Electrochemical *bottom-up* synthesis of biomass-derived carbon dots for promoting Knoevenagel condensation

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ABSTRACT

Natural raw materials such as biomass and plant wastes are the most interesting feedstocks for the synthesis of carbonaceous nanomaterials due to their high availability, environmental compatibility, and affinity with *Green Chemistry* principles. Carbon dots (CDs), a new type of carbon nanomaterials, perform an important role in this matter by serving in the development of environmentally friendly catalysts. In this study, CDs were synthesized in good yields by using the electrochemical *bottom-up* synthesis starting from the liquid phase that is separated during the hydrothermal carbonization (HTC) process involving orange peel waste (OPW). The electrochemical setup was also optimized to synthesize CDs based on 5-hydroxymethylfurfural, which represents one of the main components of the liquid phase obtained by HTC. The comprehensive optical and chemo-physical characterization of CDs samples carried out by several techniques such as SEM, TEM, XRD, PL, TGA, and FTIR, highlighted their distinctive morphological and microstructural features. The obtained CDs were successfully employed to catalyse the Knoevenagel condensation, showing excellent results in terms of yield and reproducibility. In addition, the sustainable nature of the CDs was demonstrated by recycling the catalysts up to five cycles without significant activity loss.

Introduction

In recent years, organic chemistry has come a long way in the study and application of green catalytic systems. The development of innovative, eco-friendly, and effective catalytic systems able to go towards value-added chemical transformations in environmentally benign solvents (e.g., water) is a real need.

New catalysts need to be metal-free, easy-to-prepare, obtained by cheap precursors and, if it is possible, recyclable [1]. Many efforts have been made to develop metal-free catalysts as an alternative to current catalysts for performing sustainable chemistry [2] and continue today [3]. Carbon dots (CDs) are a new class of carbon-based zero-dimensional materials, typically less than ≈10 nm in diameter. They present excellent photostability and biocompatibility, low cytotoxicity, small size, fluorescence, and have attracted a lot of attention due to their interesting properties, leading to diverse applications involving bio-imaging,

sensing, catalysis and photoelectronic devices [4]. Both natural and synthetic organic precursor molecules can be used to prepare carbon-based nanomaterials. Increasingly natural carbon sources are chosen to produce CDs because they are cheap, eco-friendly, and extensively accessible [5]. CDs can be prepared mainly by using two methods, the *top-down* and the *bottom-up* procedures. Nanoscale CDs, obtained with *top-down* methods, are synthesized by fragmentation of larger carbon-based structures such as graphite powder [6], petroleum coke [7], coal [8], carbon nanotubes [9] by using acid oxidation, microwave/ultrasonication, ultrasonic/electrochemical/chemical exfoliation or hydrothermal/solvothermal exfoliation and laser ablation strategies. Conversely, with the *bottom-up* methods, CDs are synthesized by the gradual growth of molecular precursor materials such as alcohols [10], amino acids [11] or a mixture sodium citrate with urea [12] by carbonization, hydrothermal, thermal pyrolysis, and microwave strategies (Fig. 1).
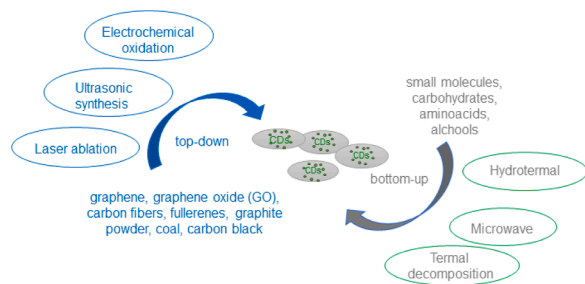
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Fig. 1. Different methods for the CDs preparation, and the *bottom-up* electrochemical approach used in this work.

Both approaches are effective in manufacturing carbon quantum dots of different sizes and characteristics. However, *bottom-up* methods generally led to the production of CDs with well-defined sizes and shapes, so the *bottom-up* approach is usually the preferred route for preparing carbon nanoparticles for catalytic applications [13]. However, most of the reported synthetic processes of CDs are complex, time-consuming and require expensive precursors or post-functionalization. Therefore, the most interesting goal is obtaining CDs from cheap and readily available substances. In this work, we present the *bottom-up* electrochemical synthesis of CDs that are obtained by using waste deriving from industrial agri-food as the starting material (Fig. 1).

Recently, the synthesis of carbon nano structures and their applications in organocatalysis and photocatalysis, have received particular attention as green non-metal-doped catalytic systems [14]. Therefore, carbon quantum dots can be considered valid interpreters to be employed as effective nano-organocatalytic and nano-photocatalytic platforms for a wide range of reactions. The useful CDs have been studied and their superior capability in catalysis applications has been reported [15]. The fundamental aspect of an active catalyst is the number of surface-active sites. The nature of the chemical functionalities on the CDs surface arises from the precursors and the operative conditions that were employed in the synthesis [16]. The presence of numerous polar groups such as carboxylic acids, alcohols, and amines plays a pivotal role in determining the chemical behaviour of these nanoparticles [17]. From the economical and eco-friendly points of view, wastes of industrial and agricultural processes are very attractive starting materials due to their low cost and the chance to recover manufacture side-products by reconverting them into useful materials such as carbon nanostructures. Therefore, the possibility to obtain CDs from crude biomass sources, through reliable and reproducible procedures, becomes an interesting prospect [18]. The waste agriculture materials are excellent precursors source for the synthesis of carbon nano structures because they are cheap and above all, contain large amounts of carbon. Typically, nanostructures synthesized from waste materials are obtained by thermal pyrolysis which requires high temperatures and very long processing times [19]. Therefore, the use of waste materials, together with greener reaction conditions, can render the overall process more attractive from the point of view of sustainability [20]. For this reason, the aqueous phases, deriving from the mild hydrothermal carbonization (HTC) treatment of agri-food waste, due to the residual presence of small added-value molecules, can be a good starting material in the synthesis processes [21]. Electrochemical processes are increasingly a consolidated technique in organic synthesis, as it allows obtaining products through redox reactions in which the electron as a reagent can be easily dosed through the passage of electric current [22].

The severe limitations of fossil fuels and limited resources have increased the studies towards more sustainable synthetic techniques. The electricity can be produced from renewable sources, and so electrochemical methods have attracted particular attention from international academia and industry as environmentally benign and cost-effective techniques [23–25] Thus, the electrochemical approach can represent an efficient and easily repeatable method for the preparation of high-quality CDs [26].

The Knoevenagel condensation reaction is one of the most important reactions for the C=C bond formation between a C=O group and an activated methylene group and has been used to synthesize important chemical intermediates, drugs, and polymers [27]. It occurs between activated methylene compounds and aldehydes to form substituted olefins by losing a water molecule [28–30]. The use of CDs to promote the Knoevenagel condensation is a very interesting metal (ion)-free catalytic methodology for developing metal-free nano catalytic systems in line with the request for more green and sustainable chemistry [31]. Owing to its very frequent utilization in organic synthesis, the Knoevenagel reaction has spurred a continuous investigation aimed to find new, more efficient, and green catalysts [32]. The classical procedures are performed in organic solvents in the presence of bases. As we have recently reported, the mechanism of the Knoevenagel condensation can proceed via the generation of the anion by deprotonation of activated methylene compounds [33,34]. Gianbastiani and co-workers reported the synthesis of multi-walled carbon nanotubes functionalized with aziridines as catalysts in the Knoevenagel condensation [35]. The reactions of ethyl cyanoacetate and different substituted benzaldehydes, an aliphatic aldehyde and a ketone were carried out by stirring the mixtures in EtOH at the reflux for 5 h. Wang and co-workers reported the use of amine-terminated CDs synthesized by pyrolysis of a mixture of citric acid and suitable diamines in 1-octanol at 180 °C (over 6 h) under argon to catalyse Knoevenagel condensation reactions in a biphasic mixture [36]. Therefore, the present study aims to design a simple method to obtain CDs by the valorisation of agri-waste materials and evaluate their applicability as catalysts in the Knoevenagel condensation reactions at room temperature under solvent-free conditions (Fig. 2).

Results and discussion

Aqueous solution (AQS) characterization

The aim of this work is the use of the liquid phase deriving from the hydrothermal carbonization (HTC) treatment of industrial orange peel waste (OPW) that is generally considered a non-exploitable material [21]. Based on our previous studies, the optimal reaction conditions to obtain an aqueous phase rich in organic compounds, useful as raw materials for further EC treatment, are carried out in HTC performed at 180 °C and 60 min [37]. The applied technique to obtain the aqueous solution (AQS) was very mild and avoids the use of organic solvents and acids typically used for these procedures. Reported data show that the main compounds are furan derivatives, especially furfural (16.69%) and 5-(hydroxymethyl)furfural (61.82%) The analysis data of AQS was obtained on ethereal extract by GC and it is reported in the SI (Fig. S1). The presence of large quantity of 5-(hydroxymethyl)furfural (5HMF) is also confirmed by the ^{13}C NMR spectroscopy which mainly shows the chemical shifts corresponding to 5HMF (^{13}C spectra in SI). The electrocatalytic 5HMF transformations have been widely studied and this research area is in its growth phase. Oxidative upgrading of 5HMF opens to future opportunities to combine biocatalysts with electrochemical methods and provides several chemical scaffolds with interesting technological and biomedical applications [38]. Thus, based on our continuous efforts and experience in both biomass valorisation [39] and the development of sustainable electrochemical methods [32–34], an electrochemical process on the AQS, rich in 5HMF, for producing CDs has been developed. It should be underlined that in the field of CDs production from biomass waste, the use of the EC method represents a highly innovative application [40,41].

Electrochemical CDs synthesis

During the HTC process, biomass is dehydrated in-situ and converted
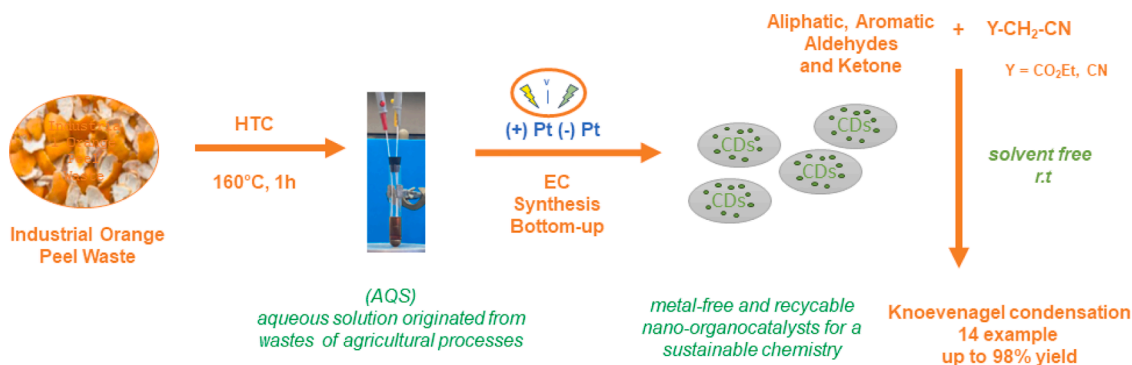
Fig. 2. Synthesis of CDs and their use as metal free nano catalysts.

mainly into three products: solid biocarbon, aqueous liquid (AQS) and non-condensable gaseous products. The CDs were prepared via alkaline-assisted electrochemical *bottom-up* synthesis starting from the cheap and non-toxic. The electrochemical *bottom-up* synthesis was carried out by using two different methods (see experimental section): the galvanostatic one and another under constant potential difference (without a reference electrode). Both methods are effective for the synthesis of nanostructures and the yields of the obtained CDs are reported in Table 1. The different electrochemical methodologies, the electrolysis time (thus, the number of Coulombs) and the purification process have been tested to study the best synthetic procedure to obtain the best yield and the best performance of chemical properties. However, the crucial aspect of the integrated process consists in the reuse of the AQS, still rich in added value molecules. The EC oxidation process allowed to obtain the derived CDs with different functions on their surface. To the aim to compare CDs from waste materials with respect from pure material we decided to synthesize CDs from 5HMF which results the main component of AQS (Table 1, CDs 5HV and CDs 5HI150). The synthesis of 5HMF-based CDs was carried out under the same conditions used on the AQS under constant potential with best yield. Using the same reaction time, the yields of CDs obtained from the 5HMF are lower than those obtained with AQS originated from the waste disposal process of OPW (see Table 1). As reported in Table 1, the best yield was obtained electrolyzing AQS under constant potential difference (two electrodes), applying a ΔE of 8 V (Table 1 CDs V8). Lower yields were obtained using ΔE of 10 or 5 V, (Table 1, CDs V5 and CDs V10) and by performing electrolysis under galvanostatic conditions for both the solutions (Table 1, CDs I150 and CDs 5HI150). However, all these electrolysis techniques, constant potential, and galvanostatic conditions employed an easy and low-cost setup with equipment available in common hardware stores. Therefore, these techniques facilitate the possibility to use those methods and can be of high interest for scale-up in the synthesis or in technical applications.

CDs characterization

In order to evaluate the properties of the synthesized CDs, the characterization tests were performed on the CDs obtained from AQS under the previously discussed optimal conditions and were compared

with the CDs obtained from 5HMF. Several techniques were used (SEM, TEM, EDX, XRD, PL, FTIR, DLS-Zero Potential and TGA) and they have revealed interesting chemical-physical properties which have suggested the use of the synthetized CDs in catalysis; moreover, many common characteristics emerge between the two samples. The SEM image (Fig. 3a) reveals the morphology and the shape of the synthesized CDs. The representative image of CDs structures shows uniformly dispersed small nanoparticles with circular shape. This agrees with TEM analysis, which confirms that the CDs were monodisperse, with a narrow size distribution of 1.47 nm and 6.67 nm for the CDs obtained from AQS (Fig. 3b, c) and less than 8 nm for CDs produced by 5HMF (Fig. 3d). In addition, the elemental composition of CDs was evaluated by energy-dispersive X-ray spectroscopy (EDX) (Fig. S2). The results of EDX indicated that the CDs contain mainly carbon, nitrogen and oxygen, and no observable impurities were detected. EDX spectra of CDs revealed a high content of O because many residual oxygenated groups remain on the surface.

To acquire deeper information regarding the evolution of the microstructure and evidence about the surface groups present, CDs samples were investigated by X-ray diffraction spectroscopy (XRD). The XRD diffraction spectrum (Fig. 4) of CDs obtained from AQS shows a broad amorphous peak centred at $2\theta = 27°$, which can refer to the graphite (002) plane and a weak peak at $2\theta = 35°$, which is clearly related to the turbostratic structure of disordered carbon coming from the (100) plane of graphite of the CDs. The XRD spectrum of CDs obtained from 5HMF also suggests the amorphous pattern. No other peaks were detected in the XRD spectra, thus confirming the amorphous nature of all CDs.

Photoluminescence (PL) spectroscopy was performed to examine the optical properties of synthesized CDs. The optical properties of CDs refer to the various types of functional groups such as hydroxyl, carbonyl and carboxyl groups and the presence of these functional groups is decisive for the origin of the CDs' PL [42]. The typical PL spectra are reported in Fig. 5a. When excited at 370 nm the two aqueous solutions show a fluorescence emission peak at 438 nm, but the CDs obtained from 5HMF show a second band centred at 520 nm. This difference is attributed to the variation of the dimensions and as reported in the literature it can be due to emission traps and the presence of different "surface states", which could also involve the variation of the density and the nature of

Table 1
Reaction conditions for the EC *bottom-up* synthesis of CDs.[a]

CDs	Starting materials	Method I/E/ΔE	Time [h]	Q [C]	CDs [mg]	Yields [%]
CDs V10	AQS 2.5 mL (0.1 mg mL^{-1}) /NH$_4$OH (30%)	$\Delta E = 10$ V	1.0	1284	80.6	30
CDs V8	AQS 2.5 mL (0.1 mg mL^{-1}) /NH$_4$OH (30%)	$\Delta E = 8$ V	2.5	2927	113.2	37
CDs V5	AQS 2.5 mL (0.1 mg mL^{-1}) /NH$_4$OH (30%)	$\Delta E = 5$ V	6	2791	67	22
CDs I150	AQS 2.5 mL (0.1 mg mL^{-1}) /NH$_4$OH (30%)	150mA	3	1620	96	32
CDs 5HV	5HMF (200 mg)/NH$_4$OH (30%)	$\Delta E = 8$ V	2.5	1350	30	16
CDs 5HI150	5HMF (200 mg)/NH$_4$OH (30%)	150mA	2.7	1485	45	23

[a] In a vial, equipped with two platinum electrodes (flat spirals, apparent area: 1 cm^2) and a magnetic stirrer at room temperature.
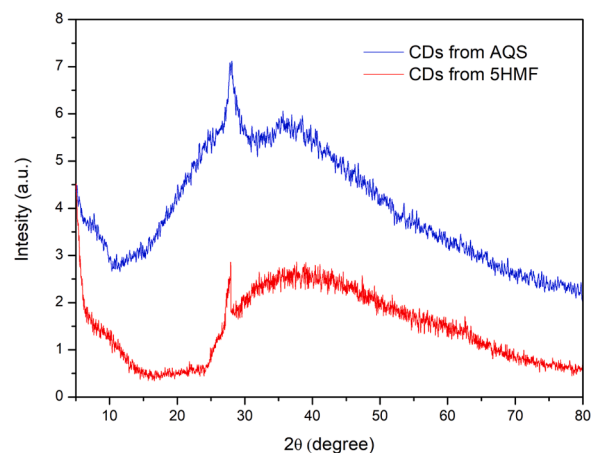
(a)

(b)

(c)

(d)
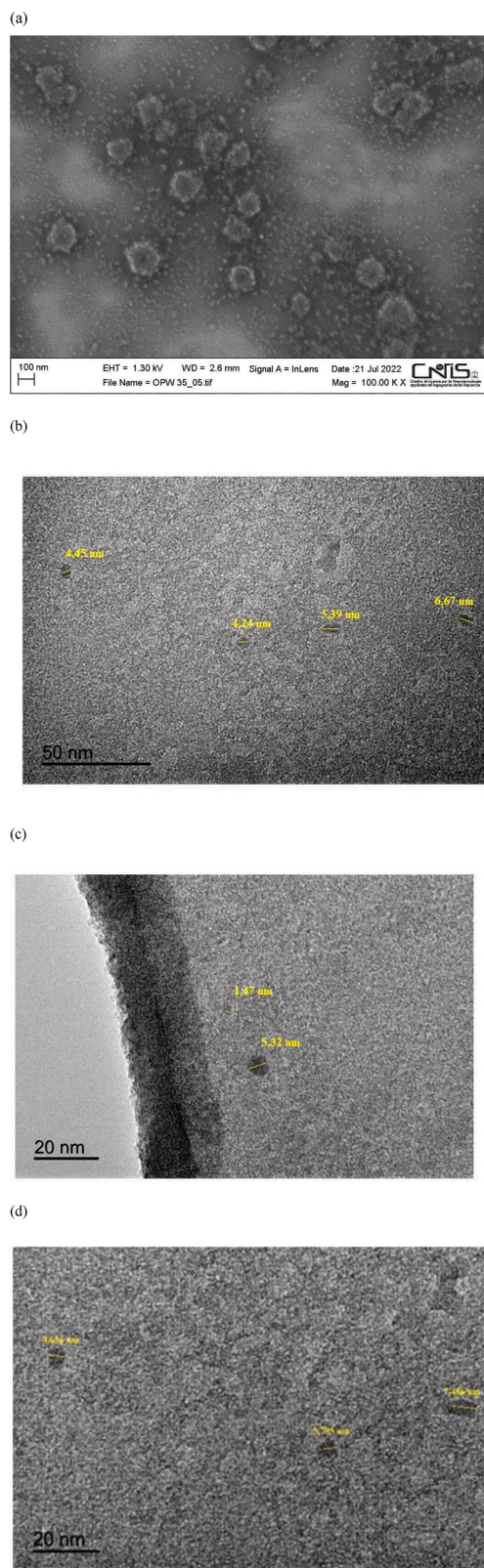
Fig. 3. SEM image (a), TEM image of CDs from AQS (b, c), and of CDs from 5HMF (d).

Fig. 4. XRD spectra of CDs from AQS and CDs from 5HMF.

the available sp^2 sites [43].

As evident from Fig. 5b, the presence of different functionalities on CDs surface was confirmed by FTIR studies. The FTIR spectrum shows the presence of d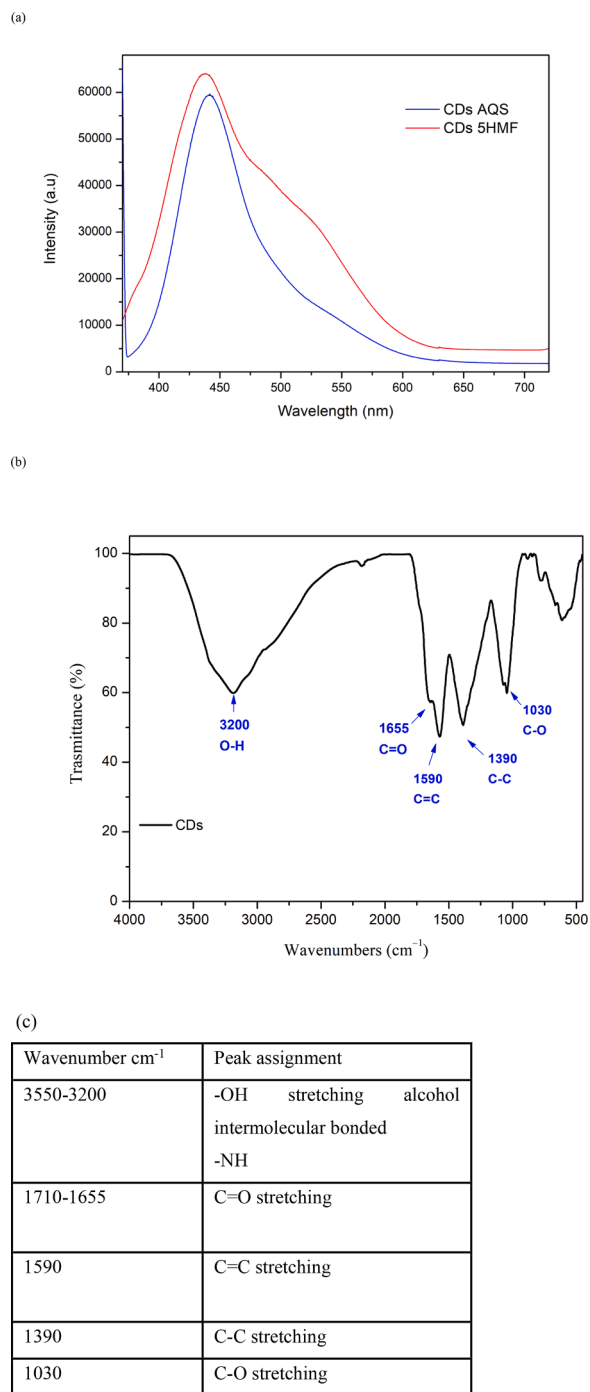ifferent groups on the surface of the nanomaterial. In particular, the band at 3200 cm^{-1} suggests the O—H stretching of hydroxylic or carboxylic functionalities, while the peak at 1049 cm^{-1} can be attributable to O—H bending of the alcohol groups. Having observed the presence of nitrogen in the EDX analysis the broad band at 3200 cm^{-1} may also be ascribed to the presence of N—H bonds of aminic and amidic groups. In addition, the presence of a peak at 1655 cm^{-1} due to the C=O bond vibrations of the carboxylic functionalities and a peak at (valore) related to the C=C stretching vibrations of the alkyl functionalities can be observed. The carbonyl peak of carboxylic acid appeared at 1595 cm^{-1} and the highly extensive O−H peak appeared at 3300 cm^{-1} [44]. All the peaks assigned to the functional groups are reported in the table of Fig. 5c. All functional groups present in the AQS-derived CDs spectra are present in the spectrum of 5HMF-derived CDs (Fig. S3), indicating that the bottom-up procedure from raw materials was useful and preferable. Thus, FTIR spectra indicate that the surface of CDs is rich in hydrophilic groups: hydroxy and carboxylic groups. As reported by Kang and co-workers, these hydrophilic groups may be due to the oxidation of the obtained carbon nanoparticles during electrochemical oxidation [45].

Dynamic light scattering (DLS) measurement, reported in Fig. 6a, confirmed the small size of the synthesized CDs and their dispersibility in water. Volume-weighted DLS measurements revealed a population centred at 10.1 nm (100 percent) for CDs from AQS and around 15 nm for the CDs obtained from 5HMF further confirming the tight particle size distribution and polydispersity index (PDI) values respectively of 0.425 and 0.611 showing the better dispersibility of CDs from AQS in water. As predictable, average DLS values are slightly higher than TEM values and this is due to the interference of the analyte with the hydrodynamic diameter. Zeta potential measurements were carried out to detect the surface potential of CDs and the suspension stability (Fig. 6b). Zeta-potential is an index of the degree of electrostatic repulsion between contiguous similar charged particles in dispersed CDs. The zeta-potentials in aqueous solution are −40 mV and −34 mV, respectively for CDs synthesized from AQS and 5HMF, indicating the repulsive strength between the nanoparticles in solution. In the investigated pH range, the CDs sample surfaces were always negatively charged, according to FTIR results, suggesting the presence of negatively charged functional groups on their surface. The more negative surface potential of CDs could be due to the surface-contained more negative ionized carboxylate radicals, which changed to less negative carboxyl groups, leading to less negative surface potential of CDs obtained from 5HMF (Fig. 6).

Lastly, the thermal degradation of the prepared CDs has been investigated using thermal gravimetric analysis (TGA) (Fig. S4). In argon atmosphere, there are two important steps of weight loss at 150 °C (≈10%) and 350 °C (≈ 50%), which may be due to the loss of water molecules associated with the surface of the CDs and a gradual loss of

(a)

(b)

(c)

Wavenumber cm⁻¹	Peak assignment
3550-3200	-OH stretching alcohol intermolecular bonded -NH
1710-1655	C=O stretching
1590	C=C stretching
1390	C-C stretching
1030	C-O stretching

Fig. 5. (a) Optical properties of CDs PL spectra, (b) FTIR spectrum of CDs, and (c) table with peak assignments.

oxygen bearing moieties including CH, respectively. The decomposition of the sample in air atmosphere took place in three main different steps. Until 400 °C the weight loss (step I) is very similar to that observed in argon atmosphere, likely due to the hydrophobic nature of the CDs, which hinders the absorption of large water quantity inside their structures. Increasing the temperature starts a large weight loss, centred around 500 °C (step II), and associated with progressive loosing of the organic components due to related to the thermal decomposition of surface functional groups. This could be further evidence that these nanodots are carbogenic nanoparticles rich in organic groups, which can be considered as the amorphous and disordered analogue of graphene oxide nanodots. The successive step III is related to surface and bulk CDs

(a)

(b)
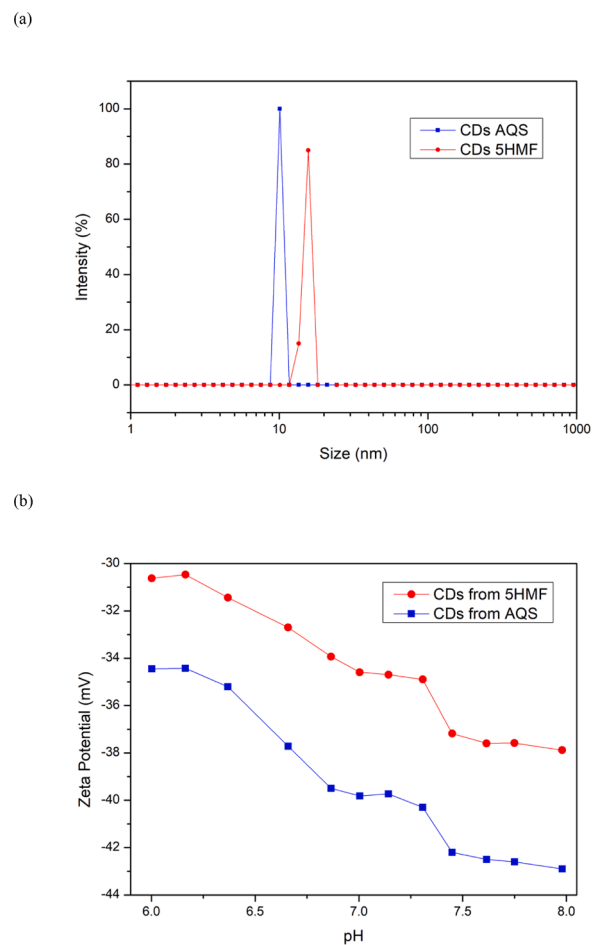
Fig. 6. (a) DLS graph and (b) zeta-potential graph at different pH values of CDs from AQS and 5HMF.

oxidation. Above 600 °C, a very small amount of residue (less than 3%) is found.

Application of CDs as catalysts

The Knoevenagel condensation is often considered as a typical probe reaction to evaluate the catalytic properties of new catalytic systems. In this work, it has been adopted to explore the catalytic properties of all CDs obtained. The obtained CDs were used of in the absence of organic solvents as catalysts and the yields of the condensation products were excellent (up to 98%). Moreover, this solvent-free procedure was able to reuse CDs for at least five consecutive runs without a significant impact in terms of product yields. For the Knoevenagel condensation, promoted by CDs catalyst, *p*-anisaldehyde **1a** as electrophile and ethyl cyanoacetate (**2a**) or dimethyl malonate (**2b**) as nucleophiles, were selected as model reagents. The model reaction was studied with respect to temperature and catalyst loading to achieve the optimized reaction conditions and all the CDs obtained were tested. The results obtained are summarized in Table 2. Obtained data shown good to excellent yields in terms of product **3aa**. The reactions proceed under solvent-free conditions at 25 °C to afford the related products **3aa** (up to 98% yield in 0.5 h) with the low catalytic loading of 10 mg. In the presence of the less reactive nucleophiles (**2a**) and in the absence of the catalyst after stirring for 12 h at room temperature, the analysis of the final mixture shows the total absence of the Knoevenagel adduct **3aa** (entry 1). As shown in the Table 2 (entry 2), minor amount of catalyst leads to a lower yield. Moreover, the photochemical activation and the influence of the oxygen presence were evaluated, and the results reported in the entries 8 and 9.

Table 2
Knoevenagel condensation catalysed by CDs from CDs I150 and CDs V8 and from CDs 5H; optimization with respect to catalyst loading and temperature.[a]

Entry	Y	Catalyst loading	Catalyst	Temp. (°C)	Reaction time (h)	Product **3**	Yields%	TOF ($mmol_{conv}$ g_{cat}^{-1} h^{-1})
1	COOEt (**2a**)	–	–	25	12	**3aa**	0	
2	"	5	CDs V8	25	12	"	23	
3	"	10	CDs V8	25	12	"	60	2.5
4	"	15	CDs V8	25	12	"	50	
5	"	10	CDs V8	45	12	"	42	
6	"	10	CDs 5H[b]	25	12	"	48	2
7	"	10	CDs I150	25	12	"	60	
8[c]	"	10	CDs V8	25	12	"	32	
9[d]	"	10	CDs V8	25	12	"	46	
10	CN (**2b**)	–	–	25	2.0	**3ab**	60	
11	"	10	CDs I150	25	0.5	"	96	93
12	"	10	CDs V8	25	0.5	"	98	
13	"	10	CDs 5H[b]	25	1	"	72	36

[a] Reaction conditions unless specified otherwise: aldehyde (**1a** 0.5 mmol), nucleophiles CN(CH₂)CO₂Et **2a** or CH₂(CN)₂ **2b** (0.5 mmol); and CDs (added of different amount) at different reaction times and temperature.

[b] CDs 5H obtained under a constant potential difference (8 V).

[c] Dark experiment conducted in the absence of visible light.

[d] Experiment carried out in an argon atmosphere.

The results show that the presence of visible light improves the reaction yield while the reaction yield appears unaffected by the presence of oxygen. Thus, the reaction produced higher yields with visible light irradiation than with that carried out in the dark. This result was analogous to those reported by Kang et al. [46], confirming a photo enhanced catalytic activity of the used CDs. Conversely, with malononitrile **2b**, that is one of most reactive nucleophiles in the Knoevenagel condensation, the reaction can proceed uncatalyzed to give a substituted 1,1-dicyanoethylene in 60% yield after two hours. (Table 2, entry 10). However, in the same reaction conditions, the reaction rate is greatly increased by the presence of the CDs, as results in Table 2 entries 11, 12, 13, where the obtained yields were respectively of 96, 98 and 72% in 0.5 h. No significant increase in yield and no formation of by-products was observed by increasing the reaction temperature (Table 2 entry 5).

The catalyst turnover frequency (TOF) was calculated for each run as millimoles of **1a** converted per gram of catalyst per hour ($mmol_{conv}$ g cat^{-1} h^{-1}) and can provide a useful indication to consider the effectiveness of our CDs in the Knoevenagel process in comparison to other functionalized carbon nanomaterials modified as reported in literature [35,36]. Moreover, the results shown that CDs obtained from raw materials have activity comparable to CDs 5H obtained from the pure material (Table 2 entries 6–13) demonstrating the advantage of using the procedure described on both the raw material and the purified material. After the initial assessment of the optimal reaction conditions, to extend the substrate scope, the feasibility of the Knoevenagel condensation involving the C—H acids, CN(CH₂)CO₂Et **2a** or CH₂(CN)₂ **2b,** was tested by using different aromatic (Table 3, entries 1–8), aliphatic (Table 3, entry 9–11) heteroaromatic (Table 3, entries 12–13) aldehydes and ketone (Table 3, entry 14).

As mentioned above, malononitrile (**2b**) resulted more reactive than ethyl cyanoacetate (**2a**) in the condensation (Table 3). The results showed that aromatic aldehydes with electron-withdrawing substituents (Table 3 entries 3–6) resulted in better yields compared to the ones with electron-donating substituents (Table 3 entries 1,2, 7–8). This is consistent with an increase in the electrophilicity of the carbonyl moiety of aldehydes bearing electron-withdrawing substituents. The feasibility of the reaction was also investigated by using aliphatic aldehydes that

resulted in moderate formation of the condensation product (Table 3 entries 9–11). Moreover, it was observed that heterocyclic aldehydes having pyridine and furan moieties (Table 3 entries 12–13) were fully compatible with the catalytic system and produced desired products in good yields. We have further extended the study of CDs catalytic activity to aliphatic ketones. The reaction of cyclohexanone with ethyl cyanoacetate occurred with only moderate yields (Table 3 entry 14). All results suggested that CDs V8 materials have exhibited excellent catalytic activities in Knoevenagel reactions.
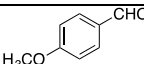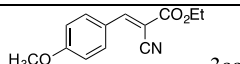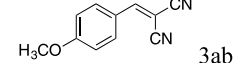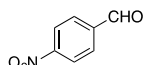
Catalyst recyclability
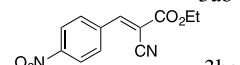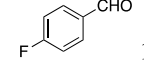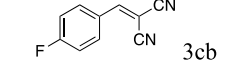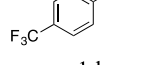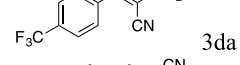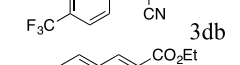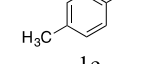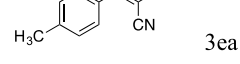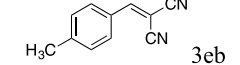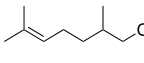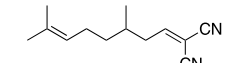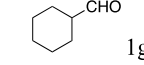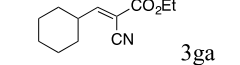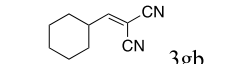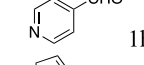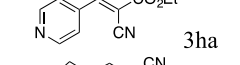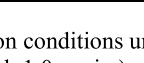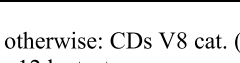
The used solvent-free procedure can also provide the reusability of CDs for at least five consecutive runs without significant impact in terms of product yields. Therefore, to test the possibility to recycle the obtained CDs, we have used the two catalysts CDs I150 and CDs V8 for subsequent catalytic reactions. among others, the advantage of CD-based AQS as a heterogeneous nano-catalyst, was that it is easily separable by simply centrifugation. After completion of each reaction, the catalyst can be easily recovered and re-used for five runs. For the most reactive malononitrile, the yields of the product **3ab** were excellent for all subsequent cycles (Fig. 7). With ethyl cyanoacetate **2a,** to give product **3aa,** a moderate loss of catalytic activity was observed (Fig. S5).

Comparison of the catalyst

To better visualize the usefulness of our CDs, a comparison was made between the efficiency of the catalyst prepared by us and some recent examples, reported in the literature, of nanomaterials to promote the Knoevenagel reaction (Table 4). To better compare the data, the reactions were conducted with the same starting substrates.

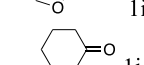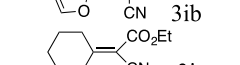The references in the Table 4, previously mentioned in the work, refer to nanomaterials such as catalysts multi-walled carbon nanotubes functionalized with aziridines [35], amine terminated CDs [36] and as a further example a comparison, a nanostructure based on a proline-Cu 1, 3,5-triazine complex coated on Fe₃O₄ magnetic nanoparticles [47]. Even if we are aware that the comparison of this type can be generic due to the

Table 3
Catalytic activity of CDs V8 for the Knoevenagel condensation of 2a and 2b with 1a-j.[a]

Entry	1	2	3	Yields 3 % [b]	TOF (mmol$_{conv}$ g$_{cat}^{-1}$ h^{-1})
1	1a (4-MeO-C6H4-CHO)	2a	3aa	60	2.5
2 [c]	1a	2b	3ab	98	98
3	1b (4-O2N-C6H4-CHO)	2a	3ba	80	3
4 [d]	1c (4-F-C6H4-CHO)	2b	3cb	93	31
5 [d]	1d (4-F3C-C6H4-CHO)	2a	3da	79	26
6 [d]	1d	2b	3db	79	26
7	1e (4-H3C-C6H4-CHO)	2a	3ea	33	1.4
8 [d]	1e	2b	3eb	82	27
9 [d]	1f	2b	3fb	86	22
10	1g (cyclohexyl-CHO)	2a	3ga	48	2
11 [d]	1g	2b	3gb	60	20
12 [c]	1h (pyridine-4-CHO)	2a	3ha	86	86
13 [c]	1i (furan-2-CHO)	2b	3ib	87	86
14	1j (cyclohexanone)	2a	3ja	11	0.4

[a] Reaction conditions unless stated otherwise: CDs V8 cat. (10 mg); aldehydes (**1a−j**; 0.5 mmol); nucleophile (**2a** or **2b**; 0.5 mmol, 1.0 equiv.); reaction time 12 h at r.t.
[b] Isolated yields.
[c] Reaction time 0.5 h.
[d] Reaction time 1.5 h.

different experimental conditions adopted in the literature for the catalytic reactions (i.e., reaction conditions, heterogenous materials), our CDs catalysts, synthesized from cheap waste materials without further modification, have shown a higher efficiency than other studied catalysts in Knoevenagel condensation in terms of better reaction yields and reaction times. The entry 3 in Table 4 results more suitable to compare with our method in terms of the solvent (H$_2$O), reaction time, and temperature conditions. On the other hand, some techniques (Table 4 entries 1, 2) were conducted by applying high reaction temperatures and (entry 1) longer reaction time with respect to our method.

Plausible reaction mechanism

A plausible mechanism for the formation of the Knoevenagel adduct is shown in the Scheme 1. The presence of carboxylic and hydroxyl groups on the CDs surface, confirmed by zeta potential measurements and FTIR, could be effective to first activate the carbonyl carbon atom making it highly electrophilic for the nucleophilic addition, leading to products under mild reaction conditions [48–50]. In fact, it is known that CDs can activate aldehydes via hydrogen bonding during nucleophilic addition reactions [46]. Thus, CDs, rush the reaction with nucleophile by activating the C=O group of the aldehyde through the formation of hydrogen bonding.

Experimental

All chemicals were commercial (Fluorochem, Aldrich) and used without further purification. NMR spectra were recorded at ambient temperature on Bruker spectrometers operating at 400 MHz, or on Spinsolve 60 spectrometer operating at 60 MHz using the solvent as internal standard. The chemical shifts (δ) are given in ppm relative to TMS. Dialysis purifications were carried out with Spectra/Por. Biotech
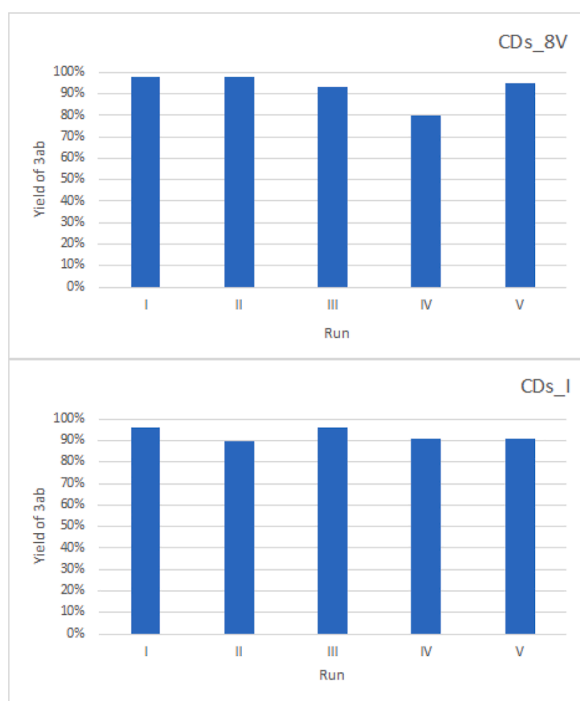
Fig. 7. Catalytic stability evaluation of the CDs used in successive reactions performed for 12 h: Yield of **3ab** with CDs I150 (CDs_I) and CDs V8 catalysts.

cellulose ester membranes (MWCO 0.1–0.5 kD) against distilled water. Electrolysis was performed using an Amel Model 552 potentiostat equipped with an Amel Model 731 integrator or using a K.E.R.T. Mod. K AT 4 VD stabilized power supply. The centrifugation systems used were an ALC Centrifugette 4206 and an ALC Centrifuge 4222 MKII.

Characterization of the AQS solution

In a model run, a blend of wet orange peel waste and deionized water at biomass: water ratio 4:1, was ultrasonically agitated for 15 min at room temperature (25 °C) and then conveyed into a 300 mL stainless steel autoclave (series 4540 Parr Instrument Company, IL, USA) for HTC. In a standard test, the reaction mixture was heated under autogenous pressure, in N_2 atmosphere, up to the reaction temperature (180 °C), at a heating rate of 5 °C min^{-1}, continuously monitored through a thermocouple placed into the autoclave and connected to the reactor controller within the whole. The residence time, after reaching the reaction temperature, was set at 60 min at a stirring speed of 750 rpm. After the HTC reaction, the autoclave was rapidly cooled. Then, the solid and aqueous solution (AQS) products were separated by vacuum filtration, with a

Buchner funnel and filter paper. Products in the aqueous liquid phase as obtained after the separation of the solid carbonaceous fraction were quantified as reported in the previous work [37]. The products contained in the AQS, as obtained after the separation of the solid carbonaceous fraction, were quantified by using an off-line Shimadzu HPLC equipped with an Aminex HPX-87-H, and the chemical content of the AQS ethereal extracted was analyzed by using a GCMS-QP2010 system (Shimadzu, Japan) equipped with a split–spitless injector. An HP-5 weak polar capillary column, 30 m × 0.25 mm i.d. × 0.32 μm film thickness, was used for GC analysis, as previously reported (Fig. S1). Compound identification was performed by comparison with spectra obtained from the US National Institute of Standards and Technology (NIST) mass spectral library.

Synthesis of carbon dots (CDs)

All CDs used were prepared via electrochemical *bottom-up* synthesis using aqueous solution (AQS) deriving from HTC treatment at 180 °C for 1 h of OPW under different electrochemical condition as reported below.

Bottom-up electrochemical synthesis under constant potential difference conditions

In a typical CDs synthesis, 2.5 mL of AQS (0.121 g mL^{-1}) was mixed with NH_4OH aqueous solution (2.5 mL; 30%) in a glass sample vial equipped with a magnetic stirrer. Two Pt wires used as both anode and cathode electrodes (flat spirals, apparent area: 1cm^2) were immersed into this alkaline solution. A Stabilizer (DC) power supply (KERT KAT4VD 1–30VDC 4 A,) was used to apply a static potential (5–10 V) between the two electrodes at ambient temperature (25 °C) for 2.5 h. The electrolysis cell setup is shown in Fig. S6.

The obtained CDs 5–10 V were then subjected to purification as
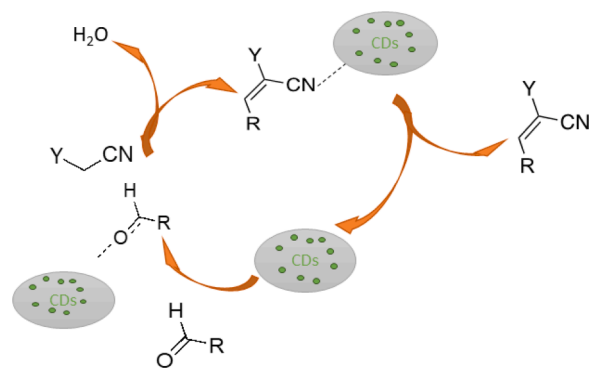
Scheme 1. Plausible reaction mechanism for the syntheses of alpha-beta unsaturated derivatives using carboxylic acid functionalized CDs based catalyst.

Table 4
Comparing the effectiveness of catalysts in the Knoevenagel condensation..

R= H, OCH$_3$
Y = CO$_2$Et, CN

Entry	Catalyst	Y	R	Solvent	Time (min)	Condition °C	Yields%	Refs.
1	MW@N^{Az}	COOEt	OCH$_3$	EtOH	300	79	73	[35]
2	DAB-CD	CN	–	1-octanol	240	45	88	[36]
3	MNP	CN	OCH$_3$	H$_2$O	60	rt	88	[47]
4	CDs V8	CN	OCH$_3$	–	30	rt	98	Our work
5	CDs V8	COOEt	OCH$_3$	–	120	rt	60	Our work

reported below.

Bottom-up electrochemical synthesis under galvanostatic conditions

In a vial, equipped with two platinum electrodes (flat spirals, apparent area: 1 cm^2) and a magnetic stirrer, 2.5 mL of AQS (0.121 g mL^{-1}) and 2.5 ml of NH$_4$OH (30%) aqueous solution were electrolysed under a constant current of 150 mA (150 mA/cm^2) for the time reported in Table 1. Electrolysis was performed at constant current using an Amel Model 552 potentiostat equipped with an Amel Model 731 integrator. The obtained CDs I150 were then subjected to purification as reported below.

Bottom-up electrochemical synthesis under constant potential difference conditions from 5 HMF

In a vial, equipped with two platinum electrodes (flat spirals, apparent area: 1 cm^2) and a magnetic stirrer, 5 mL of NH$_4$OH (30%) aqueous solution containing 200.0 mg (1.6 mmol) of 5-HMF were electrolysed under a constant potential difference (8 V) for the time reported in Table 1. The obtained CDs 5H were then subjected to purification as reported below.

CDs purification

The electrolysis solutions were purified following different procedures.

Method A: The electrolyzed solution was subjected to centrifugation for 15 min at 6000 rpm to remove large or agglomerated particles and to separate the dark solid from the supernatant. The latter was then dried at 50 °C through the Smart Evaporator apparatus. To the obtained material 5 mL of EtOH were added, stirring for at least 20 min, and then dried at 50 °C through the Smart Evaporator apparatus. After removing the liquor, the solid was further washed with EtOH, centrifuged three times, and then dried with the Smart Evaporator. Finally, after full evaporation of the solvent, pure, brown powder CDs was obtained.

Method B: the electrolyzed solution was subjected to centrifugation for 15 min at 6000 rpm to remove large or agglomerated particles and then dialyzed against ultrapure water (600 mL) through a dialysis membrane (MWCO 0.1–0.5 kD) for at least 72 h, changing the dialysis water after 24 h. The dialyzed solution was then concentrated under vacuum and dried with the Smart Evaporator.

The two methods did not show significant variations in the quality of the nanomaterials obtained; therefore, Method A was usually used, being shorter in terms of time.

The mass yield (mY) of CDs was calculated using the following equation:

$$mY, \ wt\% = \frac{mCDs, \ g}{mfeedstock, \ g} \times 100$$

where m$_{CDs}$ is the mass of CDs m$_{feedstock}$ is the dry mass of OPW.

Characterization of CDs

The CDs samples were characterized by several techniques. A high-resolution Auriga-Zeiss (Jena, Germany) Field Emission (FE)-SEM microscope; and EDS (Energy Dispersive X-ray Spectroscopy) system equipped with Bruker Quantax detector were used for the examination and analysis of the microstructure morphology and chemical composition characterizations. High Resolution Field Emission Scanning Electron Microscope (HR-FESEM, AURIGA Zeiss) operating at 10 kV and Transmission Electron Microscope (TEM, JEOL JEM 1400) operating at 80 kV, were developed to investigate the morphology and the particle sizes. The structures of synthesized CDs were investigated using the X-ray powder diffraction (XRD) using a Bruker D8 Advance A25 X-ray

diffractometer, operating at 40 kV in the range 5–80° (2θ), with an increasing rate of 0.02°/s. Photoluminescence spectroscopy was performed with a spectrofluorometer Fluoromax-3 Horiba Jobin–Yvon fluorometer (*T* = 25.0 °C) equipped with glass cuvettes (1.0 cm path length). The chemical frameworks were studied by Fourier-transform infrared spectroscopy (FTIR) and IR spectra were recorded with a Shimadzu FTIR-8400S spectrophotometer at room temperature in the range from 4000 to 650 cm^{-1} with a scanning speed of 2 mm/s. The particle size and zeta potential measurements were performed by dynamic light scattering (DLS) using the Zetasizer 3000 instrument (Malvern), equipped with a 632 nm HeNe laser, operating at a 173-degree detector angle. Thermal stability in air and inert atmosphere were evaluated by thermogravimetry (TGA) conducted with TA instruments STD600 (balance sensitivity: 0.1 mg). The samples were heated at 20 °C/min from 100 °C up to 1200 °C using a constant air flow rate (100 mL/min), after preliminary stabilization for 30 min at 100 °C to remove the eventually adsorbed water. Weight loss (%) was calculated.

General method of synthesis of Knoevenagel adduct

All products were prepared under solvent-free condition. A mixture of *p*-anisaldehyde (0.5 mmol), activated methylene compound (0.5 mmol) and 10 mg amount of CDs was stirred at room temperature in a 1.5 mL tube [32]. The reaction mixture always solidified in the vial. After the completion of reaction, or after the time indicated the product was separated by extracting with organic solvent. The mixture was then extracted with 3 × 1.5 mL of ethyl acetate to remove the product and evaporated under reduced pressure to obtain the target products. This procedure was followed for all substrates listed in Table 3.

Reusability of the catalyst

After each run, the organic product was removed from the reaction mixture by extraction with ethyl acetate (3 times); the carbon dots remained insoluble in the reaction flask. After that CDs V8 and CDs I150 were washed three times with ethyl acetate to eliminate any organic products present and were dried under vacuum and further used for the subsequent reaction cycles.

Characterization data

All known obtained products gave spectral data in accordance with those reported in the literature. All spectroscopic data are provided in the Supporting Information.

Conclusions

In this work, we have presented a useful one-step alkali-assisted electrochemical *bottom-up* synthesis of high-quality catalysts form of CDs from agri-waste materials and 5HMF. The EC synthesis process to obtain CDs, using the liquid fraction resulting from a previous HTC carried out on waste, is not known. Hence, the integration of hydrothermal and electrochemical process has proven to be an interesting and efficient synthetic strategy. In fact, the integrated process could represent a breakthrough in methods requiring long reaction time, high temperature treatments, and further treatments for functionalization. The obtained CDs by the electrochemical *bottom-up* process, without further functionalization, show the presence of functional groups on the surface revealing excellent catalytic properties providing a new high efficiency heterogeneous catalyst approach for applications in organic synthesis and eco-friendly technology. Thus, the CDs have been tested toward the Knoevenagel condensation obtaining excellent results. Accordingly, the effective catalytic activity of CDs for basic organic reactions is confirmed in addition to the already established versatile applicability of these water-soluble, non-toxic, and biocompatible fluorescent nanodots in biological, photocatalytic, and optoelectronic

device applications. The most important advantages of this study are mild reaction conditions, easy work up, and excellent recyclability which fortify carbon nanodots as effective catalysts for important organic transformations in a metal-free and green pathway. This integrated method starting from the treatment of agri-food waste is very significant in terms of recovery, recycling, and circular chemistry processes.

CRediT authorship contribution statement

Cinzia Michenzi: Validation, Visualization, Investigation, Writing – review & editing. **Claudia Espro:** Conceptualization, Methodology, Supervision, Writing – original draft. **Viviana Bressi:** Validation, Visualization, Investigation, Writing – review & editing. **Consuelo Celesti:** Visualization, Investigation. **Fabrizio Vetica:** Visualization, Investigation. **Chiara Salvitti:** Visualization, Investigation. **Isabella Chiarotto:** Conceptualization, Methodology, Supervision, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113182.

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