doi:10.2533/chimia.2017.864 Chimia 71 (2017) 864–865

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Sustainable Chemistry: From Wine Industry Waste (Wine Lees) to Luminescent Ink-jet Inks Containing Carbon Dots

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Abstract: Carbon nanodots can be obtained in good yields by direct combustion of an abundant waste from the wine industry, wine lees. The extraction of these nanoparticles followed by their chemical functionalization lead to an ink-jettable material emitting in the visible region (blue) under specific UV irradiation.

Keywords: Carbon nanodots · Luminescent material · Sustainable chemistry

Wine Lees: The Waste as Raw Material for Carbon (Nano)dots

The wine lees is one of the main residues of the wine fermentation process (about 1 g dried residue / litre of wine produced) and consists of yeasts, bacteria, tartaric acid, protein-tannin complexes and polysaccharides. Being phytotoxic, it requires adequate treatment in order to avoid uncontrolled dumping which causes environmental problems. Several valorisation solutions for this abundant waste have been proposed (yeast extraction, dietary supplement for animals, *etc.*) though not yet applied on a large scale. Therefore, alternatives to recover and transform this by-product into high value-added compounds are of special interest. We have demonstrated that the carbon-rich wine lees represents a valuable raw material for preparing carbon (nano)dots (CDs).[1]

Why Carbon (Nano)dots?

The most versatile chemical element, carbon, is not only the basis of all known living matter on Earth and a classical energy source, but also a material exhibiting multiple allotropic forms, whose secrets continue to fascinate scientists. After the considerable research interest triggered by the successive discoveries of fullerenes, carbon nanotubes and graphene, starting in 2004 it was the turn of luminescent carbon materials, also called carbon (nano)dots (CDs) or carbon quantum dots (CQDs) to provoke researchers' fascination.[2] Indeed, these quasi-spherical nanoparticles with diameters smaller than 10 nm have quite remarkable properties: strong multi-colour fluorescence, electron donor/acceptor properties, low toxicity, high chemical/photo–stability and good biocompatibility (do not contain potentially toxic components).[3] They are currently used as photocatalysts, bio-imaging agents, and optical sensors. Considerable efforts have been dedicated to replace the inorganic quantum dots, performant but toxic, with their carbon-based counterparts in various optoelectronics applications (*e.g.* light emitting diodes, supercapacitors, *etc.*) and photovoltaic devices.[4] The properties of CDs are principally influenced by three characteristics: the size, the core internal structure (mainly the type and the ratio between the 'crystalline', and 'amorphous' domains) and the surface functionalization (the number and the type of chemical functions *e.g.* carboxylic and carbonyl groups). Several materials (various organic compounds, cellulose)[5] including organic waste (shrimps, bagasse, banana juice)[6] have been identified as potential carbon-sources to prepare CD *via* various synthetic methods (combustion, pyrolysis, hydrothermal carbonisation, microwave-assisted).[7] These approaches are, however, not robust enough (any fluctuation of the reaction parameters leads to modifications of the CDs properties) and only few are appropriate for scaling-up.[8]

Compared to other wastes/carbon-sources, the wine lees are quite homogenous (a powder-like material after drying)[9] and do not need any physical pre-treatments, which is an important advantage in view of the scale-up (Fig. 1).

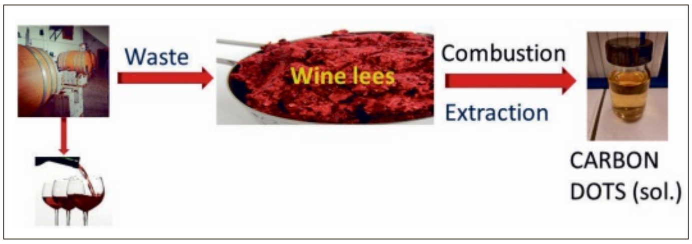

Fig. 1. The general principle of our approach.

Wine lees from white (Chasselas) and red (Humagne) wines have been tested. The dried lees is subjected to a first carbonisation step performed in an oven followed by a specific CDs extraction (ultrasound or microwave assisted solvent extractions) (Fig. 2). A screening of the solvents showed that the highest extraction yields are given, as expected, by polar protic solvents such as water and ethanol, due to the presence of polar groups on the nanoparticles surface. The microwave extraction proved more efficient than the ultrasound technique (yields of 20% and 10% respectively). In the next step, the CDs properties are finely tailored by increasing the number of carboxylic functions on the surface (oxidation of the remaining aldehydes/alcohols/phenols functions). Subsequently, the reaction of carboxylic groups with dodecylamine yields a high number of amidic linkages, ensuring in this way a good solubility in the polymerisable monomers of the UV-curable inks. As it has been reported that the presence of the amino groups on the CDs surface increases their emission properties, we have also functionalised the CDs with a short chain diamine, ethylenediamine.

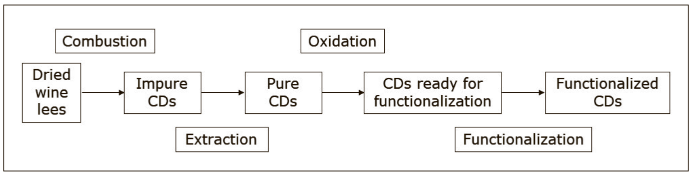

Fig. 2. General synthetic pathway.

CDs Characterisation

The CDs obtained were characterised by TEM, fluorescence spectroscopy, UV-Vis, and IR.

Even if the size distribution was difficult to estimate, the TEM observations before and after the functionalisation steps clearly show round-shaped particles with sizes in the nm range. Agglomerations are also present but their dimensions decrease after the oxidation step (Fig. 3).

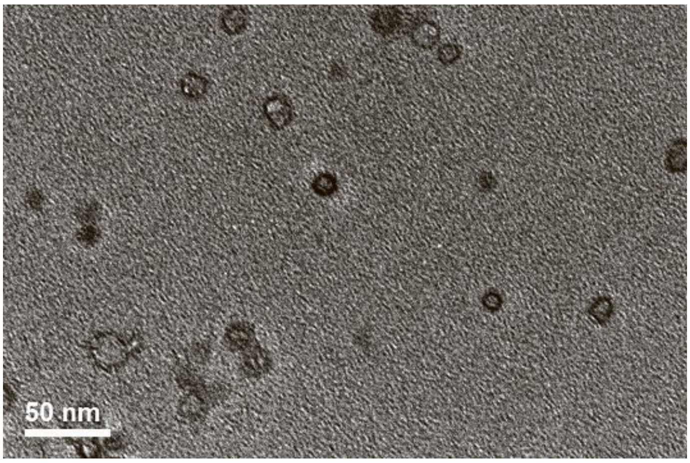

Fig. 3. TEM image showing the agglomeration of amine functionalised CDs.

The IR spectra indicate that the signal belonging to the carboxylic acid moieties[10] strongly increased after the oxidation step. After the reaction with the amine, these signals are at their weakest while the signals of the amines attached appear slightly shifted, proving the covalent bonding to the CDs surface. UV-Vis spectra indicate a maximum absorption in the near UV (between 330 and 360 nm) and the maximum of the emission is reached in the blue region. The highest quantum yields (in the range of 6%) after functionalisation are 3–4 times higher compared to those of non-functionalised CDs. The luminescent properties (quantum yields, average lifetime, radiative and non-radiative rate constants) of the CDs obtained from white wine lees are very similar to those obtained from red wine lees and this is an important advantage. The photoluminescent mechanism of CDs is not yet completely elucidated but it is well known that the emission wavelengths maxima vary with the excitation wavelengths. Typical for all CDs (carbon or metal based),[11] is the shift to longer wavelengths of the maximum emission band (in our case from 440 to 540 nm) when the excitation wavelength is increased (from 360 to 500 nm, Fig. 4).

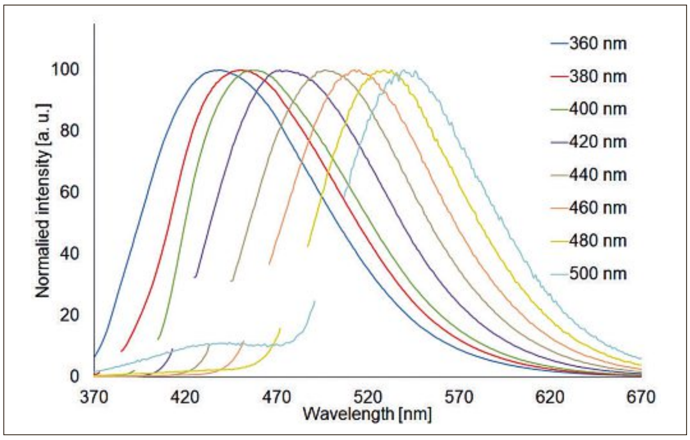

Fig. 4. Emission spectra of amine functionalised CDs at various excitation wavelengths (0.2 g/L in deionised water).

CDs as Fluorescent Pigments for Ink-jet Inks

Ink-jet printing, long confined to graphical, desktop printing, is gaining momentum amongst other industrial printing techniques (screen printing, flexography, offset). Propelling ink-droplets of a few picoliters through microsized nozzles onto different substrates has many advantages: versatility, scalability, maskless approach, short processing time, no wasted ink, and low-cost. One big disadvantage however, is the complicated ink formulation, especially when suspensions (as is the case for pigments) have to be jetted. Preventing sedimentation and formation of micro-sized agglomerates, which can clog the nozzle is a challenge. The very small dimensions of CDs combined with the passivation of their surface efficiently prevent their natural tendency to agglomerate. The CDs are therefore potential good candidates for ink-jet printing. Using various commercial acrylate bases, we prepared UV curable inks based on dodecylamine-functionalised CDs. They have been deposited on various substrates, including polystyrene sheets, with an in-house built ink-jet printer. One example is shown in Fig. 5. Almost invisible under daylight, the printed surfaces reveal a strong blue-fluorescence under UV light.

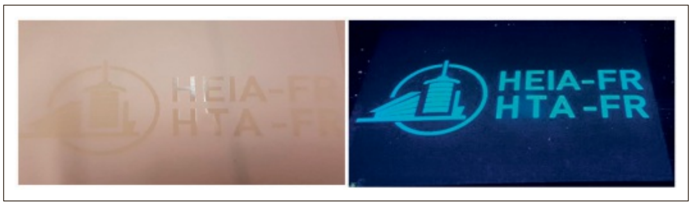

Fig. 5. Our school logo printed by ink-jet with UV curable inks containing CDs. Left: in daylight; right: under UV light (366 nm).

Conclusions

The use of wine lees, a phytotoxic, winery residue as a raw source to prepare materials with a significant added value, carbon dots, is an important step forward toward green manufacturing and sustainable chemistry. We have demonstrated a reliable efficient low cost approach to turn a problematic by-product into a valuable raw material.

Acknowledgments

P2 program of HES-SO for financial support, iPrint institute for printing the new inks, R. Erni & Y. Zhang for TEM measurements, A. Ruggi for luminescence characterisation.

Received: October 20, 2017

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