Supplementary Information - Graphene Modified with Triruthenium Acetate Clusters as Electrode for Hybrid Energy Storage System

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Supplementary Information s1

Figure s1. a) FTIR spectra for NH2Ru, rGO, rGO-NH and rGO-NHRu. b) FTIR spectra from 1580 to 1300 cm⁻¹.

Supplementary Information s2

Figure s2. Experimental and theoretical FTIR spectra for NH₂Ru. The experimental peaks are labeled with the wavenumber and the corresponding theoretical peaks are labeled with the vibration originating it. The experimental peaks labeled with * corresponds to PF₆⁻ anion which is not considered in the simulation.
Supplementary Information s3

Excited states close in energy to the excitation laser were considered for the simulation of resonance Raman. Excited states often involve contributions from several electronic transitions, so natural transition orbitals (NTOs) were calculated to obtain a compact representation of excited states as a single electronic transition from a donor orbital to acceptor orbital. The Table s1 shows the vertical electronic transition energy, the oscillation force of the excited states, and the description of excited. Whereas the Figure s3 shows a graphical representation of those electronic transitions and the experimental UV-vis spectra. The state 1 is described as a transition from the ruthenium atoms linked to pyridine ($Ru^a$ and $Ru^b$) to the ruthenium atom linked to aminopyrididine ($Ru^c$), state 2 and 3 as a transition from the ruthenium atom linked to aminopyrididine to a ruthenium atom linked to pyridine ($Ru^c\rightarrow Ru^b$ and $Ru^c\rightarrow Ru^a$ respectively). It worth to say that state 3 also involves the electronic transition found for the state 2. Furthermore, all the excited states involve changes in the electronic density of central oxygen.

Figure s3. Uv-vis spectrum of NH$_2$Ru, it is pointed out the excitation energy of the laser used for Raman spectroscopy. The main electronic transition involved in the excited states resonant with the light of the laser are represented as a simple donor-acceptor pair. The C atoms are in gray, H atoms in white, O atoms in red, N atoms in pink and orbitals as red and green shades.
Table S1. Theoretical excited states resonant with laser excitation used in Raman spectroscopy. Its oscillation force ($f_{osc}$), its description in terms of donor-acceptor pair.

<table>
<thead>
<tr>
<th>State</th>
<th>Wavelength</th>
<th>$f_{osc}$</th>
<th>Transition type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>617.5 nm</td>
<td>0.0027</td>
<td>$Ru^{a,b} \rightarrow Ru^{c}$</td>
</tr>
<tr>
<td>2</td>
<td>607.4 nm</td>
<td>0.0018</td>
<td>$Ru^{c} \rightarrow Ru^{b}$</td>
</tr>
<tr>
<td>3</td>
<td>605.2 nm</td>
<td>0.0181</td>
<td>$Ru^{c} \rightarrow Ru^{d}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Ru^{c} \rightarrow Ru^{a}$</td>
</tr>
</tbody>
</table>
**Supplementary Information s4**

The exploratory X-ray photoelectron spectra in Figure s4 shows the presence of C (39 % at.), O (42 % at.), N (7 % at.) and Na (12 % at.) in aminopyridine functionalized graphene (rGO-NH) and the presence of C (65 %), O (16 %), N (9 %), Ru (2 %), F (6 %) e Cl (3 %) in hybrid nanomaterial based on graphene and triruthenium cluster. The composition was estimated from the exploratory X-ray photoelectron spectrum. It is noteworthy that there may be some errors in the composition estimation due to the overlap between the peaks of C and Ru.

![Figure s4. XPS survey spectra of rGO-NH and rGO-NHRu samples.](image)

A summary of atomic percentage, weight percentage and unit formula calculated with EDS and XPS data is shown in Table s2. In rGO-NH the O:C ratio estimated with XPS (1:1) is higher than that estimated by EDS (3:8). Besides, in rGO-NHRu the Ru:C ratio estimated with XPS (1:34) is higher than that estimated by EDS (1:61). So, content of oxygen groups and ruthenium was higher in the surface of material.

Table s2. Chemical composition of rGO-NH and rGO-NHRu as calculated by XPS and EDS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>XPS</th>
<th>EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%at.</td>
<td>%wt.</td>
<td>#atoms</td>
</tr>
<tr>
<td>rGO-NH</td>
<td>C</td>
<td>42.2</td>
<td>44.6</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>39.1</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>7.0</td>
<td>6.5</td>
</tr>
<tr>
<td>rGO-NHRu</td>
<td>C</td>
<td>64.6</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>15.7</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8.6</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>1.9</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Supplementary Information s5

Capacity and capacitance calculations

Specific charge stored in an electrode with mass/area \( m \) can be calculated from discharge curve as:

\[
q = \frac{i \Delta t}{m} \quad (1)
\]

The specific charge stored is expressed in \( mAh \) units dividing \( q \) by 3.6 (1C = 3.6 mAh). The specific capacitance \( C_s \) of supercapacitor materials with linear discharge curve, can be calculate as:

\[
C_s = \frac{q}{\Delta V} = \frac{i \Delta t}{m \Delta V} \quad (2)
\]

Current \( i \) dependence on scan rate \( \nu \) analysis

Dependence of \( i \) on \( \nu \) can be modeled as power-law1:

\[
i = a \nu^b \quad (3)
\]

Applying logarithm:

\[
\log(i) = \log(a) + b \log(\nu) \quad (4)
\]

So, the \( b \) value corresponds to the slope calculated from a linear fit of \( \log(i) \) Vs. \( \log(\nu) \) data. \( i \) is calculated as the sum of the anodic and cathodic current peaks or at a specified potential.

\( b \) close to 1 indicate dominating capacitive processes, \( b \) close to 0.5 dominating diffusion processes:

The relationship between voltage and current for a capacitor is linear, as follows:

\[
i = C_s \frac{d \nu}{d \tau} = C_s \nu \quad (5)
\]

Also, according to Randles-Sevcik equation for an electrode with absorbed species (diffusion is not important) the peak current dependence on \( \nu \) is linear. Whereas for electrochemically reversible electron transfer processes involving diffusing species the relationship is:

\[
i = k \nu^{1/2} \quad (6)
\]

\( q_{inner} \) and \( q_{outer} \) contributions to the charge stored2:

The specific charge stored is calculated from cyclic voltammetry integrating the area below the anodic sweep trace.

\[
q = \int_{V_i}^{V_f} i \nu dV \quad (7)
\]
The charge stored can be divided in one contribution from diffusion-controlled $q_{inner}$ and capacitive or surface processes $q_{outer}$

$$q = q_{outer} + q_{inner} \quad (8)$$

As it was mentioned the diffusion controlled current contributing to $q_{inner}$ is $i = kv^{1/2}$ so:

$$q_{inner} = \int_{V_i}^{V_f} \frac{k}{v} dV = av^{-1/2} \quad (9)$$

Consequently,

$$q = q_{outer} + av^{-1/2} \quad (10)$$

$q_{outer}$ corresponds to the intercept calculated from the linear fit of $q \text{ Vs. } v^{-1/2}$ data. $q$ is calculated from cyclic voltammetry. Note that $q_{outer}$ is the value of $q$ when $av^{-1/2} = 0$, that is, when $v \approx \infty$.

$q$ increases with $v$ decrease, at the limit when $v = 0$, all the possible charge is stored ($q_{total}$). So, extrapolating to $v = 0$ an appropriate $q$ function of $v$ $q_{total}$ can be estimated. From the last equation is expected that $1/q \propto v^{1/2}$, so it is proposed:

$$\frac{1}{q} = \frac{1}{q_{total}} + bv^{1/2} \quad (11)$$

$1/q_{total}$ corresponds to the intercept calculated from the linear fit of $q \text{ Vs. } v^{1/2}$ data. Note that $1/q_{total} \neq 1/q_{outer}$. Finally, it is possible to calculate $q_{inner}$ subtracting $q_{outer}$ to $q_{total}$:

$$q_{inner} = q_{total} - q_{outer} \quad (12)$$
Figure s5. Analysis of cyclic voltammetry with scan rate variation. a) cyclic voltammetry and b) log $i$ vs log $v$ plots for NH$_2$Ru. c) and d) for rGO-NH. e) and f) for rGO-NHRu. The log $i$ vs log $v$ plots uses the peak currents of the materials or the current reached at 0.24 and 0.9 V in the case of rGO-NHRu.
Figure s6. Estimated $q_{\text{inner}}$ and $q_{\text{outer}}$ for NH$_2$Ru, rGO-NH and rGO-NHRu.

**Supplementary Information s6**

Figure s7. Comparison of cyclic voltammetry of rGO-NH and rGO-NHRu performed in KCl 0.5 mol L$^{-1}$ and KNO$_3$ 0.5 mol L$^{-1}$ + HCl 10$^{-5}$ mol L$^{-1}$

**References**
