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1 **C-nanocoated ZnO by TEMPO-oxidized Cellulose Templating for**
2 **Improved Photocatalytic Performance**

3
4 **He Xiao^a, Yiwei Shan^a, Wenyao Zhang^c, Liulian Huang^a, Lihui Chen^a, Yonghao Ni^{a,d},**

5 **Bruno Boury^{b*}, Hui Wu^{a*}**

6
7 ^a College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, 350108,
8 China

9 ^b Institute Charles Gerhardt UMR CNRS 5253, CMOS team, Université de Montpellier, CC1701,
10 place E. Bataillon, 34095, Montpellier, France

11 ^c Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L3G1,
12 Canada

13 ^d Limerick Pulp and Paper Centre, Department of Chemical Engineering, University of New
14 Brunswick, Fredericton, NBE3B 5A3, Canada

15
16 Corresponding authors: Bruno Boury (bruno.boury@univ-montp2.fr), Hui Wu
17 (wuhuifafu@163.com)

18
19 **Abstract**

20 Ultrafine C-doped ZnO/carbon nanocomposites with different photocatalytic activities
21 have been prepared using TEMPO-oxidized cellulose as a template but also as the
22 source of carbon. The result is an enhancement of the photocatalytic activity ascribed

23 to different phenomena: a high mesoporosity beneficial to mass transport, a thin
24 carbon layer onto ZnO increasing the charge transfer and hydrophobicity of ZnO, a
25 narrowing of ZnO band gap and an increase of the zinc (V_{Zn}) and oxygen (V_o)
26 vacancies effectively suppressing of the charge recombination. These are evidenced
27 by photocatalytic test of photodegradation of methyl orange (MO) achieved to assess
28 and compared the different photocatalysts. The highest rate constant value of
29 photodegradation of MO is 0.0254 min^{-1} , three times higher than that of ZnO prepared
30 without templates (0.0087 min^{-1}). The present results introduce a new vision of the
31 use of template with multiple roles in the preparation of inorganic materials and
32 specially photocatalysts.

33

34 **Keywords:** ZnO; Cellulose; Photocatalyst; Template; Carbon coating.

35

36 **Introduction**

37 Heterogeneous photocatalysis is one of the most promising processes for
38 pollution control as well as production of chemicals and fuels (Dong et al., 2015; Lee,
39 Lai, Ngai & Juan, 2016; Qu & Duan, 2013; Zhou, Yu & Jaroniec, 2014). Apart from
40 TiO_2 and few others, ZnO is one of the most popular and promising semiconductors
41 with high photocatalytic potential. It is now well documented that large exciton
42 binding energy (60 meV), low price and low toxicity are advantages of ZnO, while
43 major limitations are a wide band gap (3.37 eV), a high recombination rate of
44 photoinduced electron-hole pairs and a photocorrosion with formation of zinc

45 hydroxide(Spathis, 1995). Among the different strategies reported to overcome these
46 drawbacks, achieving nanosizing of ZnO particles is the simplest way to increase the
47 proportion of active sites of the photocatalyst by increasing the specific surface area.
48 This nanosizing also hampers the electron-hole recombination by shortening the
49 diffusion path up to the surface of the photogenerated state. Other strategies to
50 improve the photocatalytic activity, such as nanosizing of ZnO particles can be
51 associated with the presence of metal, metal oxide or sulfide particles(Vaiano,
52 Matarangolo, Murcia, Rojas, Navio & Hidalgo, 2018). Besides, combining this
53 nanosizing with an assembly of carbon (C) to obtain a ZnO/C nanocomposites is
54 emerging as the most attractive approach(Han, Yang, Weng & Xu, 2014). Carbon
55 presents the desired electrical and photophysical properties acting as a temporary
56 photoelectron reservoir to store and shuttle the photogenerated electrons from the
57 semiconductor(Li & Cao, 2011; Samadi, Shivaee, Zanetti, Pourjavadi & Moshfegh,
58 2012; Yang & Xu, 2013; Zhang, Zhang, Tang & Xu, 2012). Carbon is also envisaged
59 to improve the adsorption capability of the photocatalyst surface while improving its
60 chemical stability as an efficient shield against corrosion.

61 However, these properties can deeply vary depending on the C polymorph, e.g.
62 carbon nanotube, graphite, fullerene, graphene. Secondly, fairly different effects can
63 be expected depending on the proportion and location of carbon, varying from a true
64 doping of the ZnO crystal structure with an effect on the band gap(Yu, Zhang & Peng,
65 2016), or a photosensitization of the ZnO semiconductor(Hewlett & McLachlan,
66 2016), or a hydrophobization of the surface with modification of the adsorption

67 capacity(Hong, Lee & Ko, 2011; Yang, Weng & Xu, 2013, 2014).

68 Therefore, the C polymorph and its nanoassembly with ZnO are the keys for
69 photocatalytic activity. Numerous ways to do so already exist, but there is still a need
70 for improvements in terms of performances, sustainability, safety and cost. In this
71 context, biopolymers are increasingly used as template and C-precursors(Boury &
72 Plumejeau, 2015; Foresti, Vazquez & Boury, 2017). The interest in such biopolymer
73 template ability of relies on their efficiency to bind metal cations and achieve an
74 efficient control over the particle size of ZnO during sol-gel or solvothermal processes.
75 Furthermore, although they are removable by calcination, these biotemplates are
76 easily converted into highly porous C upon pyrolysis. So far, work in this area has
77 targeted either the complete elimination of the template upon calcination, or its
78 complete transformation into carbon upon pyrolysis. As we shall see below, we
79 hereby propose an intermediate situation. Beside water-soluble polysaccharides like
80 starch (Cheng, Ji, Wu & Zhang, 2016; Patrinoiu et al., 2016), alginic acid(Cheng et al.,
81 2018), agarose (Tran, 2016)or cellulose acetate(Olaru, Calin & Olaru, 2014; Ye,
82 Zhang, Liu & Zhou, 2011), the water insoluble cellulose is the cheapest and most
83 available polysaccharide. In addition, it is not strategical for food supply, and useful
84 for the preparation of ZnO(Lefatshe, Muiva & Kebaabetswe, 2017; Liu, Yao, Wang &
85 Ma, 2017; Yuan et al., 2017; Zhao, Zuo, Guo & Pan, 2017) and many other metal
86 oxides(Boury & Plumejeau, 2015; Foresti, Vazquez & Boury, 2017). Due to the high
87 hydroxyl content and the presence of very few carboxylic/ate functions in its fibril
88 surface, cellulose can efficiently coordinate metal cations(O'Connell, Birkinshaw &

89 O'Dwyer, 2008; Olivera, Muralidhara, Venkatesh, Guna, Gopalakrishna & Kumar,
90 2016; Wu, Lu, Zhang, Yuan, Xiong & Zhang, 2013; Xiong, Lu, Wang, Zhou & Zhang,
91 2013). Interestingly, increasing such naturally low carboxylic/ate content of natural
92 celluloses is now easily achievable thanks to the development of the regioselective
93 oxidation of the primary alcohol function in C6 position into a carboxylic function
94 using the mixture of the following reagents: NaOCl/NaBr/2,2,6,6-tetramethyl
95 piperidine-1-oxyl known as TEMPO. This chemical modification to increase the
96 carboxylic function of cellulose has recently been reported for example to enhance the
97 mineralization of cellulose with hydroxyapatite for bone tissues engineering
98 (Abouzeid, Khiari, Beneventi & Dufresne, 2018; Safwat et al., 2018). We thought that
99 this could also be an advantage in the case of the mineralization by ZnO and could
100 afford an efficient pathway to better control the nucleation process of ZnO. We have
101 reported the benefit of TEMPO-oxidized cellulose over pristine cellulose(Xiao, Zhang,
102 Wei & Chen, 2018), the improvement in photocatalytic activity was attributed to the
103 higher specific surface area obtained by controlling the growth of ZnO particles. The
104 presence of a very low level of C was also suspected of acting as a doping agent
105 lowering the ZnO band gap. At that point, we thought possible and attractive to
106 modify the preparation of the material in order to achieve a deeply different
107 nanoassembly of ZnO and C, this time targeting a true C coating of the ZnO different
108 from a C-doping. Thanks to the use of ultrasonication during the sol-gel processing of
109 ZnO templated by TEMPO-oxidized cellulose and to a careful control over the
110 temperature during the calcination that preserve a thin layer of C, we are now able to

111 report here the formation of a C-coated ZnO with very high photocatalytic activity.
112 The general strategy of preparation of the samples is summarized in Figure 1, in
113 addition to the complete characterization of materials, we present a comprehensive
114 study of the photocatalytic process of degradation with methyl orange, an
115 identification of the role of the C layer and a comparison with other C-doped ZnO.

116

117 **Materials and methods**

118 *Materials*

119 Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$), sodium hypochlorite
120 (NaClO), sodium bromide (NaBr) and sodium hydroxide (NaOH), hydrochloric acid
121 (HCl) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were of analytical grade and utilized without
122 purification. The above chemicals were acquired from Shanghai Macklin Biochemical
123 Co.,Ltd. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) agent ($\geq 98\%$) and methyl
124 orange (MO) ($\geq 96\%$) were obtained from Aladdin Industrial Corporation. Bamboo
125 dissolving pulp (α -cellulose $\geq 94\%$) was obtained from Fujian Qingshan Paper
126 Industry Co., Ltd and was used without pretreatment before experiment.

127

128 *Preparation of TEMPO-oxidized cellulose (TOC)*

129 The TEMPO-oxidized cellulose was prepared from bamboo pulps according to the
130 previously reported method (Sehaqui, Zhou, Ikkala & Berglund, 2011): Bamboo pulp
131 (2.00 g) was suspended in deionized water (200 mL) at room temperature (25 °C)
132 using mechanical stirring (400 r/min) for 1 h. Then TEMPO agent (0.04 mmol g^{-1}) of

133 dried cellulose) and sodium bromide (NaBr, 0.4 mmol g⁻¹ of dried cellulose) were
134 successively added into the above suspension. Then, sodium hypochlorite (NaClO, 12
135 mmol g⁻¹ of dried cellulose) was added dropwise to the mixture. During the
136 TEMPO-oxidized process, the pH of the mixture was maintained at 10 by adding
137 NaOH (0.1 M) with continuous stirring for 6 h. The obtained suspension was
138 homogenized by sonication (FS-1200N) at 25°C for 5 min with ultrasonic power
139 (1000W), and then centrifuged at 9000 r min⁻¹ for 15 min. The solid residue was
140 recovered, and impurities were thoroughly washed through abundant dilute
141 hydrochloric acid (0.1 M) and deionized water repeatedly. The as-prepared sample,
142 labeled as TOC, was stored at 4°C as an aqueous dispersion for further experiments.
143 Non-oxidized cellulose of bamboo dissolving pulp was denoted as NOC. Carboxyl
144 contents in the different cellulose were determined by the electric conductivity
145 titration method(Jiang & Hsieh, 2013).

146

147 *Preparation of TOC-templated ZnO (TOC-ZnO) and template-free ZnO (FT-ZnO) and*
148 *cellulose-templated ZnO (NOC-ZnO)*

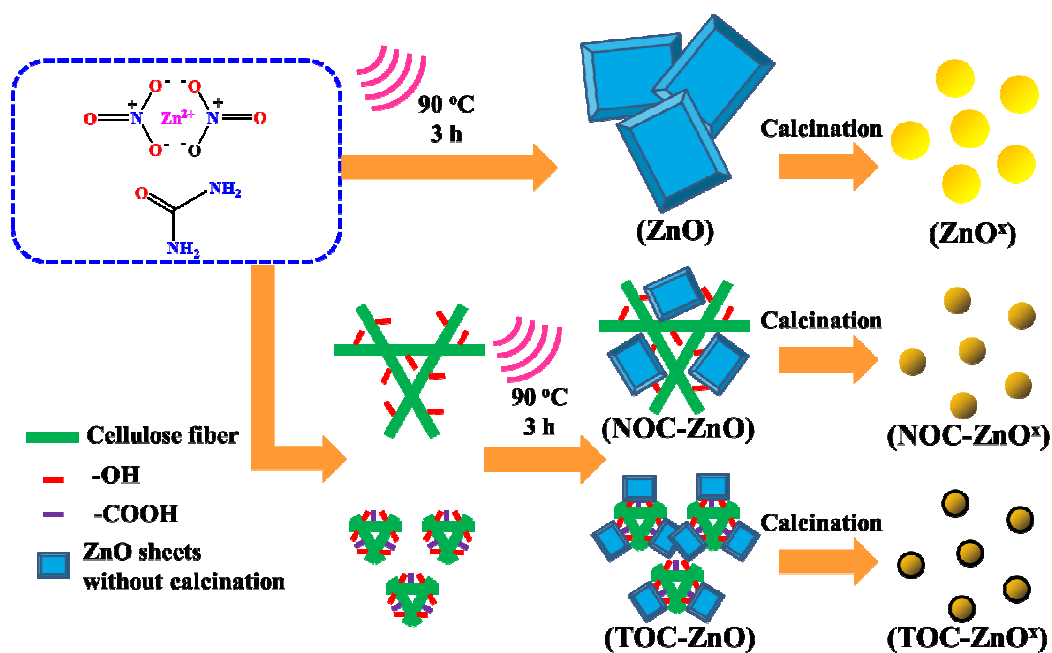
149 TEMPO-oxidized cellulose TOC (1.89 g, 11.67 mmol, 1wt % water suspension) was
150 dispersed in 100 mL deionized water for 30 min at room temperature (25°C). After
151 that, Zn(NO₃)₂·6H₂O (2.97 g, 10 mmol) was previously dissolved in 40 mL deionized
152 water, then added into the TOC suspension with continuous stirring (400 r/min) for 1
153 h at 25 °C. Subsequently, urea (0.36 g, 6 mmol, 0.6 mol L⁻¹ water solution) was
154 dropwise added into the mixtures with ultrasonic process (FS-1200N, 1000 W, 25°C)

155 for 5 min, then heated in an oil bath at 90°C for 3 h leading to the formation of a white
156 suspension. The latter was then repeatedly washed with 500 mL deionized water five
157 times in a row, centrifuged at 8000 r min⁻¹ and vacuum dried at 60 °C for 24 h labeled
158 as TOC-ZnO. For comparison, pure ZnO and ZnO/unmodified cellulose composites
159 were prepared according to the same procedure as described above FT-ZnO and
160 NOC-ZnO, respectively.

161

162 *Preparation of calcined sample TOC-ZnO^x, (x = 300, 400, 500, 600) and TF-ZnO⁴⁰⁰*
163 *and NOC-ZnO⁴⁰⁰*

164 TOC-ZnO were calcined at different temperatures (300°C, 400°C, 500°C, 600°C) in
165 muffle furnace in steady conditions without any air stream or addition for 2 h and then
166 cooled down quickly in laboratory atmosphere leading to samples respectively labeled
167 as TOC-ZnO³⁰⁰, TOC-ZnO⁴⁰⁰, TOC-ZnO⁵⁰⁰ and TOC-ZnO⁶⁰⁰. TF-ZnO and NOC-ZnO
168 were similarly calcined at 400°C in air atmosphere for 2 h denoted as TF-ZnO⁴⁰⁰ and
169 NOC-ZnO⁴⁰⁰, respectively.



170

171 **Fig.1.** Schematic illustration of the concept and general procedure for the preparation of
 172 C-covered ZnO nanocrystals templated by TEMPO-oxidized cellulose.

173

174 *Photocatalyst characterization*

175 TEMPO-oxidized cellulose was analyzed by fiber analyzer (Techpap, MorFi
 176 Compact, France) to characterize the length and width. Fourier transform infrared
 177 (FT-IR) spectra were measured by an FT-IR spectrometer equipped with an ATR
 178 accessory (Pekin-Elmer, 1600, USA) ranging the wavelength from 4000 cm⁻¹ to 400
 179 cm⁻¹. The zeta potential of 0.1 wt% aqueous bamboo dissolving pulp (NOC) and
 180 TEMPO-oxidized cellulose (TOC) suspensions were recorded with a Zetasizer Nano
 181 ZS90 analyzer (Malvern, Britain). The thermogravimetric analysis (TGA) curves were
 182 performed using STA-449 thermogravimetric analyzer (Netzsch, Germany) with a
 183 temperature range of 25-700°C at a heating rate of 10 °C·min⁻¹ in air flow (50
 184 mL·min⁻¹). Raman scattering spectra were recorded on Invia Reflex Raman

185 Microscopy (Renishaw, UK) equipped with a 532 nm laser source. X-ray diffraction
186 (XRD) analyses were recorded out by X-ray diffractometer (Rigaku, Ultima IV, Japan)
187 using Cu K α radiation, tube voltage 40 kV and tube current 45 mA. Contact angle
188 testing was measured by a dynamic drop tension meter (DSA 30, KRUSS, Germany).
189 ZnO-based photocatalysts were coated and adhered to slide glasses with tapes. Then 5
190 μ L of water drop was placed on the surface of the photocatalysts to investigate the
191 contact angle. A field emission scanning electron microscope (Hitachi, SU8010, Japan)
192 was used to observe the morphologies of carbon-doping ZnO samples. The detailed
193 microstructures of ZnO nanocrystals were investigated by using a transmission
194 electron microscopy (JEOL, JEM-2100, Japan) with a field emission gun operating at
195 200 kV. The chemical compositions of ZnO nanocrystals were determined by energy
196 dispersive spectroscopy (HORIBA, XMX 1011, Japan). Total organic carbon content
197 of calcined samples was measured by elemental analyzer (Vario EL cube, Elementar,
198 Germany). X-ray photoelectron spectra (XPS) were measured using an ESCALAB
199 250 instrument (Thermo Scientific, USA) with Al K α radiation monochromatic source.
200 The valence band (VB) values were detected by XPS scanning from 0~10 eV with
201 0.05 eV recording once. The specific surface area and pore characteristics of ZnO
202 nanocrystals were determined by N₂ adsorption-desorption measurements
203 (Micromeritics, ASAP 2020, USA). Diffuse reflectance UV-Vis (DR UV-Vis) spectra
204 were recorded on Cary 500, Varian Corporation. Electron paramagnetic resonance
205 (EPR) measurements were carried out by an EMXnano spectrometer (Bruker,
206 Germany) operating at 77 K with a frequency of 9.4 GHz. The photoluminescence

207 spectroscopy (PL) spectra of the samples were recorded using LS55
208 spectrophotometer (Perkin-Elmer, USA) with 325 nm excitation wavelength. The
209 electrochemical impedance spectroscopy measurement was performed at VersaSTAT
210 MC electrochemical workstation (Princeton, USA). The measurement was carried out
211 in a three-electrode cell with a glassy (FTO) carbon electrode as the working electrode,
212 Ag/AgCl as the reference electrode and Pt plate as the counter electrode.

213

214 *Evaluation of photocatalytic activity*

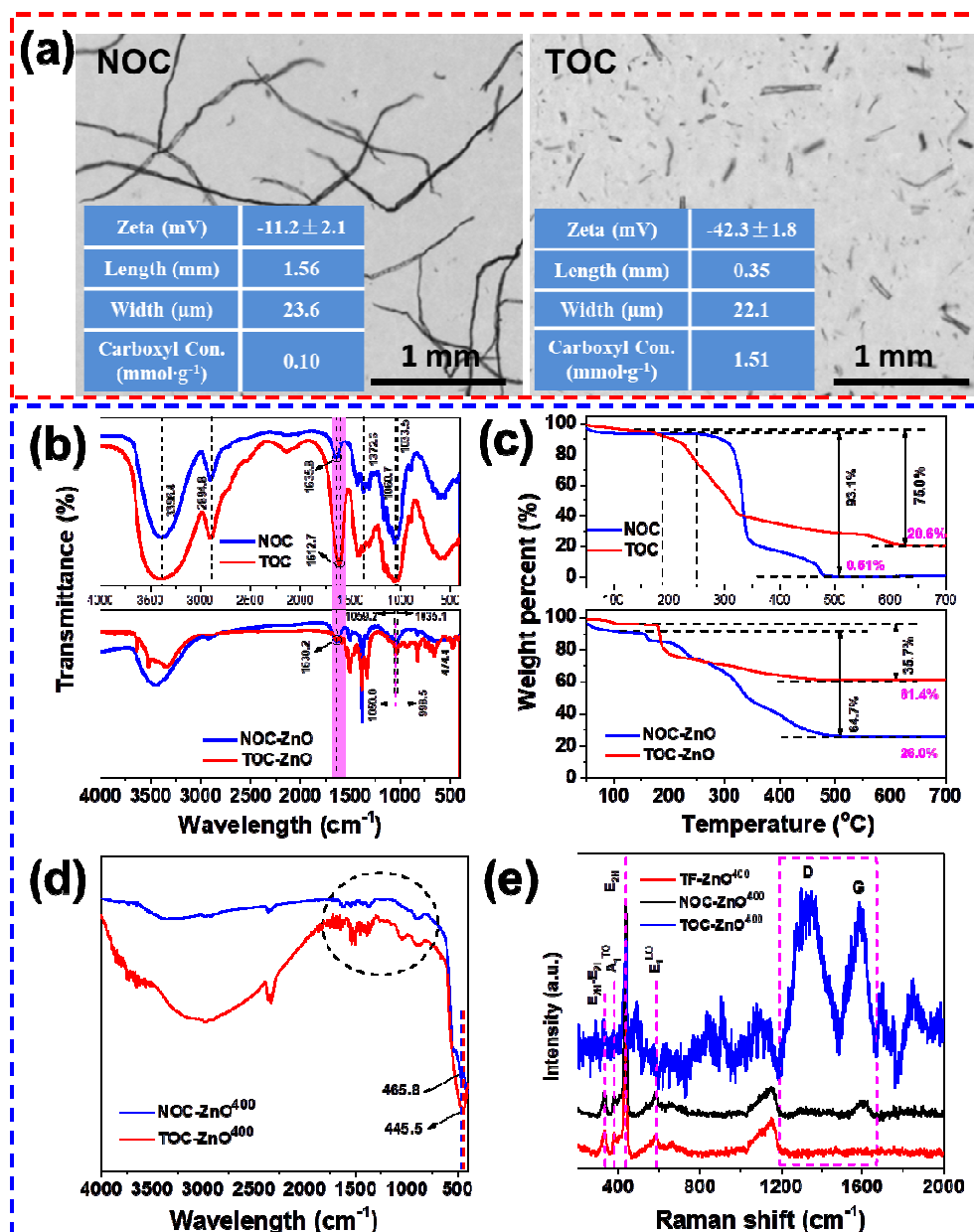
215 The ultraviolet light source is a 6 W lamp with the wavelength range of 200-400 nm
216 (Beijing Zhong Jiao Jin Yuan Technology Co., Ltd.). And the distance between the
217 light source and the reaction tube was fixed as 10 cm (Zhao, Zuo, Guo & Pan, 2017).
218 ZnO-based photocatalyst (25 mg, 0.309 mmol) were added into methyl orange
219 solution (5 mg L⁻¹, 100 mL) with continuously stirring (300 r/min) at 25°C for 30 min
220 in dark conditions in order to reach the adsorption-desorption equilibrium. Then, light
221 irradiation was turned on and aliquots (4 mL) were withdrawn and filtered through
222 PES membrane (Jin Teng Experimental Equipment Co., Ltd., 13×0.22 μm, 0.22 μm
223 pore size, Tianjin, China) at 15 min, 30 min, 60 min, 90 min and 120 min, respectively.
224 The MO concentration of the filtrate was measured by UV-Vis spectrophotometer
225 (Shimadzu, UVmini-1240, Japan) at 463 nm. To investigate the photocatalytic
226 stability of TOC-ZnO⁴⁰⁰ was used in five consecutive cycles with centrifugal
227 separation (washing by deionized water three times and vacuum drying at 40°C for 12
228 hours) after each one. The XRD characterization of the photocatalyst after five cycles

229 was also detected by X-ray diffractometer.

230

231 **Results and discussion**

232 *Synthesis and Characteristics of TOC-ZnO, FT-ZnO and NOC-ZnO.* Submicron fibrils
233 of bamboo pulp cellulose were used for controlling morphology, porosity and growth
234 of ZnO nanoparticles. Prior to reaction with zinc nitrate in urea solution, selective
235 oxidation of the primary alcohol in the C6 position was performed with TEMPO in
236 basic medium to increase the carboxylic/ate content (Isogai, Saito & Fukuzumi, 2011;
237 Pierre et al., 2017). Using the electric conductivity titration method, the proportion of
238 this group in TOC was estimated to 1.51 mmol g^{-1} , much higher than the initial
239 proportion of 0.1 mmol g^{-1} for NOC. This significant increase in the number of
240 carboxylate groups is a decisive element allowing a greater control of the intermediate
241 ZnO growth in the form of a nanoparticle more homogeneously distributed along the
242 fibers (see calculation of this distribution in Table S1).



243

244 **Fig.2** Images and main characteristics of pure cellulosic fibers and TOC (a), FT-IR spectra of
 245 cellulosic fibers and ZnO samples (b), Thermograms of cellulosic fibers NOC and TOC and of
 246 ZnO samples (c), FT-IR spectra of ZnO⁴⁰⁰ samples (d), Raman spectra of three different ZnO⁴⁰⁰
 247 samples (e).

248

249 The size and morphologies of cellulose fibers before and after TEMPO-oxidized
 250 treatment are shown in Figure 2-a,b. As observed by other(Cao, Ding, Yu & Al-Deyab,

251 2012), it is clear that the TEMPO treatment results in a shortening of the length of
252 pristine cellulose (NOC), the latter being frequently ten times longer than the
253 whiskers-like TEMPO-oxidized cellulose (TOC). However, the average width is
254 apparently not modified by the TEMPO treatment. Thus, it indicates that the side
255 reactions of TEMPO oxidation that lead to chain scission occurred mainly in some
256 specific part of the fibers resulting in their scission and subsequent length reduction.
257 The amorphous domains of the cellulose fiber are candidates for this as observed in
258 other chemical treatment of cellulose, e.g. acidic hydrolysis. A consequence of the
259 chemical modification is an important decrease of the Zeta potential from -11.2 mV
260 for NOC to -42.3 mV for TOC resulting from the increase of anionic carboxylate
261 groups on the surface of the TEMPO-oxidized cellulose.

262 The ZnO-containing materials were prepared by solvothermal process in mild
263 condition (3 h, 90°C) either without cellulose, or with cellulose or with
264 TEMPO-oxidized cellulose (Figure 1). The FTIR spectra of NOC and TOC are
265 compared in Figure 2-b. Several characteristic peaks are similar, especially those at
266 3396.4 cm^{-1} , 2894.8 cm^{-1} and 1372.6 cm^{-1} respectively due to O-H and C-H stretching
267 vibrations and C-H asymmetric deformations. Besides, the C-O stretching vibrations
268 are slightly shifted from 1060.7 cm^{-1} for C to 1033.5 cm^{-1} for TOC. However, the
269 major difference between both samples is the position and intensity of the C=O
270 stretching frequency of carboxylate groups of NOC (1635.8 cm^{-1}) and TOC (1612.7
271 cm^{-1}), both phenomena being related to the TEMPO oxidation. For NOC-ZnO the
272 characteristic peak at 1059.2 cm^{-1} and 1035.1 cm^{-1} are respectively assigned to

273 glucose ring skeletal vibration and C-O stretching vibration peak. These bands are
274 shifted for TOC-ZnO respectively to 1049.1 cm^{-1} and 992.3 cm^{-1} , this being ascribable
275 to H-bonding between cellulose and oxo- or hydroxo-Zn species in nanoparticles (Ali
276 et al., 2016). Due to the limit of the spectrometer, the maximum of band absorption
277 for the stretching mode of ZnO at 431 cm^{-1} is not observed.

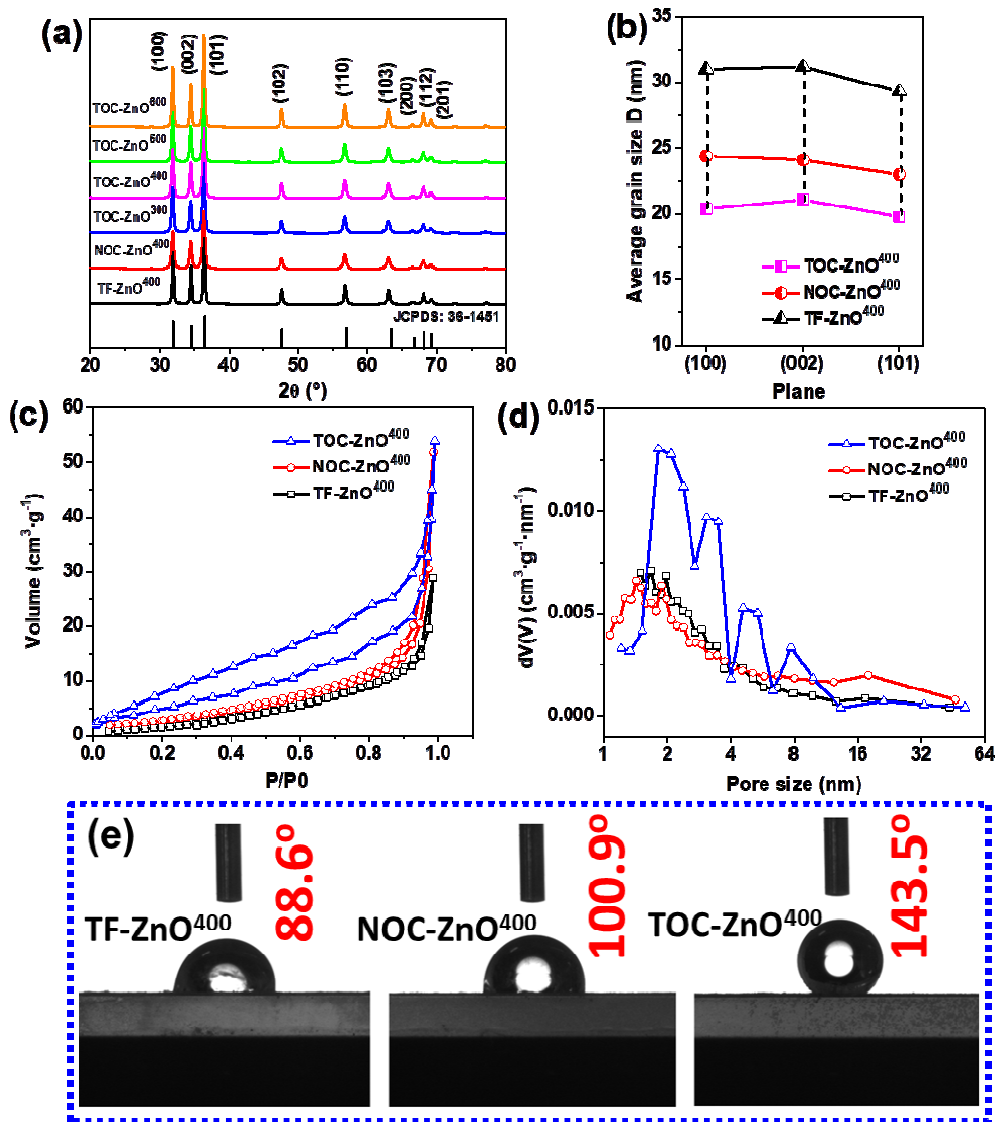
278 To evaluate the relative proportions of cellulose and ZnO in the TOC composite,
279 thermogravimetry analysis was performed on NOC, TOC, NOC-ZnO and TOC-ZnO,
280 (Figure 2-c). Weight loss starts earlier for TOC ($180\text{-}190^\circ\text{C}$) than for NOC (250°C),
281 this results from possible esterification of the abundant carboxylic and hydroxyl
282 groups in TOC compared to NOC. It can also be ascribed to dehydration between
283 residual Zn(OH) functions. For NOC alone, a 99.5% weight loss by 700°C is
284 measured, much higher than the weight loss for TOC, of up to 79.4%. This is ascribed
285 to the presence of sodium carboxylate and its decomposition upon pyrolysis result in
286 sodium oxide. When nano-assembled with ZnO, the situation is very different, and
287 TGA curves reveal that a much higher proportion of ZnO is assembled with TOC
288 (40.8% yield at 700°C for TOC-ZnO) compared with NOC (25.5% yield at 700°C for
289 C-ZnO). Additionally, these analyses indicate that the decomposition of cellulose is
290 almost complete by 500°C . Indeed, after thermal treatment at 400°C , FTIR analysis in
291 figure 2-d shows tiny peaks ranged from 1800 to 1000 cm^{-1} that cannot be attributed
292 to ZnO and are ascribed to carbonaceous residue issued from NOC or TOC. The Zn-O
293 stretching vibration peaks at 465.8 cm^{-1} for NOC-ZnO⁴⁰⁰ and 445.5 cm^{-1} for
294 TOC-ZnO⁴⁰⁰ are blue-shifted compared to the TF-ZnO⁴⁰⁰ (474.4 cm^{-1}), which is

295 ascribable to the smaller crystal size after the template preparation process(Yu, Chen,
296 Wang & Yao, 2015).

297 To further investigate the characteristics of the samples, the Raman spectra of
298 TF-ZnO⁴⁰⁰ (Figure 2-e) show that four main peaks at 331.4 cm⁻¹, 380.8 cm⁻¹, 437.4
299 cm⁻¹ and 584.4 cm⁻¹ were assigned to E_{2H}-E_{2L}, A₁^{TO}, E_{2H} and E₁^{LO}, respectively. In the
300 spectra of NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰, the peaks of E_{2H}-E_{2L}, A₁^{TO} and E₁^{LO} are all
301 blue-shifted, respectively 329.5 cm⁻¹ and 326.2 cm⁻¹ for E_{2H}-E_{2L}, 378.9 cm⁻¹ and 374.8
302 cm⁻¹ for A₁^{TO} and finally 582.6 cm⁻¹ and 574.4 cm⁻¹ for E₁^{LO}. A possible explanation is
303 the presence of a doping phenomenon as frequently reported to explain blue shift in
304 metal oxides like ZnO(Beltran, Barrero & Punnoose, 2019). Carbon arising from the
305 residue of cellulose is one candidate as evidenced by EDX analyses given below.
306 Besides, an important feature of the Raman spectrum of TOC-ZnO⁴⁰⁰ is the presence
307 of two dominant peaks at approximately 1340 cm⁻¹ and 1590 cm⁻¹, usually attributed
308 to D and G signals of graphitic carbon structure. The broadness and the low intensity
309 of the signals indicate two important points: first the thinness of the carbon domain,
310 and secondly the highly disordered structure of the graphitic carbon. An expected
311 situation if considering the low temperature of calcination. However, this is clearly
312 different from NOC-ZnO⁴⁰⁰ and TF-ZnO⁴⁰⁰ for which no signal in these regions are
313 observed.

314 The EDX analysis confirms the effect of the cellulosic oxidized template on the
315 composition of the material, namely the presence of residual carbon: 1.09% in
316 TOC-ZnO⁴⁰⁰, 0.47 % in NOC-ZnO⁴⁰⁰ and only 0.23% in TF-ZnO⁴⁰⁰, given in Fig.S1.

317 In the latter, the total organic carbon from quantitative element analysis gives slightly
318 different values: 0.45% in TOC-ZnO⁴⁰⁰, higher than 0.14% for NOC-ZnO⁴⁰⁰ and
319 0.05% for TF-ZnO⁴⁰⁰. Surface contamination by CO₂ and carbonate-related species
320 can explain the higher values obtained by EDX. However, the high C-contents are
321 clearly related to the use and decomposition of cellulosic template, samples were
322 gold-coated for analysis. The presence of such residual carbon is further demonstrated
323 below by the TEM images. This can result from the fact that tiny parts of the
324 cellulosic template are not fully accessible to oxygen and are carbonized but not
325 further oxidized into CO₂ and water. This phenomenon is favored by the relatively
326 low temperature of calcination used here (400°C) and the absence of any air stream in
327 the furnace, however, the reason why the TEMPO-oxidized cellulose leads to higher
328 C-content is not understood at present.



329

330 **Fig.3** Powder XRD patterns of samples after calcination (a) and average grain size (D) of (100),

331 (002) and (101) for TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ (b), N₂ adsorption-desorption

332 isotherms (c), pore size distribution derived from desorption isotherm of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰

333 and TOC-ZnO⁴⁰⁰ (d) and micrographs of contact angles measurements of TF-ZnO⁴⁰⁰,

334 NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ (e).

335

336 For all the samples, the X-ray diffraction pattern is in good accordance with the

337 characteristic of the hexagonal wurtzite structure ZnO (JCPDS 36-1451) with

338 characteristic peaks at 31.90°, 34.56°, 36.40°, 47.68°, 56.74°, 63.00°, 66.50°, 68.08°,
339 69.22° indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201) planes
340 respectively (Figure 3a, Table S2). However, the TOC-ZnO without calcination
341 contained ZnO with lower crystallinity as evidenced in Fig.S2. Moreover, other
342 signals of the patterns could be attributed to zinc(II) hydroxocarbonate [$\text{Zn}_4(\text{OH})_6\text{CO}_3$]
343 (PDF: 19-1458). The presence of the latter is important for further understanding of
344 the evolution, characteristics and performances of the material after calcination.

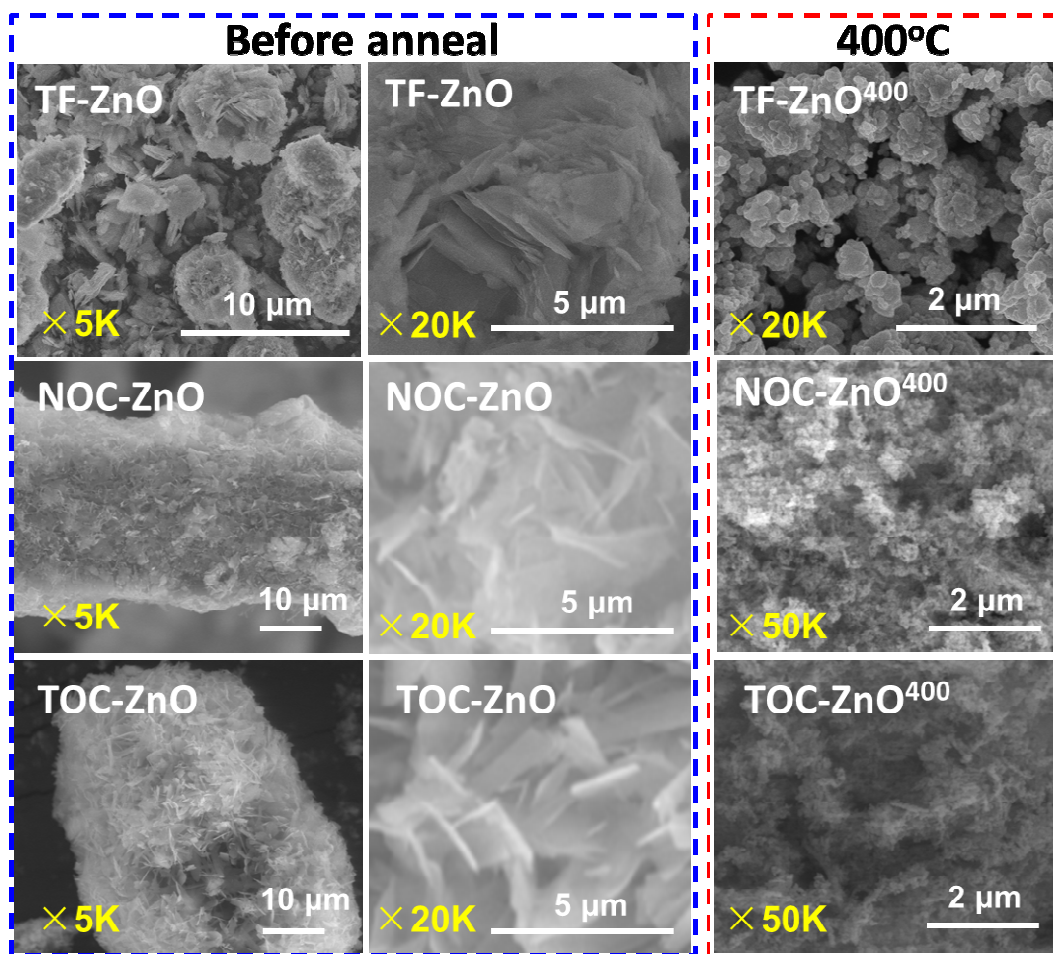
345 The effect of cellulose template on the properties of ZnO is also revealed by the
346 values of specific surface area, pore volume and pores distribution obtained from
347 nitrogen porosimetry measurements and shown in Figure 3c, d and Table S3. The
348 adsorption-desorption isotherms of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and specially
349 TOC-ZnO⁴⁰⁰ corresponded to the type IV curve with a H3 hysteresis loop, which
350 confirms the mesoporous nature of all the samples probably arising from intergranular
351 voids. From Figure 3d, as supported by the broad hysteresis loop, TOC-ZnO⁴⁰⁰ is
352 clearly less microporous than TF-ZnO⁴⁰⁰ and NOC-ZnO⁴⁰⁰ showing an important
353 proportion of pore with $\varnothing < 2$ nm, and a higher proportion of mesopores $2 < \varnothing < \approx 20$ nm.
354 From Table S3, the specific surface area and pore volume of as-prepared ZnO samples
355 was as follows: TF-ZnO⁴⁰⁰ < NOC-ZnO⁴⁰⁰ < TOC-ZnO⁴⁰⁰. There are four possible
356 driving forces for the formation of mesopores. Part of it can initially originate from
357 inter-particles voids left between the vicinal nanoparticles attached to cellulose, this
358 can be seen as an effect of the cellulose hard templating. Secondly, during the
359 calcination, these nanoparticles are prevented from collapse and sintering by the

360 presence of the carbon residues and layer (Fig.S1) that also can result in mesoporosity.
361 Thirdly, either during the hydrothermal process, or during the calcination if some urea
362 residues are included in the pre-calcined ZnO nanoparticles, their decomposition
363 generates CO₂ can also result in pore formation. This can also occur during the
364 thermal decomposition of the Zinc(II) hydroxocarbonate (identified in X-ray
365 diffraction pattern, Fig. S2) that is evidenced before calcination, and which
366 decomposition can occur by multistep mechanisms (see in Fig.S3). Another effect of
367 the use of TOC instead of NOC is a deep change of the hydrophobic/hydrophilic
368 balance of the material surface. As shown in Figure 3e, the contact angles of
369 TOC-ZnO⁴⁰⁰ (143.5°) were far larger than TF-ZnO⁴⁰⁰ (88.6°) and NOC-ZnO⁴⁰⁰
370 (100.9°) demonstrating the higher hydrophobicity of the surface of TOC-ZnO⁴⁰⁰ and
371 an additional evidence of its specificity. However, the powder formed stable mixture
372 in solution of the photocatalytic test as the result of the stirring and possibly of a light
373 photocatalytic oxidation of the C-layer taking place during the beginning of the test
374 and leading to a reduced hydrophobicity.

375 As a primary conclusion on the synthesis of the photocatalyst, it is possible to
376 underline the major effect and advantages of TOC as template in the synthesis of ZnO.
377 First, TOC combined with ultrasonic activation severely limits the growth of ZnO
378 nanocrystals. The abundant carboxyl/ate groups of the TOC probably act as efficient
379 Zn(II) binding sites that increase the number of seeding sites and decrease the ZnO
380 particles size and their aggregation. The massive elimination of TOC upon calcination
381 leads to higher specific surface area and porous volume, both beneficial to drive high

382 mass transfer during the photocatalytic process. However, the low temperature of
383 calcination (400°C) allows preserving a thin carbon layer coating the ZnO
384 nanocrystals.

385 The average grain size determined using typical crystal planes (100), (002) and
386 (101) for TF-ZnO⁴⁰⁰ are found to be similar \approx 30 nm (Figure 3b). The average grain
387 size of the characteristic planes of NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ is lower by 22%
388 and 33% respectively. This indicates that a cellulose template is very effective in
389 reducing crystal growth and agglomeration of primary grains, especially if
390 carboxylate groups have been increased like in TOC as expected; the peak positions
391 of (100), (002) and (101) have negatively shifted with the increase of the temperature
392 of calcination but the average grain size increase by 10-50% in Table S2. Such 2θ
393 shift is attributed at present to the presence of carbon, either as a C-layer or a
394 C-doping, that can generate strain upon calcination. It has been reported that for a
395 nanocrystalline material subjected to a strain, diffraction peaks can be either
396 broadened (due to nonuniform strain, “strain broadening”) and/or shift toward high- 2θ
397 value (for uniform compressive strain) or low- 2θ value (for uniform tensile
398 strain)(Cullity, 1978).



399

400 **Fig.4** SEM images of TF-ZnO, NOC-ZnO and TOC-ZnO before and after thermal treatment at

401 400°C.

402

403 The effect of the cellulose on the morphology of ZnO is evidenced by SEM

404 analysis of samples before calcination (Figure 4) and has consequences on the sample

405 afterward. As shown in Figure 4, large and disordered flake-like aggregates (2~4 μm)

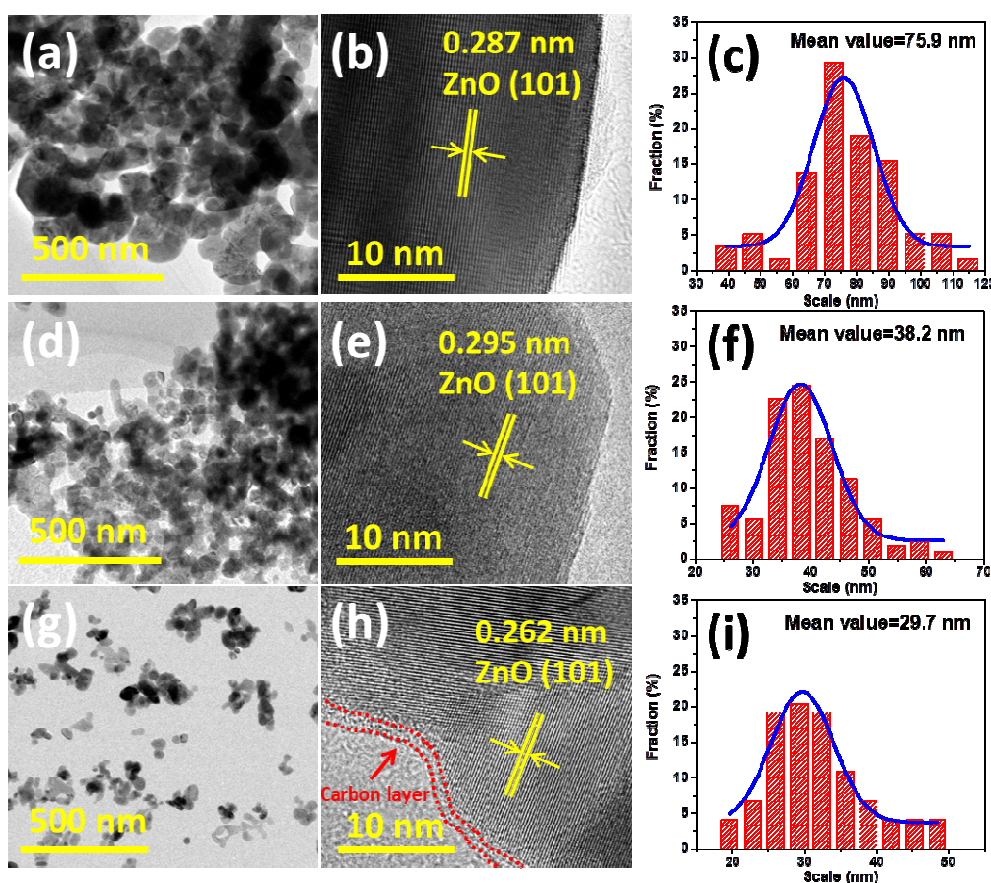
406 of ZnO are obtained in the absence of any template. The presence of NOC or TOC

407 results in a uniform deposit of smaller flakes on the surface of the cellulose template;

408 interestingly they are smaller when using TOC (~1 μm) rather than NOC (1~2 μm).

409 After calcination and removal of the cellulosic template, the original aggregates are

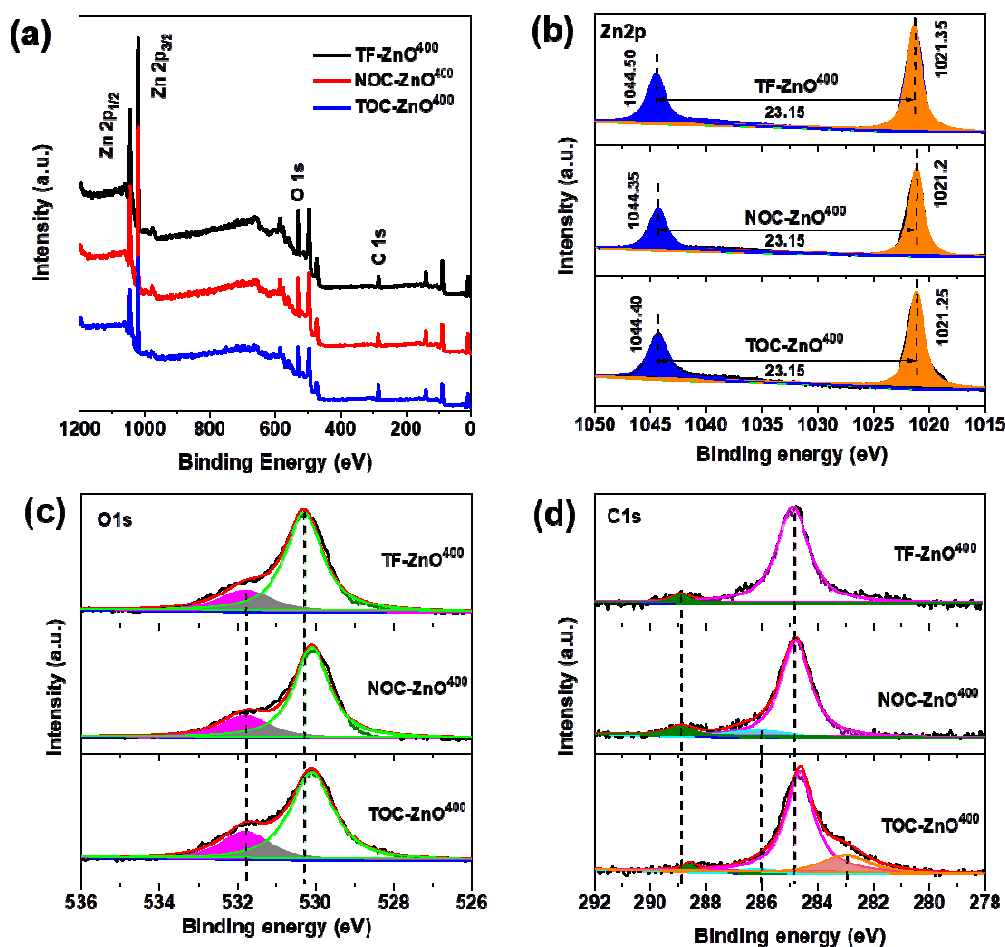
410 transformed. The calcination introduces major modifications with the increase of the
 411 temperature (300~600°C) as shown in Fig.S4; especially, the ZnO morphologies
 412 change from flakes to nanorods and to coarse rounded nano- and macro-particles,
 413 their size gradually increasing with temperature.(Li, Lan, JianPing, XiaoSong, HaiYan
 414 & JinYan; Zhao, Zuo, Guo & Pan, 2017). This modification of morphology
 415 corresponds, at least partially, with the thermal decomposition of loose flake-like
 416 basic zinc carbonate [$Zn_4(OH)_6CO_3$] resulting in ultrafine ZnO with classical nanorod
 417 morphology.



418
 419 **Fig.5** TEM images and particle size distribution of TF-ZnO⁴⁰⁰ (a, b and c), NOC-ZnO⁴⁰⁰ (d, e and
 420 f), and TOC-ZnO⁴⁰⁰ (g, h and i).

421

422 At lower scale, TEM images (Figure 5) further demonstrate the effect of the
423 cellulosic template. When absent, the corresponding sample FT-ZnO⁴⁰⁰ presents ZnO
424 nanoparticles size \approx 40-200 nm (average size=75.9 nm), much larger than the
425 nanoparticle size of NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ \approx 20-100 nm. Both values are
426 higher than the crystallite size determined by X-ray analysis suggesting that the
427 particles may not be completely crystallized or made of several crystallites. Beside the
428 size decreasing with the effect of cellulose template, lattices fringes have also
429 narrowed. In Figure 5-b and 5-e, the lattices fringes (101) measurement is 0.287 nm
430 for NOC-ZnO⁴⁰⁰ a lower value compared to 0.295 nm determined for TF-ZnO⁴⁰⁰. A
431 possible reason of that is a carbon doping in the ZnO and the XRD position (101) has
432 slightly blue shift. Meanwhile, the lattices fringes (101) of TOC-ZnO⁴⁰⁰ have reduced
433 to 0.262 nm, that is mainly caused by the presence of abundant oxygen defects in the
434 ZnO (Liu et al., 2014). Very importantly, at the highest magnification, a thin layer of
435 disorder carbon with thickness \approx 1-3 nm, can be identified especially in boundary area
436 and surrounding the dense ZnO particles.
437



438

439 **Fig.6** XPS data of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ samples: survey scan (a) and core
 440 spectra with deconvolution for Zn-2p, (b) O-1s, (c) C-1s, (d).

441

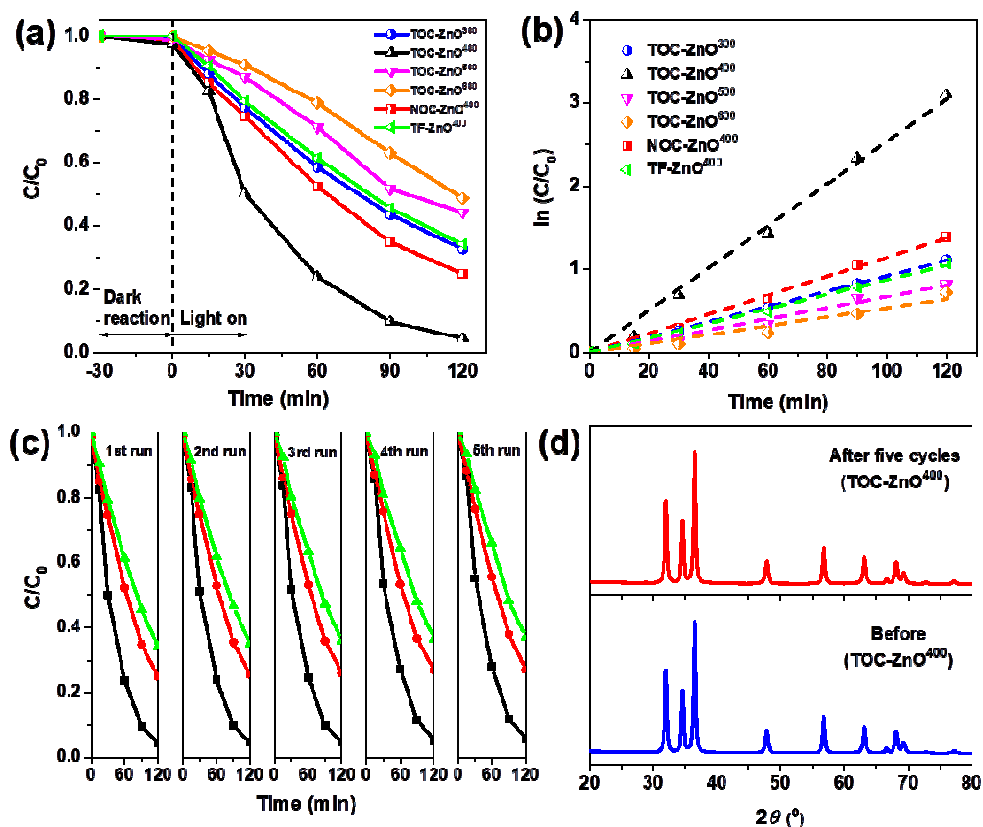
442 To confirm the elemental composition and chemical states of the samples, XPS
 443 spectra are reported in Figure 6 for samples calcined at 400°C. Two peaks at 1021.35
 444 eV and 1044.50 eV are attributed to Zn 2p_{3/2} and Zn 2p_{1/2} levels of Zn(II). For the
 445 NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰, these binding energies are slightly negatively shifted,
 446 which is due to the different chemical interactions (Ansari, Ansari, Foad & Cho,
 447 2017). Besides, the binding energies gap between Zn 2p_{3/2} and Zn 2p_{1/2} of all the ZnO
 448 samples are similar at 23.15 eV, a clear indication that the Zn atoms are in a

449 completely oxidized state. For O1s (Figure 6-c), deconvolution leads to two signals
450 one binding energy at 531.8 eV corresponding to -OH group and one at ~530.3 eV
451 corresponding to lattice oxygen Zn-O(Kotsis & Staemmler, 2006). The latter, in the
452 case of NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ is 0.2 eV lower because of chemical
453 interactions present in the samples(Ansari, Ansari, Foad & Cho, 2017). As
454 summarized in Table S4, the content of the hydroxyl group for NOC-ZnO⁴⁰⁰ and
455 TOC-ZnO⁴⁰⁰ is slightly higher than in TF-ZnO⁴⁰⁰. Meanwhile, the content of lattice
456 oxygen decreased relatively. The C1s high resolution spectra of TF-ZnO⁴⁰⁰ can be
457 divided into two peaks at 288.90 eV and 284.90 eV, while those of NOC-ZnO⁴⁰⁰ and
458 TOC-ZnO⁴⁰⁰ can be deconvoluted into three peaks (288.90 eV, 286.10 eV and 284.80
459 eV) and four peaks (288.60 eV, 286.10 eV, 284.65 eV and 283.00 eV) shown in Table
460 S5. For all the samples, the peaks located at ~288.90 eV and ~284.90 eV could be
461 assigned to the adsorbed CO₂ and graphitic sites (forming C-C group),
462 respectively(Pan et al., 2016). The satellite peak centered at 283.0 eV might be
463 attributed to the O-Zn-C bonds because of the presence of oxygen
464 vacancies(Alshammari et al., 2015; Mishra et al., 2013) and the peaks at 286.10 eV
465 for NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ might be attributed to Zn-O-C bonds(Zhang et al.,
466 2015a).

467

468 *Evaluation of the photocatalytic activity.* The photocatalytic activities of all the
469 samples were evaluated by photodegradation of methyl orange (MO) under UV light
470 irradiation. From figure 7-a and Table S6, the adsorption of MO on all the samples

471 were less than 3% after a 30 min dark adsorption. From a general point of view, the
472 photocatalytic activity follows the order $\text{TOC-ZnO}^{400} > \text{NOC-ZnO}^{400} > \text{TOC-ZnO}^{300} >$
473 $\text{TF-ZnO}^{400} > \text{TOC-ZnO}^{500} > \text{TOC-ZnO}^{600}$. After 120 min of photodegradation, 95.4%
474 of MO was removed by TOC-ZnO^{400} , while the NOC-ZnO^{400} and TF-ZnO^{400} only
475 degraded 74.8% and 65.9% of MO, respectively. Besides, photodegradation of MO by
476 TF-ZnO , NOC-ZnO and TOC-ZnO before calcination was only respectively 5.4%,
477 6.8% and 7.5% after 120 min UV light irradiation in Fig.S5, which shows that proper
478 calcination treatment improves the photocatalytic activities by the conversion of the
479 Zinc(II) hydroxocarbonate into ZnO, and by enhancing the crystallinity of the
480 material. Figure 7-b displays that photocatalytic rate of TOC-ZnO^{400} was up to
481 $2.54 \times 10^{-2} \text{ min}^{-1}$, which is 2.2 times and 2.9 times that of NOC-ZnO^{400} and TF-ZnO^{400} .
482 This can be partially correlated with the higher specific surface area of TOC-ZnO^{400}
483 (see Table S3) the rate constants (k'_{app}) for TOC-ZnO^{400} being both 1.3 times that of
484 TF-ZnO^{400} and NOC-ZnO^{400} (see Table S6). Importantly, this set of data points out
485 that there is an optimum for the temperature of calcination, indeed rate constants for
486 ZnO annealed at lower (300°) or higher (500 and 600°C) temperature are $< 1 \times 10^{-2}$
487 min^{-1} , lower than the one for a calcination performed at 400°C . Compared with other
488 reported literatures in Table 1, TOC-ZnO^{400} appears as a very attractive materials
489 avoiding the use of leachable heavy metal like Cu and very efficient a very low
490 concentration (0.25 mg L^{-1}).



491

492 **Fig.7** Photocatalytic degradation curves of methyl orange by different ZnO^x samples (a) and (b);

493 reusability assessment of TF-ZnO⁴⁰⁰ (▲), NOC-ZnO⁴⁰⁰ (●) and TOC-ZnO⁴⁰⁰ (■) for methyl

494 orange photodegradation (c); XRD patterns of TOC-ZnO⁴⁰⁰ before and after photocatalytic

495 application for methyl orange (d).

496

497 **Table 1** Comparison of photocatalytic activity of TEMPO-oxidized cellulose-derived carbon

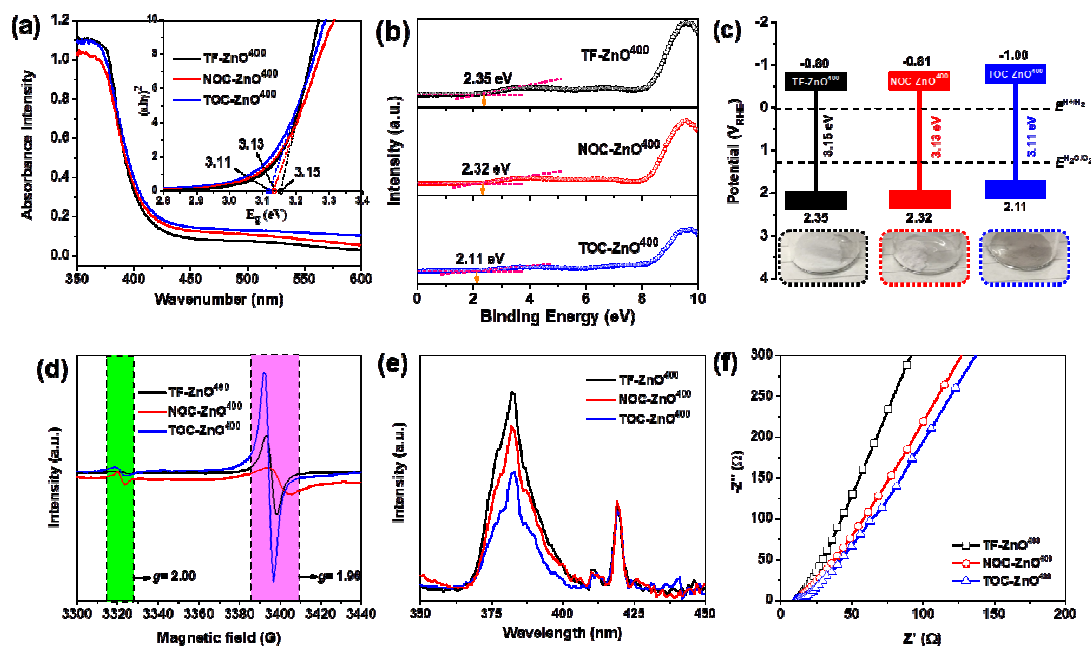
498 coated/doped ZnO with other recently reported ZnO photocatalysts

No.	ZnO samples	Cata. conc. (g L ⁻¹)	Degra. conc. (mg L ⁻¹)	Cata./degra. (g/g)	UV-ir. (min)	Degra. (%)	Ref.
1	ZnO	0.5	10 (MO)	50	180	96.5	(Li, Lu & Luo, 2017) (Gawade, Gavade,
2	ZnO	1.5	20 (MO)	75	100	81	Shinde, Babar, Kadam & Garadkar, 2017)
3	ZnO	2	10 (MO)	200	210	92	(Kumar, Kumar & Umar,

							2013)
4	Cu-ZnO	0.5	10 (MO)	50	90	99.7	(Kadam, Kim, Shin, Garadkar & Park, 2017)
5	Al-ZnO	4	10 (MO)	400	120	95	(Lee, Kim, Park, Hong & Lee, 2015)
6	C-ZnO	0.4	4.8 (MB)	83.3	60	83	(Lee, Lim, Kang & Suh, 2015)
7	C-ZnO	2.5	5 (MB)	500	120	98	(Zhao, Zuo, Guo & Pan, 2017)
8	TOC-ZnO ⁴⁰⁰	0.25	5 (MO)	50	120	95.4	This work

499

500 Photocatalytic reusability of TOC-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TF-ZnO⁴⁰⁰ were
 501 investigated by reusing the catalysis in consecutive MO degradation reactions under
 502 UV-irradiation. Before reuse, the catalysts were only washed with deionized water
 503 and vacuum dried at 40°C. Figure 7-c displays that TOC-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and
 504 TF-ZnO⁴⁰⁰ exhibit total photocatalytic durability after five cycles. Characterization by
 505 XRD demonstrated the absence of structural change for TOC-ZnO⁴⁰⁰ before and after
 506 photocatalytic performance (Figure 7-d).



507

508 **Fig.8** Characterization of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ by UV-vis DRS (a), XPS

509 spectra of all the samples for VB positions (b), VB and CB positions of all the samples (c), EPR
510 spectra (d), PL spectra (e) and EIS Nyquist plot (f).

511

512 *Photocatalytic mechanism.* To explore the mechanism of the photocatalytic activity of
513 carbon-coated ZnO obtained by calcination at 400°C, the band structures of
514 TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ have been probed. From Figure 8-a, the
515 UV-vis diffuse reflectance spectra of all the samples exhibited absorption in the UV
516 region (<400 nm). Compared with TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ have a
517 slightly red shifted absorption and possibly possess absorbance in the visible light
518 region, which is ascribed at present to the carbon doping of the ZnO nanocrystals(Jiao
519 et al., 2017; Zhang et al., 2015b). For the direct semiconductor ZnO, the band gap
520 energy was determined based on Tauc's equation(Shah et al., 2018):

521
$$\alpha h\nu = A(h\nu - E_g)^2$$

522 where α , A, γ , and E_g is the absorption coefficient, proportionality constant, light
523 frequency and band gap energy, respectively. From Figure 8-b, the band gap of
524 TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ are respectively 3.15 , 3.13 and 3.11 eV. In
525 order to measure the positions of conductive band (CB) and valence band (VB),
526 valence band potentials of all the samples were firstly detected by XPS
527 characterization. From Figure 8-b, the VB values of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and
528 TOC-ZnO⁴⁰⁰ were 2.35 eV, 2.32 eV and 2.11 eV, respectively, which was obtained
529 from tangent lines with XPS spectra. Thus, according to the formula ($E_g = VB - CB$), CB
530 values of TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ were -0.80 eV, -0.81 eV and

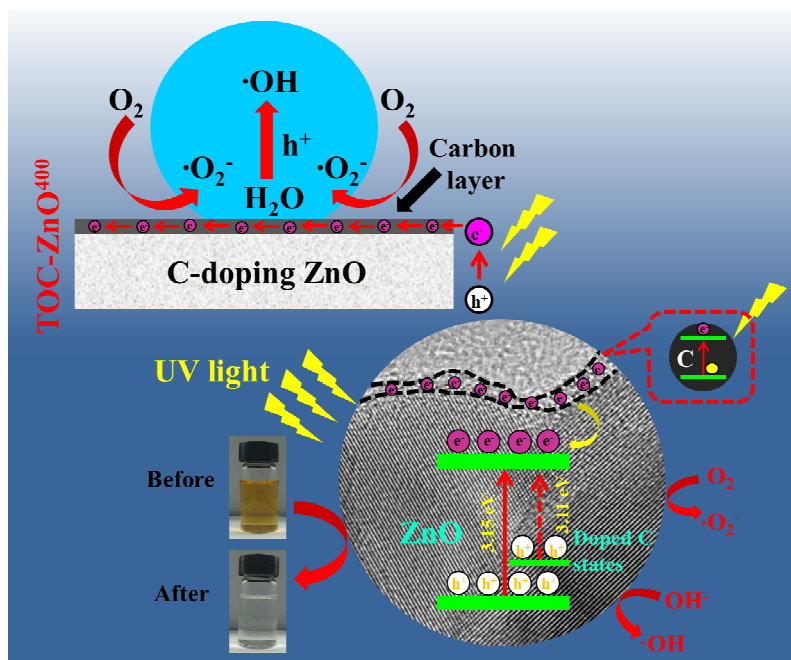
531 -0.10 eV, respectively. CB and VB positions of all the samples are displayed in Figure
532 8-c; ZnO templated by cellulose, especially by TOC template, had shifted to the lower
533 potentials with a narrower band.

534 EPR spectra were recorded in order to evaluate different defects (such as
535 vacancies and interstitials) in ZnO through detecting the unpaired electron spins(Lv,
536 Yao, Ma, Pan, Zong & Zhu, 2013). Oxygen vacancy is one of the important surface
537 defects which can be caused by atom(C)-doping or appropriate thermal
538 treatment(Polarz et al., 2006; Schneider et al., 2009) and Zinc interstitials (called Zn_i)
539 is the other defect due to the incomplete annealing of the precursor(Zeng, Duan, Li,
540 Yang, Xu & Cai, 2010). Both defects are important features of the material since it is
541 known that such surface defects modify and possibly favor the adsorption and
542 photocatalytic activities of catalysts. EPR spectra in Figure 8-d reveal different signals
543 of the TF-ZnO⁴⁰⁰, NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰ ascribed to two kinds of defects in
544 ZnO nanocrystals, namely zinc interstitials (Zn_i , $g=1.96$)(McCluskey & Jokela, 2009;
545 Selim, Weber, Solodovnikov & Lynn, 2007) and oxygen vacancies (V_o ,
546 $g=2.00$)(Polarz et al., 2006). As shown in Figure 8-d, on the one hand, TOC-ZnO⁴⁰⁰
547 and NOC-ZnO⁴⁰⁰ are assumed to have higher intensities of oxygen vacancy than
548 TF-ZnO⁴⁰⁰, because of carbon associated with the ZnO nanocrystals, which is also in
549 accordance with the XPS spectra. Abundant oxygen vacancies in the ZnO could
550 further reduce the band gap in order to enhance the photocatalytic activity(Liu et al.,
551 2014). On the other hand, the content of zinc interstitials of TOC-ZnO⁴⁰⁰ is
552 significantly higher than TF-ZnO⁴⁰⁰ and NOC-ZnO⁴⁰⁰, which might be ascribed to the

553 new bond formation of O-Zn-C as shown in Table S5. Besides, it is assumed that the
554 abundant oxygen defects and zinc interstitials also built enough vacancies and
555 exposed more active sites in order to enhance the photocatalytic activities(Kayaci,
556 Vempati, Donmez, Biyikli & Uyar, 2014; Wang et al., 2012).

557 In the photocatalytic processes, the majority of light absorption and subsequent
558 photo-excitation are usually generated on the surface of the photocatalyst, then
559 leading to the transfer and/or recombination of photo-induced electrons and holes.
560 Photoluminescence (PL) can be used to evaluate the separation or recombination rates
561 of photo-generated electron-hole carriers. A weak PL intensity reflects a low
562 recombination of photo-generated electron-hole carriers. From Figure 8-e, TF-ZnO⁴⁰⁰,
563 exhibited the strongest intensity and the PL intensity decreased in the order TF-ZnO⁴⁰⁰,
564 NOC-ZnO⁴⁰⁰ and TOC-ZnO⁴⁰⁰. Although this difference can result from different
565 phenomenon, it is clear here that the increasing carbon and defect contents in the
566 samples are concomitant with a decrease of the PL intensity(Ansari, Ansari, Foad &
567 Cho, 2017; Chen, Pang, An, Dittrich, Fan & Li, 2019). Although this C-content and
568 zinc/oxygen defects seem to reduce the recombination rates and enhance the
569 photocatalytic performance, the precise physical mechanism is not clear at present. In
570 order to get more evidences of such hypothesis, we compare the differences of
571 electron conductivity of the three samples in order to explain the transfer behavior of
572 photo-induced electrons. Electrochemical impedance spectroscopy (EIS) of ZnO
573 samples (Figure 8-f) was measured to go deeper in understanding the behavior of the
574 material and, eventually explain the difference in photocatalytic activities. The slope of

575 EIS curve of TOC-ZnO⁴⁰⁰ is lower than NOC-ZnO⁴⁰⁰ and TF-ZnO⁴⁰⁰, which indicated
576 that the former had higher electron transfer efficiency that can be ascribed to the
577 C-layer coating on the surface of the ZnO, significantly increasing electron transfer.
578 Thanks to fast transportation of photo-generated electrons, TOC-ZnO⁴⁰⁰ shows the
579 lowest PL intensity resulting from recombination of photo-generated electron-hole
580 carriers discussed above. Besides, it is known that carbon layer could adsorb more
581 ultraviolet and visible light yielding more photo-generated carriers (such as holes and
582 electrons). On the other hand, the doping of carbon in the ZnO lattice leads to the
583 formation of new mid-gap energy states above the valence band of O_{2p} orbitals of
584 ZnO mainly because of the existence of oxygen vacancies and causing to the
585 reduction of VB value(Alshammari et al., 2015; Liu et al., 2014). Above all, due to the
586 co-function of carbon coating and doping, the band gap of ZnO decreases and light
587 absorptions has a red-shift, which is favorable to the generated electrons easily
588 migrating to the conduction band. The photocatalytic reaction mechanism was shown
589 in Figure 9.



590

591 **Fig.9** Schematic illustration of the possible photocatalytic reaction mechanism of C-coated ZnO
 592 obtained from TEMPO-oxidized cellulose.

593

594 **Conclusions**

595 This study introduces new elements on the great versatility of the use of cellulose as a
 596 sacrificial biotemplate for the preparation of metal oxide/C functional nanocomposites
 597 by hydrothermal process. It confirms that carboxyl-content control the morphology,
 598 microstructures and particles size of the metal oxide, ZnO in the present case. We also
 599 show that pyrolysis is not necessary to achieve the presence of nanocarbon associated
 600 with ZnO, this can also be obtained by a careful control of the calcination of cellulose.
 601 Concerning the photocatalytic activity of these materials, it is demonstrated that a thin
 602 carbon layer onto ZnO increases the charge transfer and hydrophobicity of ZnO, a
 603 narrowing of ZnO band gap and an increase of the zinc (V_{Zn}) and oxygen (V_o)
 604 vacancies effectively suppressing of the charge recombination.

605

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613 (2019KFJJ16).

614

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