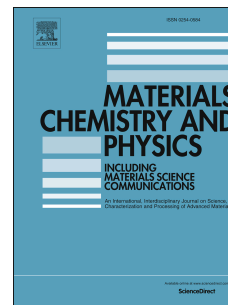# Journal Pre-proof

Field-effect transistors made of graphene grown on recycled copper foils

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Author Contributions

George M. Junior: Experiments design, graphene growth and transfer, Raman measurements, Fabrication of GFETs and recycling, GFET characterization and the manuscript and figures preparation.
Maria F. Cerqueira: Raman measurements
Jerome Borme: Experiments design, Fabrication of GFETs and the manuscript and figures preparation
Marco Martins: GFET characterization
João Gaspar: GFET characterization
Pedro Alpuim: Experiments design, the manuscript and figures preparation and supervision.

Manuscript cover page

FIELD-EFFECT TRANSISTORS MADE OF GRAPHENE GROWN ON RECYCLED COPPER FOILS

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ABSTRACT

In this paper, recycled low purity copper foils (98%) are tested after a multiple-use process for obtaining single-layer graphene (SLG). The graphene transfer technique based on water electrolysis (bubbling) is used for the preservation of the Cu foils in multiple graphene deposition cycles. Preliminary cleaning by O_2 plasma remove carbon residues from the copper surface. The Cu foils are then cleaned with hydrochloric (HCl) or acetic acid (CH_3COOH) solutions, used as chemical baths, and the results compared. Atomic force microscopy used to check the Cu foil roughness, a critical parameter for the growth of SLG, shows root-mean-square roughness of 4.61, 28.00, 3.50 nm, for new Cu foil, after acetic acid, and after hydrochloric acid treatments, respectively. Full coverage of SLG was obtained only during the third usage of Cu foils, i.e., after two recycling cycles. Carrier mobility measured on graphene field-effect transistors fabricated after each recycling cycle, show values of 814 (1728) and 1847 cm^2/Vs (1147 cm^2/Vs), for electrons (holes) after one and two recycling cycles, respectively, thus demonstrating the improvement of the quality of the graphene with the number of Cu recycling cycles. Devices fabricated with graphene grown on the initial, low-purity, Cu foil did not show transistor behavior.

Keywords: Copper purity; multiple-use, electrolysis, High-mobility, single-graphene.

1. INTRODUCTION

Single-layer graphene (SLG) has a planar honeycomb structure of sp^2 bonded atoms. The atomic structure of graphene gives rise to exceptional electrical, optical, mechanical, and thermal properties [1,2]. The high carrier mobility of graphene, and the ambipolar character, i.e., the possibility to quickly shift from electron to hole transport, makes this material attractive for innovative applications based on field-effect transistors in which the graphene is the active layer (GFETs). In these devices, a gate voltage controls the carrier concentration. The point of transition from electron to hole transport is called charge neutrality point, or Dirac point [3–5], and corresponds to the minimum conductance of the device. The position of this point in an external gate voltage scale is dependent on any charges present at or close to the surface of graphene at the microscopic scale, which modulates the carrier concentration by a mechanism called local gating. Any changes in the Dirac point position translate into changes in transistor channel resistance, for a fixed external gate voltage. Based on this mechanism, GFETs can be used as gas sensors, chemical sensors and biosensors with extreme sensitivity and record-low limit of detection.[6,7]

Single-layer graphene (SLG) can be obtained by mechanical exfoliation [8], molecular beam epitaxy (MBE) [9,10], thermal-chemical vapor deposition (T-CVD) [11,12], epitaxial growth on silicon carbide[13], among other less used techniques. Exfoliated graphene provides the highest quality material (lowest number of defects, highest carrier mobility). However, this method does not apply to large-area fabrication [12,14,15]. The graphene grown by MBE has good quality and is applicable for large-area fabrication. However, the costs involved are very high, mainly due to ultra-high vacuum conditions required [16,17] and low throughput. The elevated cost of the substrate and the difficulty in obtaining SLG [9] limit the use of epitaxial growth on silicon carbide. T-CVD deposition is most promising for large scale production of graphene devices, as it allows for the continuous deposition of graphene over large areas,[18,19] with a uniform coverage, and device grade electronic properties. T-CVD works by the decomposition at high

temperature (~1020 °C) of a carbon precursor (a gaseous hydrocarbon) onto a catalyst substrate, typically a high purity transition metal (e.g., Co, Ni, Cu, Mo) [20–22] foil or film. Copper is the most common catalyst because it has the lowest carbon solubility of all known graphene catalysts[23], which prevents carbon exodiffusion upon substrate cooling, hence enabling full coverage with single-layer graphene.

For electronic device fabrication, T-CVD graphene must be first transferred onto an electrically insulating substrate. The most common method used for the transfer of graphene implies the transition metal catalyst dissolution[2,24]. In the prospect of large scale production of graphene, efforts have been made in the reduction of the material costs, in particular the high purity metal used as the catalyst. Some have devised the reuse of the copper remaining in the etchant solution[25], while others use dry transfer technique to allow the reuse of the copper. Another transfer method, the electrochemical delamination[26] (or hydrogen bubbling), was later proposed, with prospects of enabling the reuse of the copper[27] catalyst while allowing for the use of graphene grown on both sides of the copper foil substrate. There are many studies about recycling processes for catalyst substrates. In one approach, Sodium hydroxide (NaOH) is used as the electrolyte mixed with diluted potassium persulfate ($K_2S_2O_8$) to perform a soft etch of copper[28], cleaning it from oxides and residues forming during the electrochemical process. The method was later extended to platinum foils [20], tungsten foils[29], and copper thin film on silicon[30]. While the first experiments used NaOH 1 M,[20] it was later found that a lower concentration of 0.25 M leads to a cleaner graphene transfer. [31] In another approach, a solution of sodium chloride (NaCl) and a better control of the potentials ensure a reduction of any copper oxide.[32] Y. Wang recommends the use of the $K_2S_2O_8$ for graphene transfer, using the electrochemical procedures to remove the graphene across the hydrogen bubbles[26]. In a more recent approach, Wang et al[33] proposed the use of carbonic acid during electrochemical delamination to facilitate its copper catalyst reuse and studied the quality of graphene after multiple uses of the copper.

In this work, a systematic study on the graphene quality grown on recycled Cu foils is presented, using electrolysis as the transfer method[26]. An electrochemical transfer method with $K_2S_2O_8$ was used for recycling the copper foil catalyst, and different post-transfer cleaning processes, namely using acidic and plasma treatments, for the reuse of the foil, are compared. We assess the quality of the copper foil and graphene coverage and compare the electronic properties of GFET devices made after multiple growth (up to three times) on the same catalyst substrate.

2. EXPERIMENTAL PROCEDURE

In this study, graphene is grown intentionally on low cost, low purity (98%, Goodfellow, 2% other metallic elements measured by supplier) copper foil, which leads to graphene with low electronic quality after the first release. Therefore, graphene from the first batch is discarded. The foil is then recycled according to one of the procedures described below. The experimental procedure, including the graphene growth, electrochemical delamination, and characterization of graphene, is shown on the flow chart in Figure 1. Graphene transistors are fabricated with the material resulting from depositions on recycled Cu foils, according to the schemes (A) and (B) described below.

(A) 2 samples for 1 recycling iteration with HCl or CH_3COOH, respectively;

(B) 1 sample for 2 recycling iterations with HCl.

The performance is compared with that of transistors fabricated with graphene transferred by Cu dissolution from fresh, high purity (99.999 %, AlfaAesar, 2% other metallic elements measured by supplier) Cu foils.
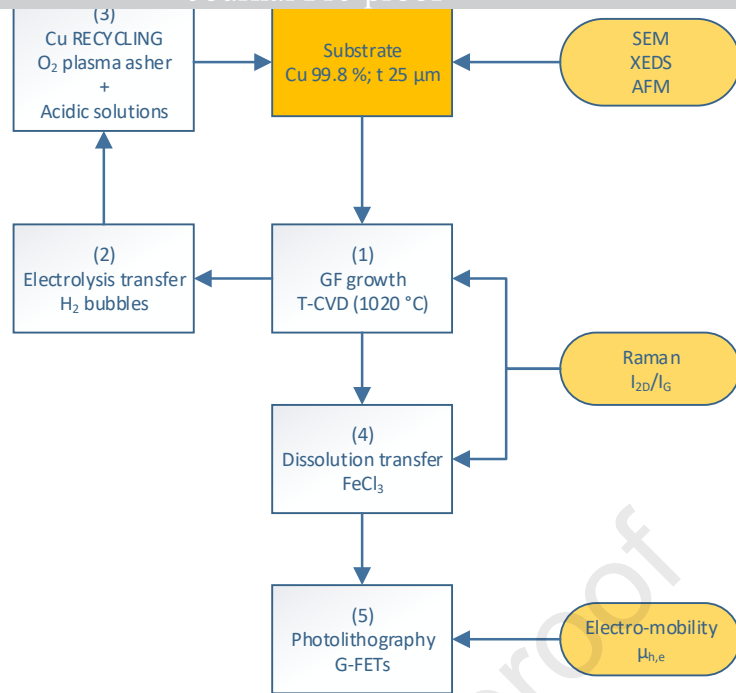
Figure 1: Workflow used in this work. The process starts with copper foil catalyst low purity for multi-layers graphene growth. The first step is the deposition at 1020 °C; the growth and dissolution transfer were characterized by Raman spectroscopy. The second step is the removal of the graphene or the thin film graphite (due to the low purity of catalyst) from the copper foil; third is to clean the surface of copper with oxygen plasma and finishing with Acidic bath to remove the residues. The analysis of copper is done by scanning electron microscope, X-Ray electron diffraction scanning), or Atomic Force Microscope. The sixth step is to transfer graphene with a dissolution method to allow the electrical characterization of graphene. The growth and dissolution transfer were characterized by Raman spectroscopy. The seventh step is to make the Graphene transistor.

A preliminary study is accomplished using 12 small pieces cut from a large Cu foil fully covered with graphene grown under the same recipe conditions (see Methods), to test all possible combinations of the values of the recycling parameters used in this study: presence or absence of oxygen plasma, two different acidic solutions (Hydrochloric acid (HCl) and acetic acid (CH_3COOH)). The duration of the copper cleaning in acidic solution is optimized. The copper surface is analyzed in three different samples, which differ in the duration of the bath:

short, medium, and extended duration. The short duration sample is removed from the bath after some change in the color of the copper surface arises. The extended duration sample is removed from the bath when the surface does not change anymore, and the medium duration is a time chosen randomly between short and long durations. Substrates are analyzed by AFM (Atomic Force Microscope), SEM (Scanning electron microscope), and XEDS (X-Ray Electron Diffraction Scanning) (see the top loop in Figure 1). After this study, it is concluded that recycling Cu foils without O_2-plasma treatment is not satisfactory (Figure 2c-d) for cleaning the surface. It is also concluded that the duration of the acidic baths lower than 30 min for HCl (Sigma-Aldrich, 37%) and 18 h for CH_3COOH (Sigma-Aldrich, ReagentPlus[©] >99%) produces poor results for cleaning the surface. Therefore in the next batch of experiments, only two combinations of the Cu foil cleaning parameters are selected: a) O_2 plasma treatment followed by HCl bath for 30 min; b) O_2 plasma treatment followed by CH_3COOH bath for 18 h.

In scheme (A), graphene is grown 2 times in subsequent depositions on the same Cu substrate. After the first growth, iteration graphene was transferred by electrolysis, thus removing it without destroying the copper. After the second growth iteration, the transfer is performed by Cu dissolution for GFET fabrication under standard conditions. In scheme (B), graphene is grown 3 times in subsequent depositions on the same Cu substrate. After each of the first two growth iterations, it is transferred by electrolysis, removing the graphene while preserving the copper foil. After the last growth process, the transfer is done by Cu dissolution for GFET fabrication using our standard process. The transistors resulting from these transfers were then compared with GFETs fabricated from high-purity Cu and transferred by substrate dissolution using the standard process.

2.1.   Growth of graphene

The new copper foils (98 % purity, 25 μm thick and $50 \times 50\,mm^2$) are characterized by scanning electron microscopy (SEM, FEI Nova NanoSEM 650) and atomic force microscopy

(AFM, Dimension Icon) for topographical analysis, and energy-dispersive scanning (XEDS, from the SEM) for compositional analysis.

Graphene was grown by T-CVD (ET3000 EasyTube FirstNano CVD Corporation) on the copper substrates characterized before. Briefly, the growth steps are (i) heating of the copper foil at 1020 ºC for 40 minutes in a H_2 atmosphere, followed by (ii) methane/hydrogen (50/300 sccm) atmosphere for 45 minutes. Both steps, annealing, and deposition, are done at a pressure of 0.5 Torr. Immediately after growth, graphene is characterized by Raman spectroscopy on the native copper substrate.

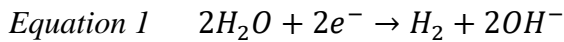- Characterization, growth, and use of graphene

The Raman spectra were obtained, in the backscattering geometry, with a Witec Alpha300R confocal Raman microscope using a 532 nm frequency-doubled Nd:YAG laser for excitation with P_{laser} = 1.5 mW incident on the sample. The number of graphene layers is obtained from the intensity ratio between the 2D (ω_{2D} ~2700 cm^{-1}) and G (ω_G ~1590 cm^{-1}) modes, where monolayer of graphene is associated to $I_{2D}/I_G > 1$ [34]. The intensity of the D mode (ω_D ~1350 cm^{-1}) and corresponding intensity ratio between D and G modes are used to estimate the presence of defects [35].

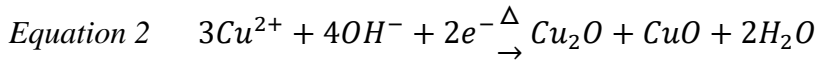## 2.2. Electrolysis transfer

After the graphene growth and characterization on copper, both sides of the copper foil are spun with a 630 nm layer of polymethyl methacrylate (PMMA, positive resist for e-beam lithography, model AR-P 679.04, Allresist). This polymer layer supports the graphene during all the steps of the transfer process, forming a membrane.

Electrochemical delamination is performed in an aqueous solution of potassium sulfate (K_2SO_4 [0.05 mM], Sigma-Aldrich, ReagentPlus$^©$ >99%) by applying a voltage of 10 V between the electrodes into glass Duran$^®$ container supported by vertical tweezer as the positive electrode. The current was in the range of 1 mA. The release of graphene from the Cu
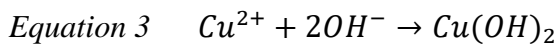
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foil is due to the H$_2$ bubbles that form at the interface graphene/copper by water splitting, when copper is the cathode, following the reaction: [26]

Equation 1 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

The anode half-reaction is:

Equation 2 $3Cu^{2+} + 4OH^- + 2e^- \xrightarrow{\Delta} Cu_2O + CuO + 2H_2O$

With the formation of copper hydroxides [26]:

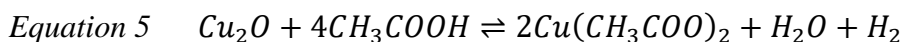*Equation 3* $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$

The floating graphene/PMMA samples are recovered from the electrolytic solution, cleaned in ultrapure water, and then transferred and dried the same way as in the case of the copper dissolution.
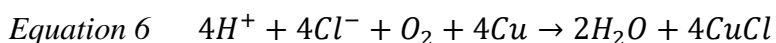
2.3.   Copper foil recycling

Half of the copper samples for recycling were submitted to an oxygen plasma treatment and followed to the chemical bath. The plasma eliminates possible carbon residues on the Cu surface, which would influence the copper evaporation during the high-temperature annealing and deposition, resulting in a Cu roughness increase [36]. However, the O$_2$ plasma causes the formation of copper oxides at the surface. Because these oxides, grown under harsh plasma conditions, in general cause a reduced quality graphene growth[37], they were removed.

The samples are submitted to either one of two cleaning baths: 2 % acetic acid[38] or 2 % hydrochloric acid [39,40]. These acidic solutions cause the removal of oxides present at the surface. They also etch part of the copper. The reaction equations that describe these cleaning procedures are:

Equation 4 $CuO + 2CH_3COOH \rightleftharpoons Cu(CH_3COO)_2 + H_2O$

Equation 5 $Cu_2O + 4CH_3COOH \rightleftharpoons 2Cu(CH_3COO)_2 + H_2O + H_2$

for CH$_3$COOH cleaning and,

Equation 6 $4H^+ + 4Cl^- + O_2 + 4Cu \rightarrow 2H_2O + 4CuCl$

for HCl cleaning.

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The duration of the immersion in the acidic bath was 5, 20, and 30 min in the case of HCl and

1, 6, and 18 h for CH$_3$COOH.

After the chemical bath, each copper foil was characterized as described above for the new Cu

foil, and used for the next graphene growth batch process.

2.4. Transfer by dissolution

The transfer by dissolution is used as the last transfer step after the foil was already used

multiple times. It serves at the same time as a reference transfer method, [41] since it is known

to provide excellent coverage of the final substrate.

After graphene growth, the copper is spin-coated on one side with 630 nm PMMA at 1000

rpm, then baked at 80 °C for 8 minutes. The opposite side of the copper is treated with an

oxygen plasma, removing the graphene that grew on that side. The copper foil is then left

floating on a solution of iron chloride 0.5 M at 35 °C for 30 min until the copper dissolves.

The floating PMMA with graphene attached at the bottom side is transferred to a solution of

2% HCl for 30 min, then to a de-ionized (DI) water bath for 30 min. The HCl and DI-water

cleaning steps are repeated 5 times.

The pre-patterned substrate is then used to scoop the floating graphene/PMMA film. Before

this step, the substrate was primed with Hexamethyldisilazane (HMDS, Merck >99%) vapor

to increase its hydrophobicity and adhesion. Water between the substrate and PMMA is

gently pushed away using a nitrogen gun, and then the sample is dried at 180 °C for 12 h in an

oven. After the sample cools down, PMMA is removed by an acetone bath for 2 h.

2.5. Photolithography

The final substrates for graphene transistors, i.e., the substrates with source, drain, and gate

contacts are fabricated by optical lithography (Heidelberg DWL 2000, laser 405 nm, 120 mW

maximum power, head 4 mm, 200 mm monocrystalline silicon wafer size, 1 μm resolution).

The substrates have a buried gate contact (50 nm of tantalum) covered with 200 nm of SiO$_2$

deposited by CVD. The access vias to the gate contact were performed by reactive ion etching

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(SPTS APS). The source and drain contacts (Cr(5nm)/Au(50nm)) were lithographed on the SiO$_2$ insulator by ion-milling (Nordiko 7500). The GFETs were designed to have channel width-over-length ratios, *W/L*, of 1 (*W* = 50 μm, *L* = 50 μm) or 3 (*W* = 75 μm, *L* = 25 μm). The final substrate of 25 × 25 mm^2 contains 416 GFETs.

The Graphene layer is patterned by photolithography using positive photoresist (AZ1505, MicroChemicals) photoresist then etched by a plasma ashing process. After patterning, the photoresist is removed in an acetone (Sigma-Aldrich) bath for 2 h without ultrasounds.

2.6 Electrical characterization

The carrier mobility of graphene grown from recycled copper foil is compared with the mobility of graphene monolayer from new copper foil catalyst high purity (99.999%). The carrier mobility is extracted from transistor transfer curves that are obtained in a three probe measurement station using a Picoammeter Keithley 6487 (Drain-source circuit) and a Source-meter Keithley 2410 (Gate-drain circuit), and custom software to automate the measurement loop. The transistors are characterized by forcing a 100 μA current between source and drain while sweeping the gate voltage between -50 and +50 V. The carrier density and carrier mobility for electrons and holes are obtained by fitting the transfer curves to the transconductance model described by Equation 7.

Equation 7 $I_{DS} = \mu \frac{W}{L} C(V_{GS}) V_{DS}$

I$_{DS}$ is drain-source current, μ is the carrier's mobility, *W* is the width, *L* is the length, *C* is the geometric gate dielectric capacitance (200 nm of SiO$_2$ as shown section 3.3) and V$_{GS}$ and V$_{DS}$ are gate-source and drain-source voltages, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Cu surface

Figure 2 shows images of a copper foil after a first graphene deposition, transfer, and recycling using the procedure with an acidic bath of CH$_3$COOH (Figure 2c), or HCl (Figure 2d), and also by a combination of O$_2$ plasma followed by CH$_3$COOH (Figure 2e), or HCl

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(Figure 2f). Figure 2a shows the XEDS spectra, taken at 10 kV, of selected areas indicated in the SEM images 2c and 2d. The SEM images were done under an electron beam accelerated between 5 -10 kV. The magnification of the pictures was at 50000 times. Figure 2b is a SEM image of a used Cu foil, shown for comparison, where the inset shows the same Cu foil after O_2 plasma. For each chemical bath, the effect of a preliminary cleaning step with O_2 plasma can be seen in Figure 2e and Figure 2f, for CH_3COOH and HCl, respectively.
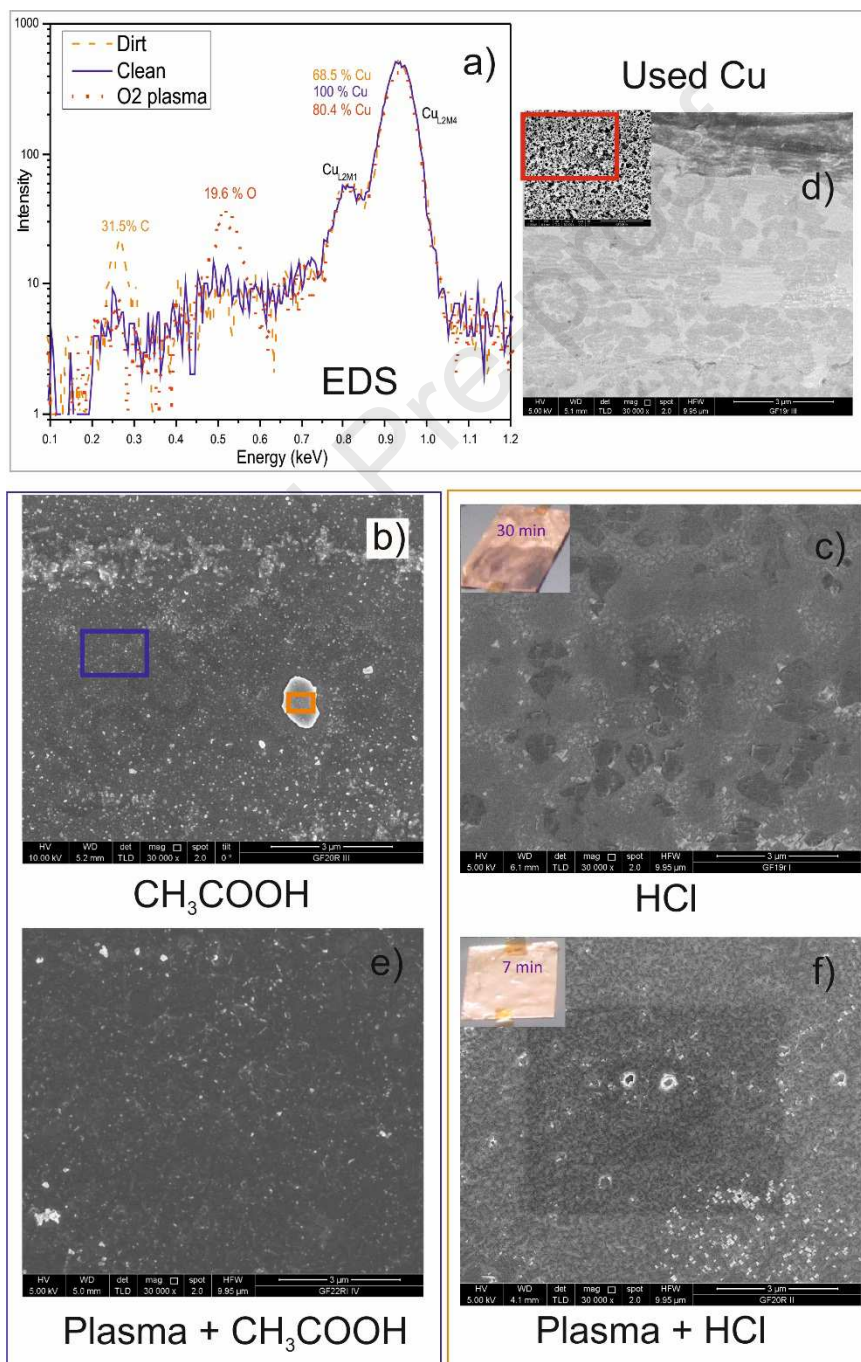
Figure 2: Effect of O₂ plasma and acidic treatment in the recycling process. a) XEDS analysis of the copper foil recycled with CH₃COOH [2 %] treatment from selected areas in c) and of the copper surface after O₂ plasma of the inset in b); b) SEM image of a used copper foil and inset of a copper foil submitted to O₂ plasma showing selected area used for the XEDS analysis in a) is shown in the inset; c) SEM image of copper foil recycled with CH₃COOH [2 %], for 18 h showing selected areas used for the XEDS analysis (in a); d) SEM image of copper foil recycled with HCl [2 %], for 30 min, and optical image of copper foil is shown in the inset; e) SEM image of a copper foil recycled with O₂ plasma and with CH₃COOH [2 %]; f) SEM image of a copper foil recycled with O₂ plasma and HCl [2 %] solution, and optical image of the copper foil after 7 min in the HCl [2 %] solution inset. (XEDS Oxford x-act / SEM FEI Nova NanoSEM).

The blue curve (a cumulative spectrum of the area inside the blue rectangle of Figure 2c) shows an effectively cleaned copper area, with no or residual O and C peaks. The dashed orange curve (a cumulative spectrum of area inside the dashed orange rectangle of Figure 2c) shows a prominent C peak, from contaminating residues. The dotted red curve (a cumulative spectrum of the area inside the dotted red rectangle of Figure 2b) shows an O peak attributable to oxide formation due to plasma cleaning. Figure 2e-f shows the SEM images of a copper foil recycled with O₂ plasma followed by CH₃COOH (Figure 2e) and HCl (Figure 2f) for 18 h and 30 min, respectively. Comparing the figures corresponding to treatment with the same acidic solution (CH₃COOH in Figure 2c and Figure 2e and HCl in Figure 2d and Figure 2f), the O₂ plasma process followed by acidic bath improves the Cu foil quality. Concerning the SEM images in Figure 2b, Figure 2e-f, it is clear that the Cu surface after one recycling process, independently of the acidic solution used, becomes more homogeneous, presenting a minimum quantity of residues when compared with the used Cu foil. Moreover, the HCl solution originates some holes, as seen in Figure 2f.

The surfaces of the recycled Cu samples were studied by AFM in tapping mode at 512 kHz. Figure 3b-c presents the AFM images of two recycled Cu foils using O₂ plasma and CH₃COOH solution (Figure 3b) and O₂ plasma and HCl solution (Figure 3c). For comparison, images of a new copper foil are also presented (Figure 3a).
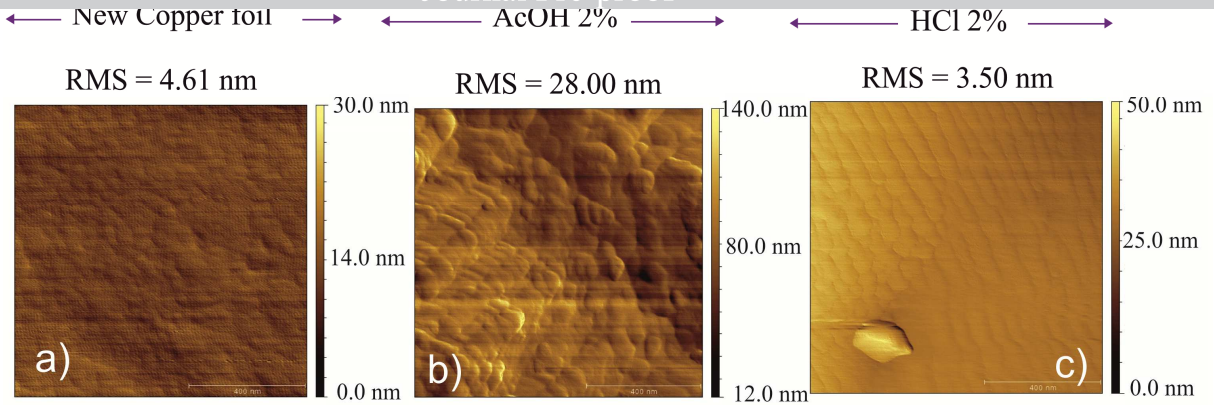
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Figure 3: Effect of recycling with O_2 plasma and acidic solutions: a) AFM height image of a new copper foil; b) AFM height image of a Cu-recycled with O_2 plasma and CH_3COOH [2 %] solution; c) AFM height image of a copper foil recycled with O_2 plasma and HCl [2 %] solution. The AFM and SEM measurements were not performed at the same sample area. (Bruker Dimension Icon, tip: Nanosensors PPP-NCHR tapping mode, 324 kHz). The SEM image scale of the copper foil is doubled than the recycled coppers.

The peak-to-peak amplitude (A_{pp}) and root-mean-square roughness (r_{RMS}) were measured on the pristine sample and after the recycling process (Figure 3a-c). The AFM characteristics for the pristine copper foil are $A_{pp} = 28.3$ nm and $r_{RMS} = 4.61$ nm. The peak-to-peak amplitude and roughness obtained for Cu substrate recycled using CH_3COOH sharply increases to $A_{pp} = 146.4$ nm and $r_{RMS} = 28$ nm, whereas, the parameters obtained for Cu recycled using HCl gives almost the same values as obtained with the pristine Cu foil: $A_{pp} = 28.9$ nm, $r_{RMS} = 3.50$ nm.

According to these results, the copper recycling using O_2 plasma and acidic solutions (HCl and CH_3COOH) leads to a clean, although irregular surface. Moreover, the AFM study reveals that after sample cleaning using HCl, the surface roughness becomes equivalent to that of the pristine Cu foil. Therefore, the combined use of hydrochloric acid solution and O_2 plasma treatment is the right approach for copper recycling.

3.2. Graphene characterization by Raman spectroscopy

Figure 4 shows the Raman spectra of graphene samples while still on the catalyst (Figure 4a and b) and after transfer to the final Si/SiO_2 substrates (Figure 4c and 4d). The Raman signal of graphene on Cu substrate shows a broad background band associated with the reflection of

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light from the Cu substrate (Figure 4a-b), which is absent for the final substrate. The Raman peaks at 2700, 1590, and 1350 cm^{-1} are vibrational modes assigned to for graphene. The peak at 1590 cm^{-1} (with integrated area I_G) corresponds to the in-plane stretching vibration of the sp^2 carbon bonds, like in graphite. I_D is the integrated intensity of the peak at 1350 cm^{-1} and corresponds to the breathing modes of six-atom rings, requiring a defect or an edge for its activation. I_{2D} around 2700 cm^{-1} is an overtone of the D mode only visible in graphene, due to single-layer confinement. The electron mobility increases with larger crystallite size and less graphene numbers of layers, so less intensity at 1350 cm^{-1} peak and more intensity in the 2700 cm^{-1} peak is desirable. Single-layer graphene is characterized by a ratio of $I_{2D}/I_G > 1$.

Figure 4a and Figure 4c show Raman spectra representative of the graphene grown on one-time recycled Cu foil (2nd use of Cu foil). Figure 4b and d show Raman spectra representative of the superior quality graphene grown on two times-recycled Cu foil (3rd use of Cu foil). The Witec system was set up in 1.5 mW on a 532 nm wavelength laser.
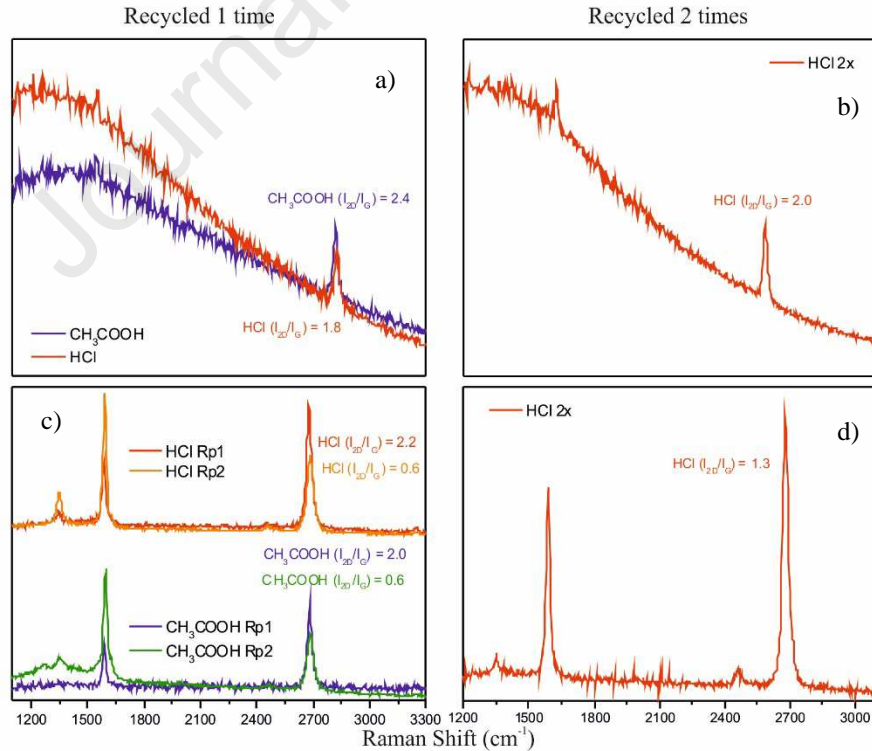
Figure 4: Representative Raman spectra of the graphene grown on a) 2ⁿᵈ use copper foil (after the 1ˢᵗ recycling process); b) 3ʳᵈ use copper foil (after the 2ⁿᵈ recycling process); Raman spectra of graphene after transferring from c) 2ⁿᵈ time used copper foil and and d) 3ʳᵈ time used copper foil. The different Raman curves presented in a) and c) correspond to different samples. The curve in d) was measured on the same graphene film as in b).

It is seen that the graphene quality improves with the increasing of the number of Cu recycling cycles observed only on graphene Raman spectral after transfer and Figure 4c-d, because the copper foil has metal luminescence from itself avoiding a precise analysis. For the graphene on one time-recycled Cu foil Raman spectra the 2D peak was observed as well as ion the copper foil recycled 2 times.

Important to note, after the 1ˢᵗ-recycling process of the low-purity copper foil, the graphene quality is already reasonable, independently of the Cu recycling process used, as shown by the Raman spectra in Figure 4a and Figure 4c. Indeed, the I_D defects peak is not seen in the Raman spectra taken on Cu, while monolayer graphene is detected. After transfer to the Si/SiO$_2$ substrate using the PMMA membrane, the peak of the defects becomes apparent (Figure 4c). A remarkable improvement is observed in the Raman spectrum typical of SLG with few defects shown in Figure 4d, obtained from graphene on SiO$_2$ from the Cu 2ⁿᵈ-recycling process, using HCl [2 %] solution. Similar spectra are obtained in all analyzed points of this sample.

3.3. Electrical characterization of GFETs

Figure 5a shows histograms with statistical results of the channel resistance, R_{ch}, of 563 GFETs selected from 3 batches of 416 devices each (1248 devices in total). The devices are fabricated using graphene transferred from copper recycled using three different pathways, according to schemes (A) and (B) in section 2. The selection criterion was arbitrarily set to $R_{ch} < 10$ kΩ, which separates the transistors considered of good quality from the others ($R_{ch} > 10$ kΩ), which were discarded. The yield is the ratio between the number of devices with $R_{ch} < 10$ kΩ and 416. The results are distributed as follows: 157 devices (yield = 38%) using HCl cleaning and scheme (A), i.e., after 1 recycling of the Cu foil (red columns); 334 devices

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(yield = 80%) using CH₃COOH cleaning also following scheme (A) (green columns), and 72

devices (yield = 17%) using HCl cleaning following scheme (B), i.e., after 2 recycling

processes of the Cu foil (black columns). Figure 5b shows the statistical results of the channel

resistance in 388 GFETs (yield = 93 %) using graphene from a new copper foil, Alfa Aesar
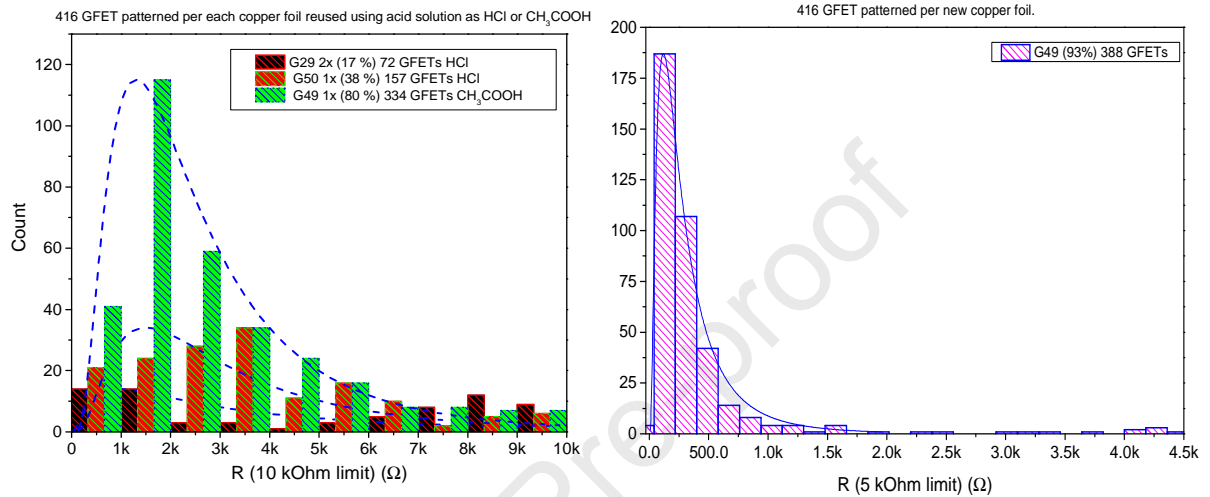
(99.999 % of purity).

Figure 5 a) Histogram showing GFET-channel resistance using graphene grown on copper recycled using CH₃COOH (1ˢᵗ recycling) and HCl (1ˢᵗ and 2ⁿᵈ recycling). The data selection (563 GFET, of which 334 of HCl 1 time, 157 of CH₃COOH, and 72 of HCl 2 times) was made based on the resistance (<10 kΩ). b) Histogram showing GFET-channel resistance using graphene grown on new copper foil.

For processes following method in (A) and HCl cleaning (1-time cleaning and 2-times

cleaning, as shown in section 2), the mode of the experimental distribution is 3.5 kΩ, and

90% of the devices have R < 5.8 kΩ (157 devices). For the CH₃COOH cleaning, the most

probable resistance of the 334 GFETs is 2.8 kΩ, and the 90ᵗʰ percentile is 4.9 kΩ. When using

the HCl process 2 times on the same copper foil, following scheme (B), the average resistance

is 4.8 kΩ, and the 90ᵗʰ percentile is 8.4 kΩ for 72 GFETs. The statistical results of the

resistance for 388 GFETs fabricated with graphene grown on high-purity Cu foils, for

comparison, show an average of 0.4 kΩ the 90ᵗʰ percentile is 1.0 kΩ.

In Figure 6 the transfer normalized curves in gate voltage for different transistor sets

originating from the three Cu treatments processes are shown: 21 GFETs originating from Cu

substrates treated with CH₃COOH according to the scheme (A) (black color); 11 GFETs

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treated with HCl according to the scheme (A) (blue color), 30 GFETs treated with HCl according to the scheme (B) (red color). It is seen that the graphene grown on treated copper foil has a relatively high mobility even after the first recycling treatment in HCl or CH_3COOH: 1147 cm^2/Vs and 814 cm^2/Vs for electrons, and 889 cm^2/Vs and 1728 cm^2/Vs for holes, respectively. As discussed earlier, the copper foil roughness, after CH_3COOH treatment is higher than after HCl treatment, then these transfer curves indicate that the roughness of catalyst substrate is not the only factor dictating the performance of the device. The electrical study confirms that, for growing graphene, the surface quality of recycled copper foil increases with multiple uses. As shown in Figure 6, the transfer curves of the GFETs using graphene grown on Cu foil recycled twice with HCl show higher mobility (1847 and 997 cm^2/Vs, for holes and electrons, respectively) and a better shape than those from devices fabricated from graphene on Cu recycled only once with HCl. The results are comparable with those from devices made of single-layer graphene obtained from high purity new copper foil, with 1393 and 1875 cm^2/Vs for holes and electrons, respectively, as shown in Figure 6d.
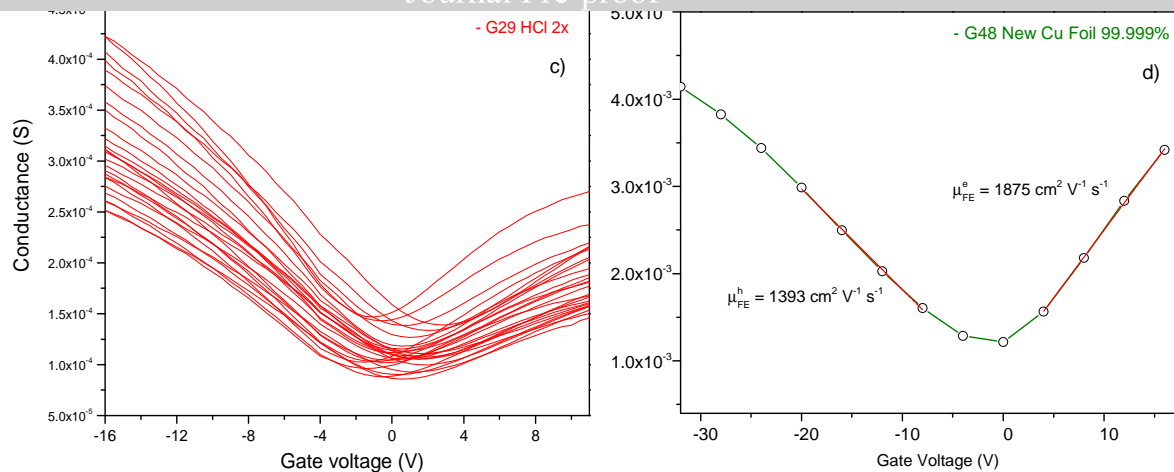

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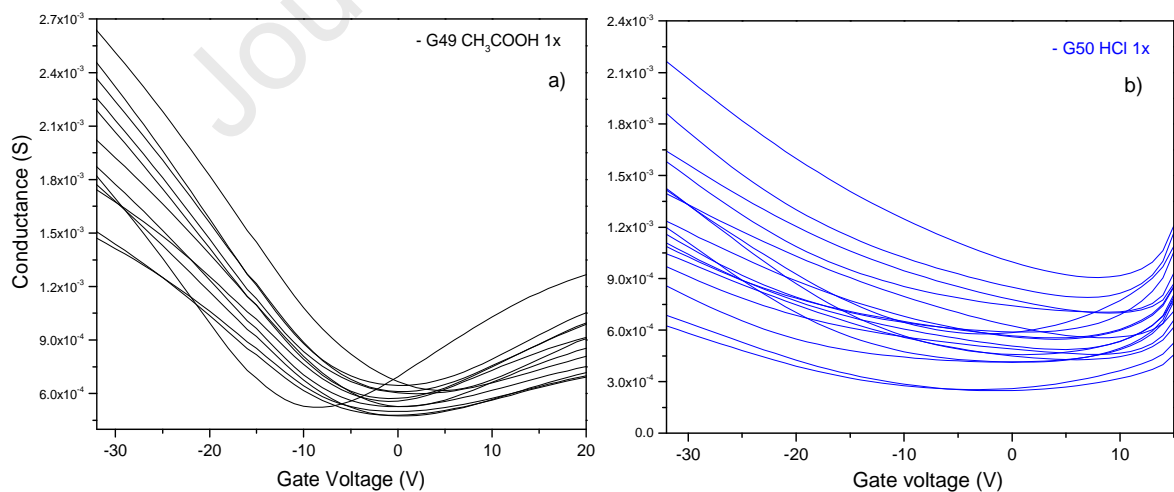
Figure 6: Representative transfer curves normalized in gate voltage of the transistors with different graphene from different copper foils catalyst provided by different acid bath recycling. a) CH_3COOH solution 1 time, b) HCl solution 1 time, c) HCl solution 2 time, d) Single layer graphene transfer curve grown on new copper foil with outlined slope to extract the carriers' mobility.

Copper foil roughness and surface homogeneity determine graphene quality. In the recycling process of Cu foils, using O_2 plasma treatment previously to a chemical bath is essential for surface homogeneity, as shown by SEM results. The quality improves because the copper foil after cleaning has less surface impurities, making the carbon less soluble on the catalyst surface. We assume that the native copper oxides concentration on the catalyst surface is the same in new copper foil as in recycled copper foil and that they are removed in the annealing step that precedes graphene deposition. When recycling Cu multiple times, HCl chemical bath prepares a better Cu surface for graphene growth than CH_3COOH chemical bath, as shown by AFM results. The quality increase probably because the treatment of the copper foil removes the contamination from the surface turning the carbon less soluble on the copper. The annealing step does not remove impurities as seen by the growth of amorphous carbon thin film on low purity copper.

4. CONCLUSION

Both single layer and multilayer graphene were grown on Cu foil recycled once using HCl or CH_3COOH. Full coverage of single-layer graphene (without the presence of the multilayer) was only achieved on Cu foil after the second recycling iteration with HCl, demonstrating the

increasing quality of Cu foil to grow graphene with multiple recycling cycles. The treatment is essential to the reusable process because cleaning the surface allows the growth without blocking zones due to a dirty surface. The annealing step does not remove the dirty particles that determines the purity of the catalyst.

The transistors made of single-layer graphene grown on recycled copper had the highest carrier mobility with values of $1847 \, cm^2/Vs$ and $1147 \, cm^2/Vs$ for holes and electrons, respectively. In conclusion, the recycling process of the low purity copper foil (98 %) allows for multiple uses of the same copper foil for graphene deposition with an enhancement of the carrier mobility, and with increasing quality as the number of cycles of the copper recycling also increases.

5. ACKNOWLEDGMENTS

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Highlights

- SLG were obtained using low purity Cu foils (98%) after multiple graphene growth.

- Water electrolysis was used for catalyst recycling combined with acidic solutions for cleaning the Cu foils.

- Atomic force microscopy and Raman spectroscopy were used to check Cu foil roughness and graphene structure, respectively.

- Carrier mobility measured are 814 cm^2/Vs and 1847 cm^2/Vs for electrons after one and two recycling cycles, respectively.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: