

# Preparation of activated carbon-metal (hydr)oxide photocatalysts under different heating conditions. Chemical aspects.

## Preparación de fotocatalizadores carbón activado-(hydr)óxidos metálicos en diferentes condiciones de calentamiento. Aspectos químicos.

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### Abstract

This study deals with the preparation of activated carbon (AC)-metal (hydr)oxide (MO) photocatalysts from commercial AC and  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SnCl}_2$ ,  $\text{TiO}_2$  and  $\text{WO}_4^{2-}$  in water, with special emphasis on the chemical changes produced along the process. Overall, three series of samples were obtained by first soaking at 80 °C and oven-drying at 120 °C (S1) and by subsequent heating at 200 °C (S2) or 850 °C (S3) in  $\text{N}_2$  atmosphere. pH of the impregnation solution/suspension was 2.91 with  $\text{Al}^{3+}$ , 1.54 with  $\text{Fe}^{3+}$ , 5.16 with  $\text{Zn}^{2+}$ , 1.37 with  $\text{SnCl}_2$ , 5.84 with  $\text{TiO}_2$  and 9.54 with  $\text{WO}_4^{2-}$ . Data of the process yield at the three temperatures and of the ash content are reported. For S1, yield varies by  $\text{SnCl}_2 >> \text{Fe}^{3+} > \text{WO}_4^{2-} > \text{Zn}^{2+} = \text{TiO}_2 > \text{Al}^{3+}$ .

### Resumen

Se estudia la preparación de materiales de carbón activado (AC)-(hydr)óxido de metales (MO) a partir de un carbón activado comercial y de  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SnCl}_2$ ,  $\text{TiO}_2$  y  $\text{WO}_4^{2-}$  en disolución/suspensión acuosa, con especial énfasis en los cambios químicos producidos a lo largo del proceso. En total se han preparado tres series de muestras mediante remojo a 80 °C y secado en estufa a 120 °C (S1) y posterior calentamiento de estas muestras bien a 200 °C (S2) o a 850 °C (S3) en  $\text{N}_2$ . El pH del líquido de impregnación fue 2.91 con  $\text{Al}^{3+}$ , 1.54 con  $\text{Fe}^{3+}$ , 5.16 con  $\text{Zn}^{2+}$ , 1.37 con  $\text{SnCl}_2$ , 5.84 con  $\text{TiO}_2$  y 9.54 con  $\text{WO}_4^{2-}$ . Se aportan los datos del rendimiento del proceso y el contenido de cenizas de las muestras. Para las muestras de la serie S1, el rendimiento del proceso varía según  $\text{SnCl}_2 >> \text{Fe}^{3+} > \text{WO}_4^{2-} > \text{Zn}^{2+} = \text{TiO}_2 > \text{Al}^{3+}$ .

### 1. Introduction

The technological and economic importance of photocatalysis has increased considerably over the past decades because of the practical interest in air and water remediation, self-cleaning surfaces, self-sterilizing surfaces, and hydrogen generation using green energy of sunlight [1]. In 2009 the global market for photocatalytic products was \$848 million and with an annual growth rate of 14.3 % a global volume of \$1.7 billion was expected in 2014 [2].  $\text{TiO}_2$  is by far the most frequently employed photocatalyst, owing to the advantages of earth abundance, low toxicity, and thermal and chemical stability, besides being cheap, insoluble under most conditions, and photostable [3]. In photocatalytic reactions, metal

oxides are generally suspended in the liquid phase or dispersed over high-surface-area materials. The former process is handicapped by filtration of  $\text{TiO}_2$  fine particles and effective absorption of ultraviolet-visible radiation. In the latter process, activated carbon has been extensively researched and used as a support for  $\text{TiO}_2$  [4]. Semiconductor metal oxides are not only  $\text{TiO}_2$  but also  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ , and  $\text{WO}_3$ . The preparation methods and applications for these metal oxides supported on AC were critically reviewed before [5]. Here, mainly for comparison purposes (see Ref.: 6-8), the chemical and mass changes originated as a result of the impregnation process of AC with  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SnCl}_2$ ,  $\text{TiO}_2$  and  $\text{WO}_4^{2-}$  in water and of the subsequent heat treatment of the resulting products are examined.

### 2. Experimental

Table 1. Preparation of the AC-MO catalysts. Yield and ash content.

Tabla 1. Preparación de los catalizadores AC-MO. Rendimiento y contenido de cenizas.

Series	Sample	Yield / wt%	Ash content / wt%
	AC	-	4.72
S1	A120	102	7.11
	F120	114	13.63
	Z120	103	9.73
	S120	149	27.31
	T120	103	8.82
	W120	106	9.46
S2	A200	93	8.86
	F200	94	13.55
	Z200	91	9.45
	S200	96	27.21
	T200	96	8.05
	W200	96	9.93
S3	A850	90	5.68
	F850	81	14.66
	Z850	84	6.18
	S850	68	2.34
	T850	98	9.33
	W850	95	11.54

Activated carbon (AC) from Merck (1.5 mm average particle size) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (Panreac; reagent grade), and anatase powder (Aldrich; particle size lower than 44  $\mu\text{m}$ ) in water were used in the preparation of the AC-MO. pH of the impregnation solution was in turn 2.91, 1.54, 5.16, 1.37, 5.84 and 9.54. The preparation of the samples was undertaken by wet impregnation in two successive soaking (80 °C, 5 h) and oven-drying (120 °C, 24 h) steps (S1) and subsequent heating at 200 (S2) or 850 °C (S3) for 2 h in  $\text{N}_2$  atmosphere. The yield of the process of preparation of the catalyst samples was estimated by the following expression:

$$Y(\%) = \frac{M_f(g)}{M_i(g)} \cdot 100 \quad (1)$$

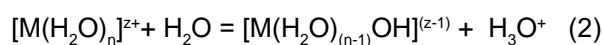
where  $M_i$  is the initial mass of AC or of the samples of series 1 and  $M_f$  is the final mass of product. The codes assigned to the catalyst samples are shown in Table 1, which also lists yield values. The ash content was determined by incineration of the samples at 650 °C for 12 h. Composition data are also compiled in Table 1.

### 3. Results and discussion

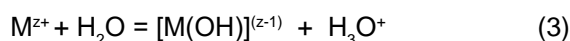
#### 3.1. Preparation of the samples

##### 3.1.1. pH of the impregnation solution

In the preparation of the AC-MO materials from AC and  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SnCl}_2$ ,  $\text{WO}_4^{2-}$  or  $\text{TiO}_2$  in water, the pH of the impregnation solution gives idea of speciation, which is an essential factor because it controls the loading process and as a last resort the mass change produced in AC. As shown in Table 1, the measured pH varies by  $\text{SnCl}_2 < \text{Fe}^{3+} < \text{Al}^{3+} < \text{water} \approx \text{Zn}^{2+} \approx \text{TiO}_2 < \text{WO}_4^{2-}$  and in the wide range between 1.37 for  $\text{SnCl}_2$  and 9.54 for  $\text{WO}_4^{2-}$ . For the  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  ions, the pH variation is consistent with the tendency exhibited by these metal ions to undergo hydrolysis. Metal ions, especially in high oxidation state, in aqueous solution undergo hydrolysis by the reaction (2):



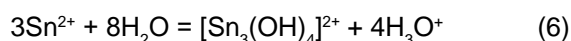
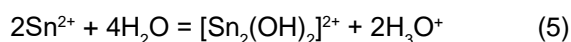
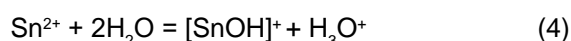
that for the sake of brevity this reaction is often written



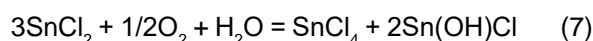
In this reaction, a proton from a water molecule in the coordination sphere of the metal ion is transferred to a water molecule in the solvent. The aquo-cation behaves as a Brönsted's acid, whereas the water molecule does as a Brönsted's base. As a result of the hydrolysis reaction, in general, metal ions in aqueous solution are found as metal aquo complexes and metal hydroxo complexes of formula  $[\text{M}(\text{H}_2\text{O})_n]^{z+}$  and  $[\text{M}(\text{H}_2\text{O})_{n-m}(\text{OH})_m]^{(z-m)+}$ , the chemical composition of these complexes being dependent on the solution concentration (i.e., 0.27 mol  $\text{L}^{-1}$  for  $\text{Al}^{3+}$ , 0.25 mol  $\text{L}^{-1}$  for  $\text{Fe}^{3+}$  and 0.34 mol  $\text{L}^{-1}$  for  $\text{Zn}^{2+}$ ) and pH. The hydrolysis of  $\text{Fe}^{3+}$  begins at about pH 1 with formation of  $[\text{Fe}(\text{OH})]^{2+}$ . Likewise, the species  $[\text{Fe}(\text{OH})_2]^+$ ,  $[\text{Fe}_2(\text{OH})_2]^{4+}$ , and  $[\text{Fe}_3(\text{OH})_4]^{5+}$  were identified, usually at higher pH.

$\text{Al}^{3+}$  can be hydrolyzed extensively to form solutions of polynuclear hydroxides complexes and very large polymeric or colloidal species. Mononuclear species  $[\text{Al}(\text{OH})]^{2+}$  and  $[\text{Al}(\text{OH})_4]^-$  are also formed, the former appearing above pH 3.  $\text{Zn}^{2+}$  hydrolyzes only sparingly in acid media to produce  $[\text{Zn}(\text{OH})]^+$  and  $[\text{Zn}_2(\text{OH})]^{3+}$  before precipitation commences in the neutral region. In basic media,  $[\text{Zn}(\text{OH})_4]^{2-}$  and perhaps  $[\text{Zn}_2(\text{OH})_6]^{2-}$  are formed [9].

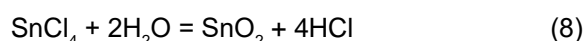
Although  $\text{SnCl}_2$  is mainly covalent in nature the electronegativities of Sn, Cl and O indicate that the Sn-Cl and Sn-O bonds possess a relatively high ionic character and therefore  $\text{SnCl}_2$  is readily soluble in water, i.e. 178 g of  $\text{SnCl}_2$  in 100 g of water at 10 °C [10]. Furthermore, it may take part in a number of equilibrium reactions depending on factors such as pH, concentration, presence of aerial oxygen, and storage time [9, 11-15]. First, in solutions at  $\text{pH} < 2$ , the acidic cation  $\text{Sn}^{2+}$  easily hydrolyses by



and  $\text{Sn}^{2+}$  hydroxichlorides are formed, the trimeric species being the predominant one [9, 11, 12]. In fact, the strength of  $\text{Sn}^{2+}$  as an aqueous acid is principally as a result of the rapid polymerization of the mononuclear conjugate base [13]. At pH near 2,  $\text{SnO} \cdot \text{H}_2\text{O}$  should precipitate and transform into  $\text{SnO}$ . However, in the presence of chloride ion basic salts precipitate first [9, 12] and  $\text{SnO}$  is formed then at higher pH [14, 15]. Second, as the main hydrolytic species of  $\text{Sn}^{2+}$ ,  $[\text{SnOH}]^+$ ,  $\text{Sn}(\text{OH})_2$  and  $[\text{Sn}(\text{OH})_3]^-$  mononuclear species with diluted  $\text{Sn}^{2+}$  solutions ( $5 \times 10^{-7}$  mol  $\text{L}^{-1}$ ) and  $[\text{Sn}_2(\text{OH})_2]^{2+}$  and  $[\text{Sn}_3(\text{OH})_4]^{2+}$  polynuclear species for higher  $\text{Sn}^{2+}$  concentrations ( $10^{-3}$  and  $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ) were also reported [16 and citations therein]. Third,  $\text{SnCl}_2$  is a fair reducing agent that is slowly oxidized in aqueous solution by atmospheric oxygen [17]:



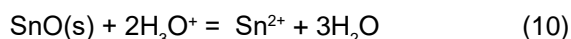
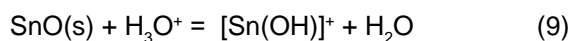
Because  $\text{SnO}_2$  is a weak base,  $\text{SnCl}_4$  in aqueous solution is hydrolyzed to considerable degree, substantially according to:



with the resulting white  $\text{SnO}_2$  remaining in solution in colloidal form. Simultaneously, HCl to some extent combines with un-reacted  $\text{SnCl}_4$  and hexachlorostannic acid,  $\text{H}_2[\text{SnCl}_6]$ , is formed [17]. Finally, during the storage of acidic  $\text{SnCl}_2$  solutions, a small precipitate was gradually formed which became visible only after 30-45 days had elapsed since their preparation. After isolation, the precipitate was made up of the phases of  $\text{Sn}(\text{II},\text{IV})$  hydroxichlorides and other oxo- and hydroxo-complexes [18]. Needless

to say, the low pH of the SnCl<sub>2</sub> solution (i.e., 1.37) used in the impregnation of AC advocates for a predominance of reactions such as (4) and (8), because of a more favourable generation of HCl. In the case of the reaction (8), however, it should be taken into account that the presence of Sn<sup>4+</sup> as colloidal SnO<sub>2</sub> in such a solution should be minor due to the low concentration of O<sub>2</sub> (i.e. presumably ~ 1.3 x 10<sup>-3</sup> mol L<sup>-1</sup> [18]) as compared to SnCl<sub>2</sub> (i.e. 0.44 mol L<sup>-1</sup>) and also the slow kinetics of the reaction (7) [17]. As a result of the very short storage time of the SnCl<sub>2</sub> solution (in fact, it was used immediately after preparation) before using it in the impregnation of AC, in addition to un-reacted SnCl<sub>2</sub> and ions coming from its dissociation, it should primarily contain Sn<sup>2+</sup> polynuclear species rather than Sn<sup>2+</sup> and Sn<sup>4+</sup> polymeric species.

After the SnCl<sub>2</sub> solution was brought into contact with AC, i.e. the measured pH of the point of zero charge (pH<sub>pzc</sub>) for this carbon was as high as 10.50, at the onset of the soaking step, pH should increase because of the protonation of AC basic sites [19] and SnO should then be formed. The following reactions will account for the solubility of SnO in water in an acidic medium [9, 20]:



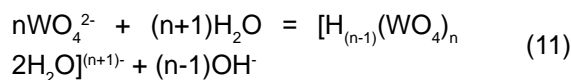
and therefore autoxidation likely went on by further embracing increased amounts of [Sn(OH)]<sup>+</sup> and Sn<sup>2+</sup>. Stannous oxide exhibits a high ability to oxidation and as a result special care was observed in its preparation to protect it from oxygen since the Sn<sup>2+</sup> ion changes very rapidly to Sn<sup>4+</sup> ion in the presence of atmospheric oxygen [20]. Of course, like for the SnCl<sub>2</sub> solution, the extent to which the oxidation process occurred during the soaking step was conditioned by the small amount of O<sub>2</sub> present in the medium. However, the opposite applies to the subsequent oven-drying step at 120 °C, which was performed in air atmosphere and therefore without no restriction to the O<sub>2</sub> availability, apart from its low solubility. This is 3.08 cm<sup>3</sup> (gas at STP) in 100 cm<sup>3</sup> H<sub>2</sub>O at 20 °C [21], although in the SnCl<sub>2</sub> solution under the temperature conditions in the soaking step it should decrease not only because of the higher operating temperature (i.e. 80 °C) but also because of the presence of various inorganic chemical species in the medium. However, relating to the presence of SnCl<sub>2</sub> in the medium, pH should not affect the O<sub>2</sub> solubility as Cl<sup>-</sup> is the conjugate base of the strong acid HCl. During the oven-drying step, it is likely that at the beginning the sudden water evaporation from the wetted-freshly impregnated AC prevented O<sub>2</sub> from entering AC porosity and that, after a certain time had elapsed, the access of O<sub>2</sub> to AC porosity was favored because of the O<sub>2</sub> mobility and thereby diffusion ease at 120 °C.

In connection with the autoxidation of SnCl<sub>2</sub> it was stated before that its study is complicated by the presence of a large number of ionic equilibria involving dissociation, hydrolysis and complex formation [22]. It is a thermal and photochemical chain reaction,

showing peroxide formation, induced oxidation of other molecular species present in the solution, and great sensitivity to positive and negative catalysts. The complex HSnCl<sub>3</sub> or H<sub>2</sub>SnCl<sub>4</sub> was described as playing an important role in the oxidation of SnCl<sub>2</sub> [23]. Furthermore, one such positive catalyst is activated carbon, which accelerated the reaction but not in proportion to the weight used [24]. Air-induced oxidation of organic and inorganic systems goes through free radical processes. Autoxidation reactions are usually subdivided into initiation, propagation and termination reactions. Two types of initial reactions can take place: abstraction of H atoms from various bonds and addition of O<sub>2</sub> to the free radical sites [25]. Molecular oxygen adds and gives peroxy radicals, yet O<sub>2</sub> can also act directly as an oxidant (i.e., electron acceptor) [26]. Since chemical species such as peroxides are stronger oxidants than molecular O<sub>2</sub> (i.e., as a guide, E° is 1.776 V for H<sub>2</sub>O<sub>2</sub> and 1.229 V for O<sub>2</sub> [10]), it can be presumed that in the autoxidation of SnCl<sub>2</sub> AC behaved simultaneously as a catalyst of the reaction and as a reactant that could also be oxidized.

Titanium dioxide (anatase) shows a high tendency to hydroxylation [27]. For hydrated titania obtained by hydrolysis of titanium salts it was assumed that its surface is completely hydroxylated. However drying, even at room temperature, leads to irreversible dehydroxylation [28]. Water adsorption on strongly dehydroxylated anatase takes place in two ways: part of the water molecules are dissociated forming hydroxyl groups again, while the major part of water is adsorbed molecularly [29]. Repetition of the hydroxylation and dehydroxylation cycles leads to a decreasing concentration of the sites for dissociative adsorption, probably owing to surface reconstructions [30]. Accordingly, it seems that after the contact with water already hydroxylated anatase only underwent a slight hydroxylation, in accord with the small pH change produced for the TiO<sub>2</sub> suspension in respect to deionized water.

According to the Pourbaix's diagram for tungsten, the only ionic species stable in aqueous solution at basic pH is the tungstate ion, WO<sub>4</sub><sup>2-</sup>; whereas the existence of pertungstic ion WO<sub>5</sub><sup>2-</sup> remains hypothetical [31]. Because of hydration, structures such as [WO<sub>2</sub>(OH)<sub>4</sub>]<sup>2-</sup> and [W(OH)<sub>8</sub>]<sup>2-</sup> were proposed as well for the WO<sub>4</sub><sup>2-</sup> ion in aqueous solution at pH ≥ 6 [32]. The pH of 9.54 measured for the Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O solution falls within the range of pH values between 9.15 and 10.5 reported in the literature for molar solutions prepared from Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and purified water [33]. The alkalinity of the WO<sub>4</sub><sup>2-</sup> solution may be due to the presence of excess alkali (i.e., NaOH) in commercial Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O or to Na<sub>2</sub>WO<sub>4</sub> hydrolysis and polymerization in accord with the postulated basic mechanism in the formation of iso- and heteropolytungstates from WO<sub>4</sub><sup>2-</sup> [33]:



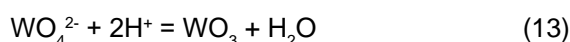
### 3.1.2. Yield

The yield of the impregnation process of AC for S1 data in Table 1 is higher than 100% for all samples and strongly dependent on the MO precursor. Thus,

it varies in the wide range between 102 wt% for A120 to 149 wt% for S120 by S120 >> F120 > W120 > Z120 = T120 > A120 and is markedly higher for F120 and very especially for S120 than for the rest of the samples belonging to S1. Probably, two important factors with influence on the process yield are the diffusion of the MO precursor in pores of AC and the metal density. Diffusion will be mainly dependent on the size of the MO precursor, which may be found as a hydrated, hydrolyzed or polymerized metal ion and also as a hydroxylated MO in the aqueous system. In the case of S120, mass balance is consistent with the involvement of small size tin species (e.g., Sn<sup>2+</sup> and [Sn(OH)]<sup>+</sup>), generated from SnCl<sub>2</sub>, in the diffusion process and with their subsequent oxidation catalyzed by AC, which should ultimately give tin species with a high oxygen content such as SnO<sub>2</sub>. For Fe<sup>3+</sup>, polynuclear hydrolyzed species may be formed in the 0.25 mol L<sup>-1</sup> solution by the reaction [34]:



Likewise, WO<sub>4</sub><sup>2-</sup> should transform into WO<sub>3</sub> by:



despite the high pH of the WO<sub>4</sub><sup>2-</sup> solution and AC's surface (i.e., pH of the point of zero charge is 10.5 for AC). Probably, the reaction (13) was favoured by the evaporation of water during the oven-drying step. Finally, from the low yield for T120 it is evident the influence of particle size on the impregnation process of AC. On the other hand, the latter is also an important factor in connection with the process yield because of the wide set of metal precursors used in the study. Density is a function of the metal atomic mass, which determines the weight of a given amount of sample and for the here used MO precursors it ranges between 26.981 for Al and 183.85 for W [33]. On the other hand, yield varies between 91-96 wt% for S2 and 68 - 98 wt% for S3, and therefore in a wider range for S3 than for S2.

### 3.1.3. Ash content

As can be seen in Table 1, for a large number of AC-MO samples, the ash content is about twice higher than for AC. For S850, however, it is noticeably lower than for AC. For S1, the ash content varies by S120 > F120 > Z120 > W120 > T120 > A120, the correlation with yield being as a rule good. The slightly different ash contents for homologous samples of S1 and S2 argue for a reversible desorption of water and partial dehydroxylation of S1 in the preparation of S2, because of the 200 °C-low heat treatment temperature. On the contrary, for S3 the ash content varies by F850 > W850 > T850 > Z850 > A850 > S850 and widely between 2.34 wt% for S850 and 14.66 wt% for F850. The ash content is low not only for S850 but also for A850 and Z850, whereas it is high for F850 and W850. Accordingly, it is attributable to the carbothermal reduction of M<sub>n</sub>O<sub>m</sub>:



that originates CO release and M. Lower-melting

point metals (i.e. Sn, 231.93 °C; Zn, 419.53 °C; Al, 660.32 °C) will melt and vaporize, whereas higher-melting point metals (i.e. Fe, 1538 °C; W, 3414 °C) will remain unaltered in the samples. This influenced the ash content as both metals should be oxidized again to M<sub>n</sub>O<sub>m</sub> during the incineration process of the samples.

## Conclusions

The preparation of AC-MO photocatalysts from AC and Al<sup>3+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, SnCl<sub>2</sub>, TiO<sub>2</sub> or WO<sub>4</sub><sup>2-</sup> in water has been thoroughly studied by taking into account the concentration and pH, and thereby speciation, of the impregnation solution. For S1, the process yield varies by S120 >> F120 > W120 > Z120 = T120 > A120 and ranges between 102 wt% for A120 and 149 wt% for S120. The mass changes as a rule are stronger for S1 and S3 than for S2. The ash content is higher for F120 and especially for S120 than for the remaining samples. A number of metal oxides are carbothermally reduced at 850 °C and the resulting metal may melt and vaporize, depending on melting temperature relative to heat treatment temperature. The ash content becomes as low as 2.34 wt% for S850.

## Acknowledgements

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