Electronic Supplementary Information.


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S1. Ethanol electro-oxidation in alkaline media with Ni Foams as WE

Here we briefly study the electro-oxidation of ethanol in alkaline media using a Nickel Foam as working electrode and a platinum wire as counter with respect an Ag/AgCl reference electrode. Electro-oxidation of ethanol in alkaline media with nickel electrodes has been developed by Fleischmann and collaborators\textsuperscript{1,2}, extremely important in the synthesis of carbon quantum dots from ethanol in alkaline media. According to Fleischmann et al the electro-oxidation of simple chain alcohol in such circumstances it's a $4e^-$ mediated process, this process involves the formation of oxides in the working electrode as a reversible process and some radical intermediates.

\[
\begin{align*}
    OH^- + \text{lower oxide} & \overset{\text{fast}}{\leftrightarrow} \text{higher oxide} + H_2O + e^- \\
    (\text{organic substrate})_{\text{sol}} & \overset{\text{on higher oxide}}{\leftrightarrow} (\text{organic substrate})_{\text{ads}} \\
    \text{Higher Oxide} + (\text{Organic Substrate})_{\text{ads}} & \Rightarrow \text{lower oxide} + \text{radical intermediate} \\
    \text{Radical Intermediate} + (n-1)\text{higher oxide} & \Rightarrow (n-1)\text{lower oxide} + \text{product}
\end{align*}
\]

This is a general route for the electro-oxidation of simple chain alcohols in alkaline media, with different metal catalyst. Recently, Barbosa et al\textsuperscript{3} take this same approach and using an FTIR they determined the different participants involved in the electro-oxidation of ethanol on polycrystalline nickel in alkaline media; according to their findings we can establish:

- Lower oxide = Ni (OH)$_2$ = Nickel Oxide (II)
- Higher Oxide = NiO (OH) = Nickel oxide hydroxide
- Organic Substrate = CH$_3$CH$_2$OH = Ethanol
- Radical Intermediate = CH$_3$CHO = Acetaldehyde
- Product = CH$_3$COOH = Acetic Acid (Acetate for pH>10)

Yielding the next 5 equations for the electrode dynamics:

\[
\begin{align*}
    OH^- + \text{Ni(OH)$_2$} & \overset{\text{fast}}{\leftrightarrow} \text{NiO(OH)} + H_2O + e^- \\
    (CH_3CH_2OH)_{\text{sol}} & \overset{\text{on higher oxide}}{\leftrightarrow} (CH_3CH_2OH)_{\text{ads}}
\end{align*}
\]
3) \[ \text{NiO(OH)} + (\text{CH}_3\text{CH}_2\text{OH})_{ads}^* \xrightarrow{\text{ads}} \text{Ni(OH)}_2 + \text{CH}_3\text{CHO} \]

*rate determining hydrogen extraction

4) \[ \text{CH}_3\text{CHO} + (n-1)\text{NiO(OH)} \xrightarrow{\text{yields}} (n-1)\text{Ni(OH)}_2 + \text{CH}_2\text{COOH} \]

5) \[ \text{CH}_3\text{COOH} + \text{OH}^- \xrightarrow{\text{yields}} \text{CH}_3\text{COO}^- \]

In order to study ethanol electro-oxidation, we perform several Cyclic Voltagrammetries in a 3-electrode set-up of a solution of 1M NaOH and 0.5 M EtOH. Figure S1A shows a schematic of the experimental set-up. Nickel Foam is used as a working electrode and a platinum wire as counter electrode. The reference voltage is set trough an Ag/AgCl reference electrode. Figure S1B shows a cyclovoltammetry measurement of ethanol electrooxidation on a Nickel foam. Control group without ethanol is added for completeness. Ethanol can be electrooxidized to Acetate in a 0.55-0.85 V window with respect to an Ag/AgCl reference electrode using Ni foam as a working electrode. The presence of Nickel Oxides is critical to the electro-oxidation of ethanol because these oxides are participants in all the intermediate reactions.

**Figure S1.** (a) Experimental set-up for study electrochemical oxidation of ethanol. (b) Ciclic Voltagramm of Nickel Foam in a NaOH 1M+ EtOH 0.5 M (in red) and Control Experiment (black) without EtOH.
S2 Insights into the Electrooxidation of Ethanol and CQDs formation.  Section S1 and Figure S1 discusses the electrooxidation reaction of ethanol and exhibits cyclic voltagramm (CVs of the electrochemical reactions occurring at the anode). Carbon nanoparticles are produced in a bottom-up synthesis through dehydration and carbonization of ethanol during electrooxidation. These carbon nanostructures are generated at the interface of the working electrode in a media composed of a mixture of ethanol and 0.1 M NaOH which is subjected to 30 V for 1 h. One of the main products of electrooxidation of ethanol is acetaldehyde. When Ni is used as the working electrode, the preferred pathway of electrooxidation is a 4-electron mediated process where acetaldehyde and acetic acid are generated as intermediate and final product, respectively. In the presence of Na and in a strong alkaline media, acetic acid deprotonates to form sodium acetate which precipitates upon saturation. Acetaldehyde is generated in large amounts upon ethanol electrooxidation and is the starting block in the bottom-up synthesis of CQDs through electrochemical oxidation of ethanol. During the synthesis, the concentration of acetaldehyde begins to build up at the interface of the working electrode as well as in the solution; eventually leading to an aldol addition and condensation process. During aldol condensation, the conjugate base of an aldehyde adds to the carbonyl group of another aldehyde. This mechanism gives a new α, β-hydroxyl aldehyde which is dehydrated to form an α, β-unsaturated carbonyl compound. In the case of acetaldehyde, the aldol addition product is 3-hydroxybutanal, which could be dehydrated to yield crotonaldehyde. The aldol condensation of acetaldehyde is catalyzed by hydroxide ions (the main source in this case) via the formation of Ni (OH)₂ / NiO (OH) at the anode, offering basic sites for the process to occur and giving different self-regenerating phases of Ni (OH)₂ that push large amounts of acetaldehyde to enhance the process. This situation promotes the aldolization of crotonaldehyde with acetaldehyde resulting in the formation of hexa-2,4-dienal. Repeating this process of aldol condensation produces higher molecular weight compounds that catalyzed, by the Ni, could give rise to a mechanism of cycloaddition. Also, different adsorbed species (for example –CH₂CHO) bonded to α, β unsaturated moieties could produce branched, long-chain molecules that are supported on the anode surface and that we could see as sub product of the synthesis in the HRTEM characterization. Metal oxides are crucial to the production of acetaldehyde and the subsequent aldol condensation of the product, because there are less efficient catalysts when compared to Pt regarding the ethanol electrooxidation process. When Pt is used as a working electrode the preferred oxidation pathway leads to CO₂. This could be the reason why Liu et al⁷ observed no CNs formation in their set up even though Deng et al⁸ reported specifically on that manner.
Figure S2. Branched, long-chain molecules as subproduct during electrooxidation of ethanol (a) and their corresponding FFT (b) showing amorphous phases.
Figure S3. HRTEM image of another region of the sample (a). Digital zoom into the ROI showing different crystallographic directions (b). FFT of ROI.
Figure S4. HRTEM image (a) in another zone of the aforementioned sample, different ROIs color coding is established in order to assess the crystallinity of different carbon nanoparticles. FFT of four ROI are color coded in green (b), blue (c), violet (d) and red (e).
S5. Comparative simulated UV-Vis spectra and emission properties of pyrene and pyrene + 2OH

<table>
<thead>
<tr>
<th># Rings sp² Domain</th>
<th>PAH</th>
<th>Emission Wavelength (nm)</th>
<th>Emission Energy (eV)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Pyrene</td>
<td>336.5</td>
<td>3.684</td>
<td>H-1 ↔ L (0.432897)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H ↔ L+1 (0.562973)</td>
</tr>
<tr>
<td>4</td>
<td>Pyrene + 2 OH</td>
<td>365.6</td>
<td>3.391</td>
<td>H-1 ↔ L (0.78822)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H ↔ L (0.033505)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H ↔ L+2 (0.150889)</td>
</tr>
</tbody>
</table>

Figure S5. Simulated Uv-Vis Spectra and emission properties for Pyrene and Pyrene + 2OH

**Figure S6.** Simulated molecular orbitals for coronene+ charged carbonyl.
S7. Survey XPS spectra (0-600 eV) and C/O content for CQDs

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak (eV)</th>
<th>FHWM (eV)</th>
<th>Area (CPS * eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>286.06</td>
<td>3.06</td>
<td>152991.76</td>
<td>76.77</td>
</tr>
<tr>
<td>O1s</td>
<td>532.6</td>
<td>3.74</td>
<td>78740.38</td>
<td>16.35</td>
</tr>
<tr>
<td>Na1s</td>
<td>1072.33</td>
<td>3.04</td>
<td>66694.39</td>
<td>6.88</td>
</tr>
</tbody>
</table>

**Figure S7.** Survey XPS spectra (0-600 eV) for CQDs.
Table S1. The Table compares our work with the Literature indicating the photocatalyst, dye, light source and power, and degradation rate and time. NR stands for not reported.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Light source</th>
<th>Wavelength</th>
<th>Power</th>
<th>Degradation rate</th>
<th>Irradiation time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multilayer-GQDs</td>
<td>MB</td>
<td>Led</td>
<td>520 nm and 470 nm</td>
<td>1 W.mm⁻²</td>
<td>93%</td>
<td>60 min</td>
<td>Ref⁹</td>
</tr>
<tr>
<td>GQDs and polymer-modified GQDs</td>
<td>MB</td>
<td>Xe lamp</td>
<td>Visible (cutoff λ&gt;400 nm)</td>
<td>300 W</td>
<td>45%</td>
<td>100 min</td>
<td>Ref¹⁰</td>
</tr>
<tr>
<td>GQDs</td>
<td>MB</td>
<td>Sun light</td>
<td>Whole spectrum</td>
<td>NR</td>
<td>45%</td>
<td>100 min</td>
<td>Ref¹¹</td>
</tr>
<tr>
<td>N-CQDs</td>
<td>MB</td>
<td>Xe lamp</td>
<td>Visible (cutoff λ&gt;400 nm) all spectrum</td>
<td>500 W / (54 × 10³ ± 5000 lm)</td>
<td>97%</td>
<td>60 min</td>
<td>Ref¹²</td>
</tr>
<tr>
<td>N-CQDs</td>
<td>MB</td>
<td>Sun light</td>
<td>Whole spectrum</td>
<td>-</td>
<td>95%</td>
<td>180 min</td>
<td>Ref¹³</td>
</tr>
<tr>
<td>TiO₂/N-GQDs</td>
<td>MB</td>
<td>UV lamp</td>
<td>UV irradiation</td>
<td>400 W</td>
<td>85%</td>
<td>70 min</td>
<td>Ref¹⁴</td>
</tr>
<tr>
<td>GQDs</td>
<td>Rh G</td>
<td>Sun light</td>
<td>Whole spectrum</td>
<td>NR</td>
<td>80%</td>
<td>80 min</td>
<td>Ref¹⁵</td>
</tr>
<tr>
<td>GQDs</td>
<td>MB, MO</td>
<td>CFL and LED</td>
<td>400 and 750 nm</td>
<td>1000 lm</td>
<td>79% / 52%</td>
<td>120 min / 120 min</td>
<td>Ref¹⁶</td>
</tr>
<tr>
<td>GQDs/Polymeric Carbon nitride</td>
<td>Rh B</td>
<td>Xe lamp</td>
<td>Visible (cutoff λ&gt;420 nm)</td>
<td>300 W</td>
<td>100%</td>
<td>80 min</td>
<td>Ref¹⁷</td>
</tr>
<tr>
<td>S,N-GQDs</td>
<td>Crystal violet and Alizarin yellow</td>
<td>Xe lamp</td>
<td>Visible irradiation</td>
<td>400 W</td>
<td>91% / 64%</td>
<td>100 min</td>
<td>Ref¹⁸</td>
</tr>
<tr>
<td>TiO₂/GQDs</td>
<td>Reactive Black 5 (RB5)</td>
<td>Sun light</td>
<td>Whole spectrum</td>
<td>NR</td>
<td>100%</td>
<td>30 min</td>
<td>Ref¹⁹</td>
</tr>
<tr>
<td>Crystalline CQDs</td>
<td>MB</td>
<td>Hg lamp</td>
<td>250-750 nm</td>
<td>100 W</td>
<td>95%</td>
<td>5 min</td>
<td>This study</td>
</tr>
</tbody>
</table>

This study
References:


