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Direct growth of 2D and 3D graphene nano-structures over large glass substrates by tuning a sacrificial Cu-template layer

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ABSTRACT

We demonstrate direct growth of two-dimensional (2D) and three-dimensional (3D) graphene structures on glass substrates. By starting from catalytic copper nanoparticles of different densities and using chemical vapour deposition (CVD) techniques, different 2D and 3D morphologies can be obtained, including graphene sponge-like, nano-ball and conformal graphene structures. More important, we show that the initial copper template can be completely removed via sublimation during CVD and, if need be, subsequent metal etching. This allows optical transmissions close to the bare substrate, which, combined with electrical conductivity make the proposed technique very attractive for creating graphene with high surface to volume ratio for a wide variety of applications, including antiglare display screens, solar cells, light-emitting diodes, gas and biological plasmonic sensors.

1. Introduction

Graphene, a two-dimensional (2D) carbon material, has a wide variety of potential applications due to its unique electrical and optical properties, mechanical strength, flexibility and chemical stability. Since its discovery, several techniques have been developed to grow it with high quality and over large area substrates. These include chemical vapor deposition (CVD) and plasma-enhanced CVD (PECVD) usually carried out on transition metal foils that act as catalysts to favor the dissociation of a hydrocarbon gas. An important factor to control the number of graphene layers is the carbon solubility of the catalyst, as it enables different growth mechanisms (carbon adsorption, absorption or segregation). In the case of Cu, single layer graphene can grow in a controlled manner because of the adsorption mechanism due to low carbon solubility. For this reason, 25 to 35 μm -thick Cu foils have

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become the standard surface for CVD or PECVD graphene growth [1]. The graphene is then transferred to the desirable substrate, e.g. glass in our case, by using sacrificial layers, the most common one being polymethyl methacrylate (PMMA). Often, the electrical, optical and mechanical properties of the transferred graphene are affected by organic residues. To avoid time consuming, cumbersome transfer and poor performance associated to residues, direct growth on dielectric substrates has been investigated. For example, it has been achieved by using an interfacial ultrathin metal film that acts as a catalyst and retracts during growth leaving graphene on the dielectric area. As a final step the residual metal can be completely removed using simple etching processes [2–5].

Recently, more complex three dimensional (3D) structures with high quality and large surface-to-volume ratio have been obtained starting from 3D-shaped catalytic templates. Also, it was demonstrated a significant control of size and shape thanks to the catalyst morphology, which can be modified to obtain, for example, graphene spheres, tubes or networks [6,7]. Ni foams are an example of a 3D-shaped catalyst that produces high quality 3D-graphene (3D-G) networks with excellent conductivity [8,9]. Other studies have demonstrated the growth of 3D-G by using more specific catalysts, e.g. MgO, Ni-coated pyrolyzed films and metallic salts. Of interest are structures grown by PECVD while a voltage is applied, which are known as “carbon nanowalls” [10,11]. If good quality is preserved, 3D-G structures are attractive as they possess 2D-graphene properties with a larger “effective” surface area. In addition, the combination of 3D-G with other functional materials could lead to the development of new surfaces for a wide variety of applications, including antiglare display screens, solar cells, light-emitting diodes (LEDs), supercapacitors, batteries, gas and biological sensors [12]. The challenges associated to grow 3D-G structures consist in extending the aforesaid technique to different catalyst materials and geometries and, similarly to 2D graphene, avoiding transfer processes that usually involve etching of the metal catalyst, use of polymers and lithography.

In this work we address these challenges and demonstrate 2D- and 3D-G structures starting from properly defined catalytic Cu templates. Nano-structuring of the initial Cu structures is achieved using lithography-free methods that allow to process large areas (up to 2x2 inches). Notably, Cu deposition and nano-structuring can be carried out on a wide range of substrate materials and inside the same CVD chamber as that used for the subsequent graphene growth, these being clear advantages for future industrialization. To demonstrate the versatility of the proposed technique, we investigated the growth of three graphene structures with different properties, optical, electrical and morphological, obtained by proper tailoring of the initial Cu template: (i) the arrangement of non-aggregated Cu nanoparticles (Cu NPs) in different layers that produced the formation of a 3D-G sponge-like structure (3D-GS); (ii) one layer of isolated Cu NPs that produced 3D-graphene nanoballs (3D-GB); (iii) the aggregation of Cu NPs forming larger catalytic structures that produced 2D graphene (2D-G) networks.

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3 It is worth noting that in previous work the Cu NPs tended to coalesce during graphene growth
4 making it difficult to control the size and shape of the catalyst particles. Instead, our process allows
5 control of Cu NPs template. Along the way, we have improved adhesion by surface treatment or by
6 partially embedding the Cu template in glass. The resulting high quality graphene nano-structures
7 present low defects sites, high surface to volume ratio, high optical transmission while still preserving
8 electrical properties.
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13 14 15 16 **2. Experimental procedure**

17 **2.1. Cu deposition on glass substrate**

18 Fused silica substrates from Corning Inc. (High Purity Fused Silica, HPFS[®]) with a size of 2x2 inches
19 were used in this work. The substrates were cleaned using conventional organic solvents followed by
20 O₂/Ar (50:50) plasma cleaning at 50 W for 3 min, thus obtaining an hydrophilic surface (contact angle
21 below 5 degrees) which ensures a good adhesion of the Cu template. For the production of all
22 graphene structures, Cu has to be first deposited onto the substrate. For 3D-GB and 2D-G, Cu was
23 deposited from a copper (II) oxide (CuO) suspension in water (Nanophase Technologies or Alpha
24 Aesar, 46.8%) onto cleaned glass. The dispersion was mixed and then sonicated for 10 min. After that,
25 samples were located inside a dipping vessel. For both structures, the primary particle size of the
26 dispersion was 17-23 nm. The deposition of CuO NPs on glass was carried out through varying
27 concentration (1-10 wt/wt%) by diluting the stock solution and dip speed at 224 mm/min without
28 additional modification of the solution. High concentrations resulted in multilayer coatings but at
29 lower concentrations we observed a discontinuous (island type) coating deposition with few layers of
30 particles in some regions with agglomerates with 100 nm heights, larger than 100 nm agglomerates
31 were also seen. This was the procedure for obtaining CuO NPs for 3D-GB production. However, for
32 producing bigger CuO particles for 2D-G structures, we observed that increasing the number of lower
33 withdrawal speed dip runs (50-150 mm/min) led to an increase in particle density without addition of
34 multilayers. Adhesion of CuO NPs for 2D-G was increased by embedding the particles in the glass.
35 This was performed by running various temperature profiles inside a Vulcan furnace using air at
36 temperatures 850-1100°C. The optimal temperature for particle adhesion was ~975°C for 1 h. After
37 that, for both CuO NPs structures, a reduction step for the catalyst activation was performed inside an
38 oven or CVD at 600°C for one hour or longer. Reduced Cu(0) nanoparticles were observed as a
39 plasmon resonance at 586-590 nm in the absorption spectra. The ability to do the in situ reduction and
40 graphene growth in a CVD reactor helps reducing the sample handling and process steps were reduced
41 inside an oven or CVD using H₂ at 600°C for approximately one hour.
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58 For 3D-GS, Cu was thermally evaporated on glass slides. Samples were located inside a quartz tube or
59 CVD equipment at vacuum ($5 \cdot 10^{-3}$ mbar) and 1100°C where Cu was evaporated from a Sigma Aldrich
60 foil with a thickness in the 25 to 35 μm range. The foil was located at the center of the quartz tube

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3 while the fused silica substrate at the extremity of the chamber. By changing the position of the
4 substrate, Cu NPs of different diameters could be obtained, thus allowing different size graphene
5 structures. We located the sample approximately 6 inch away from the Cu foil located in the center,
6 where the substrate temperature was 250°C and Cu NPs had a mean diameter ($\bar{\varnothing}_{\text{CuNPs}}$) of 100 nm.
7 The corresponding 3D-GS structure will have dimensions similar to the Cu template.
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13 2.2. Graphene growth on Cu NPs by CVD

14 Graphene was grown by CVD (Black Magic 4-inch, AIXTRON) under the following conditions:
15 CH₄:H₂ (1:4, for 2D-G and 3D-GB) and C₂H₂:H₂ (1:0, 1:2, 1:4, for 3D-GS), 0.2 mbar for 3D-GS and
16 25 mbar for 3D-GB and 2D-G, heating rates of 50-75°C/min, temperatures of 900°C for 3D-GS and
17 1000°C for 3D-GB and 2D-G, and time of 30 minutes.
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23 2.3. Cu removal from graphene structures

24 For 2D-G and 3D-GS structures, the Cu catalyst is removed by sublimation. An increase of
25 temperature up to 1100°C is performed under Ar/H₂ environment for 10 minutes. In the case of 3D-
26 GBs, the Cu pre-pattern is removed by wet etching using diluted ammonium persulfate for 10 min.
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31 2.4. Cu NPs and graphene structures characterization

32 The evolution of the growth was monitored by means of Atomic Force Microscopy (AFM,
33 Bruker/Veeco Dimension 3100) and FEI-Scanning Electron Microscopy (FE-SEM, FEI Inspect F).
34 Structural characterization was carried out by energy-dispersive X-ray spectroscopy (EDX, Oxford
35 INCA) to confirm that Cu catalyst was removed. EDX measurements were carried at 10 different
36 points. The accelerating potentials varied between 5kV and 15kV, depending on the nature of the
37 sample. Complementary information was obtained by Raman spectroscopy at 532 nm excitation
38 wavelength using a 100X microscope lens (Renishaw inVia). The spectra were acquired in 1100 to
39 2900 cm⁻¹ Raman shift range. For all structures, the surface was statistically studied through mapping.
40 Electrical sheet resistance measurements (Rs) were carried out using a 4-point probe equipment.
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49 3. Results and discussion

50 The synthesis of 3D and 2D graphene structures (3D-GB, 3D-GS and 2D-G) are illustrated in Fig. 1.
51 Using Cu as a common catalyst for all structures, the growth consisted in three steps: (i) Cu pre-
52 patterning by dip-coating of CuO particles on the substrate or by thermal evaporation of Cu from a Cu
53 foil (see previous section 2 for more details); (ii) catalytic CVD graphene growth; and (iii) removal of
54 residual Cu by wet etching, sublimation or both.
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59 In the following we present characterization results for all structures obtained in this work.
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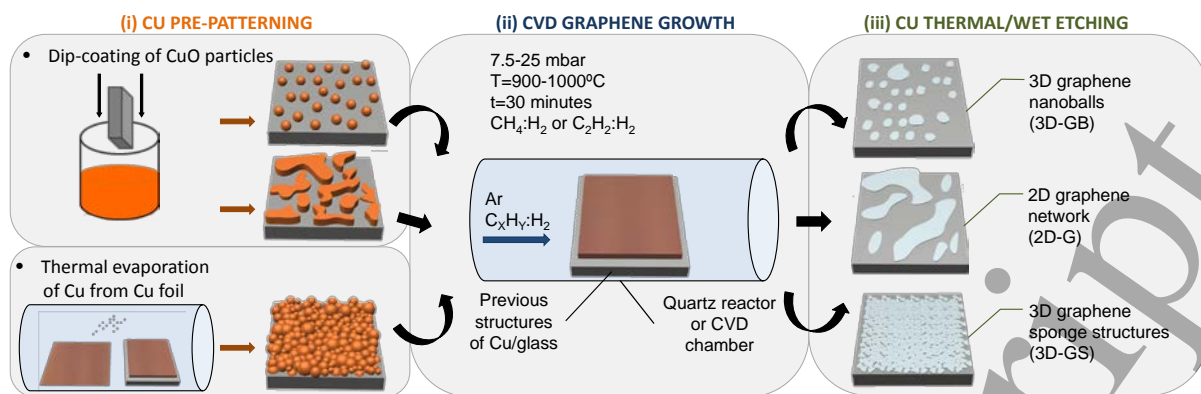


Figure 1. Fabrication of 3D and 2D-graphene structures. (i) Cu template formation on the substrate by CuO particles dip-coating or by thermal evaporation from a Cu foil. Pictures on the right side show the final Cu structures on the substrate: isolated, large Cu NPs embedded in glass or multi-layer Cu NPs. (ii) CVD growth of graphene on the Cu template. (iii) Removal of residual Cu by wet etching or thermal sublimation.

3.1. 3D Graphene nanoballs (3D-GB)

The 3D-GB structures required a systematic control of the initial Cu template before graphene growth. Figure 2 (a-b) shows top and 30° SEM pictures of the Cu NPs after deposition and subsequent H₂ reduction. It can be observed that Cu NPs are spread over the surface presenting a distribution similar to that in solution and, contrary to previous work [13], without large aggregation. This was achieved by having cleaned glass surface to reduce the contact angle to <5°, thus easing the deposition of NPs and improving their adhesion to the substrate. Glass is typically cleaned using Semiclean™ KG solution soaks at 70 °C in an ultra sound wash and ultrasound rinse in DI water. Then the substrates are dried in air at 80 °C. Prior to the coating process the glass were plasma cleaned (March PM-100, Nordson) at 50 W for 3 min using an O₂/Ar (50/50 mix) to ensure the removal of any organics on the surface after the washing or storage steps. This cleaning process and the concentration of CuO solution and dip-coating parameters (withdrawal speed, immerse time) allow the controlling of the monolayer deposition, Cu NPs density and aggregate size. For example, Fig. 2 (a) shows a $\bar{\varnothing}_{\text{CuNPs}}$ dispersion centered at 150 nm after H₂ reduction of CuO particles in the CVD reactor. Graphene is deposited in situ in the CVD reactor. Figure 2 (b) and (c) show the 30° tilted view of the Cu NPs before and after graphene deposition, respectively. One can appreciate the morphological change with the particle reducing their surface contact angle, getting closer to each other and graphene growing in between. After graphene deposition, the sample was dipped in diluted ammonium persulfate solution to etch Cu. The resulting 3D-GBs are shown in the SEM picture of Fig. 2(d) presenting diameters similar to those of the original Cu NPs. In addition, they are completely catalyst-free, as confirmed by the EDX spectra in Fig.S1 (see supplementary information, SI).

To assess the quality of the 3D-GBs, Raman measurements were performed. The inset of Fig. 2(e) shows a representative Raman spectrum where the typical three graphene peaks are clearly evident: D,

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G and 2D bands, at 1350, 1580 and 2700 cm^{-1} , respectively. According to the graphene monolayer criteria [14,15], graphene quality can be measured in terms of intensity ratio (I_D/I_G) between D and G peaks. The lower the I_D/I_G the higher the quality, while the ratio (I_{2D}/I_G) between 2D and G peaks is expected to be equal or higher than 2. By Raman mapping over a large area ($20 \times 20 \mu\text{m}^2$), we could confirm that 3D-GBs were homogeneously distributed (see SI, Fig.S2). Fig. 2(d) shows a Gaussian distribution of I_{2D}/I_G with a mean value of 2.25 in a representative area of the sample. This value confirms that 3D-G structures are single layer. Moreover, it is important that the graphene structures are less defective if compared to previous literature, where a high D peak value was reported [13,16]. Also, it is worth to comment that a tiny D' peak is present on the right of the G peak due to structural defects [17]. Finally, optical transmission measurements were carried out at the different steps of the growth process. The initial Cu NPs produce a strong plasmonic dip in transmission which explains the pale red color of the samples, while the high transmission in the near-infrared is expected as in that region the wavelength becomes much larger than the particle size. The growth of graphene reduces only slightly the transmission that in fact changes mostly because of the rearrangement (size and surface distribution) of the Cu NPs. As expected the most dramatic transmission change took place after wet etching of Cu. The final 3D-GB structures show very little absorption with respect to the initial fused silica substrate (Fig. 2(f)). At 550 nm, the transmittance is approximately 90%. If one considers the reflection (7%), the absorption is about 3%. This value is close to the theoretical absorption of single-layer graphene (2.3%). Because the 3D-GBs are isolated and the substrate is electrically not conductive, Rs could not be measured.

The 3D-GBs may have applications where large surface to volume ratios are advantageous, such as supercapacitor, electrochemistry and catalytic chemistry. The electron confinement associated to the nanoballs could also produce localized surface plasmon resonances (LSPRs). We did not observe those as they are expected at large wavelengths (in the mid infrared region) and require graphene doping beyond the intrinsic levels. In the future we plan to electrical gate the nanoballs by, for example, adding an additional graphene layer to create a common electrical contact and obtain in this way the doping level to observe LSPR. LSPRs are very attractive for chemical and biochemical sensing [18].

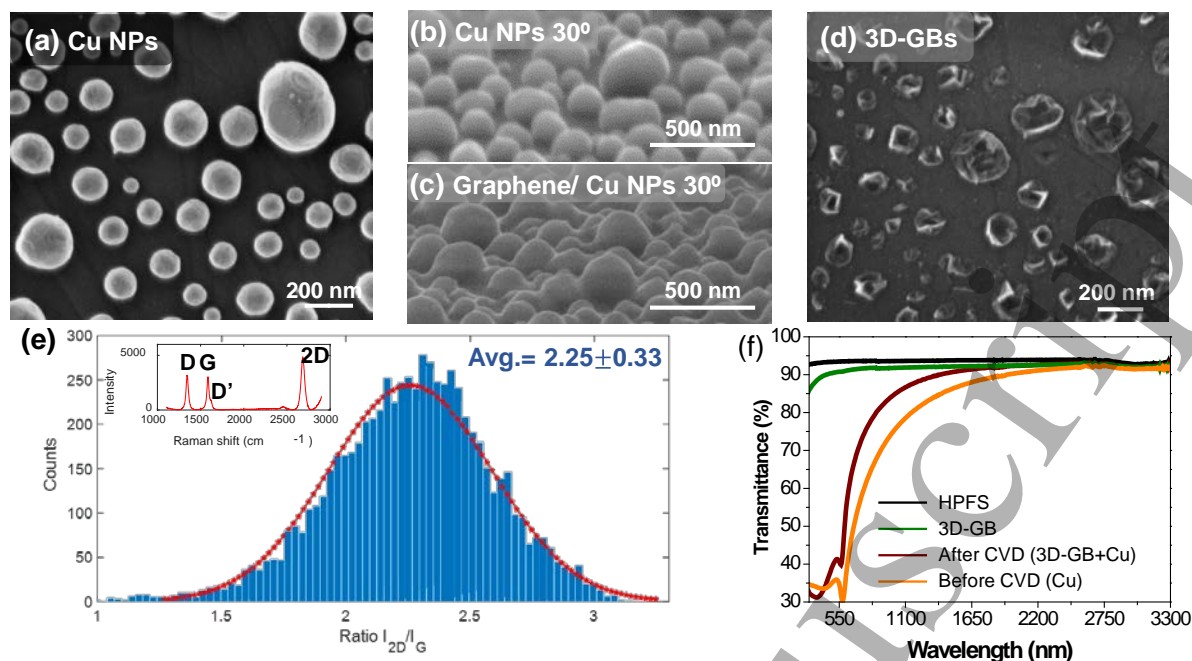


Figure 2. Characterization of 3D-GB structure. (a) SEM image of Cu NPs deposited on glass and after H_2 reduction process. (b) and (c) SEM at 30° of deposited Cu NPs without and with graphene, respectively. The particles profile in (c) is smoother due to NPs change and graphene coverage. (d) 3D-GB after Cu removal. (e) Statistical distribution of Raman I_{2D}/I_G peak ratio, with average value of 2.25 ± 0.33 , over an area of $20 \times 20 \mu m^2$. For I_D/I_G peak ratio, the average value was 1.32 ± 0.21 . In the inset, a representative spectrum shows the three typical Raman peaks of graphene (D, G and 2D) with an additional D' peak as a consequence of defects in the graphene structure, (f) Optical transmittance measurements of: Cu NPs as deposited on glass after H_2 reduction (orange), Cu NPs covered with graphene (wine), 3D-GB after Cu removal (green) and bare substrate (in black).

3.2. 3D Sponge-like graphene (3D-GS)

The 3D-Gs can meet the requirement of large scale applications: high quality, uniformity, transparency and conductivity. As previously mentioned, an accurate control of the evaporation time and location of the sample within the reaction chamber allowed tailoring the size of the resulting Cu NPs. As an example, Fig. 3 (a) shows the Cu NPs structure with a narrow size distribution centered at 30 nm diameter and 75 nm height, (see SI, Fig.S3(a)). By increasing the reaction temperature to $800^\circ C$, the particles aggregated and increased their diameter and height up to 200 nm (see SI, Fig.S3(b)). After graphene deposition at $900^\circ C$, the Cu template was sublimated at $1100^\circ C$ leaving no detectable Cu, as shown by EDX measurements (see SI, Fig.S4). The resulting 3D-GS structures are shown in Fig. 3(c). They present a sponge finger-like interconnected structure. It is worth noting that Raman mapping on these structures seems to reproduce the sample surface, for example in Fig. 3(d) we see the intensity mapping related with the 2D peak. This indicates continuity and homogeneity of

the graphene. In contrast to other samples, the mappings do not show any feature that can be related to surface motifs, and intensity fluctuations are likely to be related to variations of graphene density or quality. The corresponding distribution of I_{2D}/I_G is shown in Fig. 3 (e) and is a narrow peak with mean value of 0.5. This suggests the presence of few-layer graphene as can be also seen in the representative Raman spectra, see the inset. The graphene structure thus resembles the Cu template, closely packed and formed by several layers.

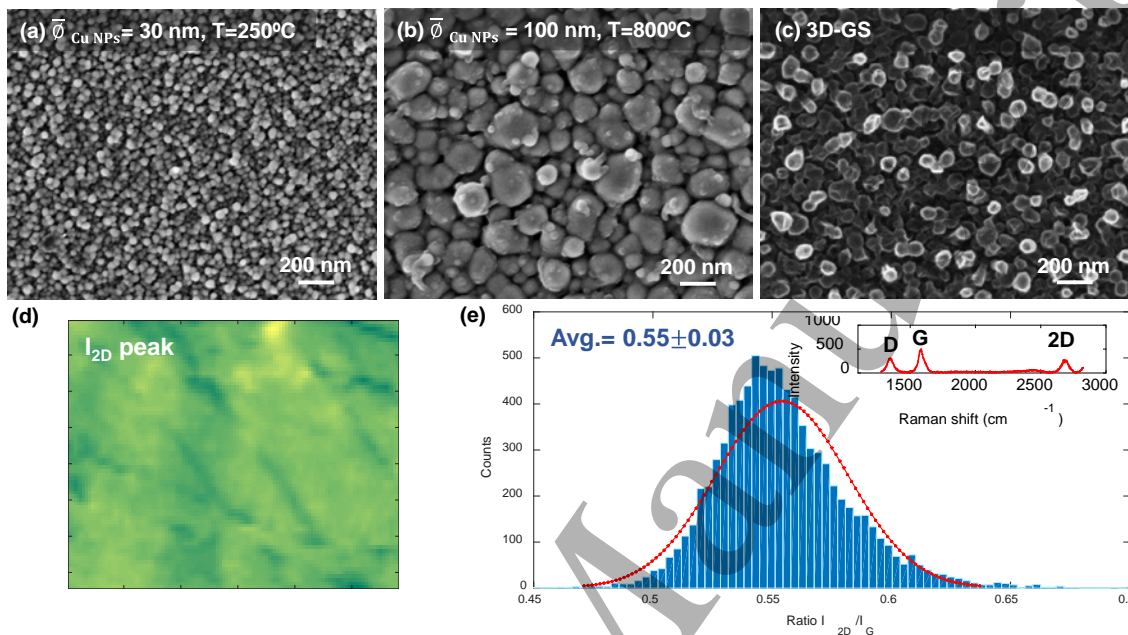


Figure 3. Characterization of 3D-GS. SEM of: (a) Cu NPs as deposited at 250°C, and (b) after being treated at 800°C. Note the size increase. (c) 3D-GS after CVD coating of graphene at 900°C for 30 minutes and the consequent thermal sublimation of Cu at 1100°C for 30 min. (d) Raman mapping over $20 \times 20 \mu\text{m}^2$ area showing the intensity of 2D peak (I_{2D}). (e) Distribution of I_{2D}/I_G extracted from the Raman mapping in (d) with an average value of 0.55 ± 0.03 . For I_D/I_G ratio, the average value was 0.80 ± 0.05 . The inset shows a representative spectrum of Raman mapping.

Another important fact is that the overlap between the different layers forming the nano-structures enables electrical conductivity. Rs of these structures can be tuned from 1 to 20 kOhm/sq depending on the thickness and morphology of the Cu template; i.e. process conditions. Note that optical transmittance and sheet resistance are closely related (see SI, Fig.S5 for a summary of structures obtained with slightly different process conditions). The structures previously described and obtained at $\text{C}_2\text{H}_2:\text{H}_2$ 1:1 gave a range of transmittance of 47-70% at 2-5 kOhm/sq. However, the change of gases ratio can increase the transmittance up to a value of 80% while Rs values vary from 3 to 20 kOhms/sq.

3.3. 2D graphene (2D-G)

By modifying the initial Cu template we were able to promote the growth of 2D dimensional graphene using similar process conditions as those described above for 3D-GB. The increase of dip coating steps of CuO particles on glass, followed by the corresponding reduction under H₂ flow, resulted in the large Cu isolated motifs shown in Figure 4(a). As in previous procedures, part of the Cu NPs would evaporate before graphene deposition due to the high reaction temperatures. To avoid this, a surface treatment of the glass was necessary. It consisted in embedding the Cu particles into the glass surface as previously described in section 2.1. The graphene was then deposited, and the Cu is finally sublimated at 1100°C. The result is a transparent substrate covered with 2D-G, see Figs. 4(b) and (c). The slight curvature of the substrate confirms the effective embedding of initial Cu structures. Raman mapping was performed giving a distribution of I_{2D}/I_G with an average value of 1.13, Fig. 4(d). The typical spectra (in the inset) reveal high quality graphene as the D peak is very low. Within the lateral resolution of our Raman spectrometer, the maps (see SI, Fig.S6) indicate full surface coverage of the 2D-G structure. Regarding electrical measurements, the 2D nanostructure was not measured as it was difficult to contact on the dielectric substrate. Future work could contemplate the gating of the graphene nanostructures by using Si/SiO₂ as the initial substrate. The optical transmittance before CVD (orange) and after Cu etching (green), together with bare substrate is shown in fig. 4 (e). Values up to 90% (at 550 nm wavelength) were observed, very close to the initial bare glass substrate. The high optical transmittance confirms the complete removal of the Cu template (see also EDX in SI, Fig.S7), a very promising feature for a wide range of applications, such as transparent electrodes and interfacial layers.

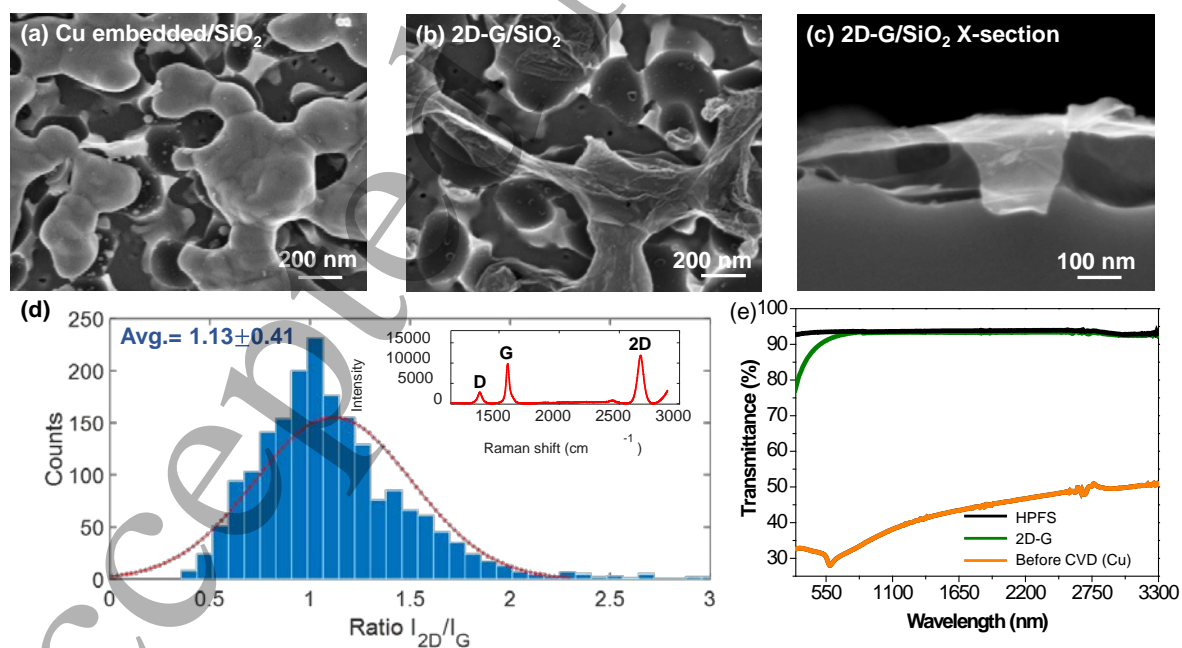


Figure 4. Characterization of 2D-G structure. (a) SEM images of Cu embedded particles in glass before graphene deposition. (b-c) Top and cross section SEM of graphene after thermal

sublimation of Cu. (d) Raman distribution of I_{2D}/I_G with an average value of 1.13 ± 0.41 over an area of $20 \times 20 \mu\text{m}^2$. For I_D/I_G ratio the average value was 0.79 ± 0.16 . Inset: Raman spectra of 2D-G on Si/SiO₂. (e) Transmittance measurements of the embedded Cu (orange line), 2D-G after Cu removal at 1100°C (green line) and the initial bare substrate (black line).

Table 1. Summary of main properties related to 2D and 3D graphene structures developed by CVD technique and tuning the Cu template catalyst.

Properties	Graphene structure		
	3D-GB	3D-GS	2D-G
Catalyst	Isolated Cu NPs	Layered Cu NPs	Large Cu NPs
Graphene growth	1000°C, 30 min, CH ₄ :H ₂ (1:4)	900°C, 30 min, C ₂ H ₂ :H ₂ (1:1)	1000°C, 30 min, CH ₄ :H ₂ (1:4)
	I_{2D}/I_G	2.25 ± 0.33	0.55 ± 0.03
I_D/I_G	1.32 ± 0.21	0.80 ± 0.05	0.79 ± 0.16
Transmittance, 633 nm (%)	91.2	46.5	92.2
Rs (kOhms/sq)	- (*)	2.2	- (*)

(*) Rs was not measured as the structures are isolated/not continuous over a dielectric.

4. Conclusions

We have demonstrated a new technique to grow 2D and 3D graphene structures on glass substrate by starting from a predefined catalytic copper particle template. Different morphologies with a high surface to volume ratio can be produced, from sponge-like to nanoball and conformal graphene structures, with also very high transparency. These can find important application in antiglare display screens, solar cells, light-emitting diodes, gas and biological plasmonic sensors.

Acknowledgments

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