTC-210–3 | 297.7     | 329.0      | 417.9      | 8.7                    | 8.3                     | 480.5                                           | 6.09         |
| Ag$_{10}$@HTC-180–3 | 303.3     | 332.4      | 426.0      | 15.3                   | 10.3                    | 498.1                                           | 6.16         |
| Ag$_{10}$@HTC-240–3 | 300.6     | 332.5      | 423.7      | 8.3                    | 11.7                    | 510.6                                           | 6.09         |
| Ag$_{10}$@HTC-210–1 | 303.4     | 344.0      | 413.2      | 13.9                   | 7.7                     | 493.6                                           | 5.71         |
| Ag$_{10}$@HTC-210–6 | 304.7     | 334.8      | 426.0      | 10.1                   | 9.5                     | 514.8                                           | 6.12         |
3.3. FTIR analysis of gas products

The gaseous products during the combustion process of different hydrochars were analyzed by using TG-FTIR technique. Figure 8 shows the three dimensional spectrum of gas products from combustion of HTC-210–3 and AgSO4@HTC-210–3. The appearance of absorbance peaks with time is basically consistent with the weight loss in the above DTG curve. The characteristic infrared absorption peaks of the released volatiles around the maximum weight loss temperatures of zone 2 and 3 are presented in Figure 9.

According to the FTIR spectrum and previous reports, a summary of the identified gaseous products is listed in Table 5. A few permanent gaseous components, such as H2O, CO2 and CO, could be readily identified on the basis of their characteristic FTIR bands [38]. The band at 4000–3500 cm⁻¹ correspond to the stretching vibration of O–H bond presenting the formation of H2O. The generation of CO2 is assessed from the stretching vibration of C=O at bands of 2400–2250 cm⁻¹ and 750–600 cm⁻¹. The absorption band at 2250–2000 cm⁻¹ represents the formation of CO. The generation of CO2 and CO could be mainly attributed to the combustion
reactions of hydrochars and the breakage of ether bond, respectively [39, 40]. And CO₂ was the dominant gaseous products during the combustion of hydrochars.

A small amount of organic components can also be identified between the wavenumber of 1900 and 1440 cm⁻¹. The absorption band at 1900−1650 cm⁻¹, corresponding to the stretching vibration of C=O, are relative complex and identifying each compound is difficult. Previous studies have pointed out that these bands indicate the presence of ketone, aldehyde and acids [40]. The absorbance bands between 1600 and 1440 cm⁻¹ can be assigned to the C=C stretching vibration and benzene skeleton vibration [41], which indicating the production of aromatics during the combustion of hydrochar. Besides, by comparing the HTC-210−3 and Ag₅₀@HTC-210−3 samples from figures 8 and 9, it could be observed that the relative concentrations of produced gases are different. This phenomenon is mainly ascibed to the immobilization of AgNPs on the hydrochar.

In order to further evaluate the effect of AgNPs immobilization during combustion process, the evolution of absorbance intensity of the identified gaseous products with combustion temperature are compared and presented in figure 10. The release of H₂O from combustion of HTC-210−3 occurred in a wide temperature range with two peaks at 366 °C and 563 °C. As for the Ag₅₀@HTC-210−3 sample, H₂O was released in a narrowed temperature range with a decreased peak temperature of 484 °C. It was reproted that the H₂O was mainly derived from the dehydration stage or the combustion reactions between oxygen and hydrogen elements in the oxidative stage [42]. In this respect, the immobilized AgNPs reduced the barrier for hydrochar combustion, as reflected by the decreased peak temperature for H₂O release. For the HTC-210−3 sample, the evolution profiles of CO₂ (at 2354 cm⁻¹ and 671 cm⁻¹) and CO exhibit the similar shape within the release temerature range of 300 to 700 °C. While the absorbance intensity of CO₂ is approximately 15 times higher that of CO. There are two evolution peaks for the release of CO₂ and CO, a dominant peak at around 550 °C with a shoulder peak at around 370 °C. This suggested that the emission of CO₂ and CO during the char combustion stage was higher than the combustion process of volatile components [43]. However, an obvious change was observed for the release profiles of CO₂ and CO As for the Ag₅₀@HTC-210−3 sample. The release temperature range narrowed, ranging from 300 to about 560 °C with only one dominant peak at around 460 °C. In addition, the maximum absorbance intensity of absorbance peak of CO₂ increased while the intensity for CO decreased. Generally, the intensity of absorbance at a specific peak is linearly dependent to the relative concentration of the corresponding component. This result suggested that the immobilized AgNPs may enhance the intensity of char combustion by acting as a catalyst, resulting in the reduced emission of harmful gas CO and the narrowed release temperature range.

The evolution of organic components, such as ketone, aldehyde, acid and aromatics is shown in figures 10(d) and (e). As for the HTC-210−3 sample, the C=O contained organic compounds were mainly released at lower temperatures, ranging from 250 to 490 °C with a maximum emission at 360 °C. The release of aromatic components increased gradually with a peak also at 360 °C, and then decreased slowly. The generation of organic compounds were mainly in the devolatilization and combustion stage, associated to the fracture of alkyl side chains, acyl groups and the bonds in esters in the hydrochar [42, 44, 45]. The immobilization of AgNPs had moderate effect on the emission of C=O and C=C contained organic compounds. The released amount was decreased while the emission temperatures were not significantly changed. This observation of the gas release may indicate that the immobilization of AgNPs played a catalytic effect especially during the char combustion process of hydrochar, thereby decreasing the corresponding combustion temperature and the release of harmful gas CO.

4. Conclusions

In summary, tobacco stem (TS) was converted into hydrochar by hydrothermal carbonization (HTC). Meanwhile, AgNPs were immobilized onto hydrochar through a facile one-pot co-HTC of TS and metal precursor. EDS, XRD and TEM analysis indicated that single-phase AgNPs were successfully formed during the hydrothermal process and evenly distributed on the hydrochar sample. Volatile matter of hydrochar decreased with the increasing concentration of silver precursor, while the fixed carbon exhibited the opposite trend. Remarkable difference of combustion behavior was observed between hydrochar and AgNPs immobilized hydrochars. The ignition temperature, burnout temperature and maximum rate temperature for char combustion have been decreased after the immobilization of AgNPs, indicating an enhanced oxidative reactivity due to the catalytic effect of AgNPs. Furthermore, the different release behavior of gaseous products during combustion process also indicated the immobilized AgNPs played a catalytic role especially in the char combustion stage.
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Conflict of interest

The authors declare no competing financial interest.

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