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Direct Conversion of CO_2 to Multi-Layer Graphene using Cu–Pd Alloys

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A straightforward one-step process was developed, in which CO_2 gas is directly converted into multi-layer graphene via atmospheric pressure chemical vapor deposition (APCVD). A bimetallic alloy film based on Cu and Pd was employed as the catalyst and substrate. In this study, we found that the quantity of Cu required for the CO_2 conversion process is high (>82 at%). The findings gained in this study serve as a foundation for further studies of metallic alloys for the thermo-reduction of CO_2 to graphene under CVD conditions.

Introduction

Since the first report of graphene obtained by mechanical exfoliation, it has become one of the most promising carbon-based materials owing to its extraordinary properties, such as high intrinsic mobility, thermal conductivity, and optical transmittance.[1–3] Up to now, graphene can be obtained by different methodologies that are classified as top-down and bottom-up approaches.[4,5] The top-down methodology normally involves the exfoliation of bulk graphite by overcoming the van der Waals forces. Nevertheless, this procedure presents some issues, such as defects caused by the re-agglomeration of the graphene sheets,[6] low yields, and limited size patches of graphene.[7] Conversely, bottom-up approaches involve the synthesis of graphene from a molecular carbon source (e.g., methane, ethylene), a reducing agent, and a substrate. Examples of these are chemical vapour deposition (CVD), epitaxial growth, or electrochemical methods.[6,8]

In the framework of green chemistry, few studies have addressed the conversion of CO_2 into graphitic material. For example, in 2013 Luo et al. presented a methodology involving a two-step conversion of CO_2 to graphene.[9] The first step involved the activation of CO_2 by passing a mixture of CO_2 and hydrogen gases through a Ni catalyst, leading to the production of more reactive carbon-based species. The second step consisted of the reduction of the reactive carbon species on Cu foil at high temperature, thus producing graphene. Furthermore, approaches based on electrochemical methodologies using heterogeneous catalysts have been developed.[10,11] For example, Hu et al. reported the graphitization of CO_2 through an electrochemical approach via molten salts.[10] However, whereas the authors obtained some graphene-like material, most of the product resulted in amorphous carbon. More recently, it was shown that CO_2 can be electrochemically reduced to carbonaceous species at room temperature employing ceria catalysts.[12] In this regard, herein we present a one-step synthesis of graphene using CO_2 gas, as carbon feedstock, and Cu–Pd substrates, employing an atmospheric pressure chemical vapour deposition (APCVD) reactor. Our results show that the Cu–Pd alloy acts not just as the catalyst for the CO_2 reduction and conversion, but also as the substrate for the graphene growth. Through this approach, we demonstrate that the activation energy of CO_2 can be overcome by combining the catalytic ability of the metals Cu and Pd, with the reductive power of H_2 and the high temperatures of the CVD furnace (Figure 1).

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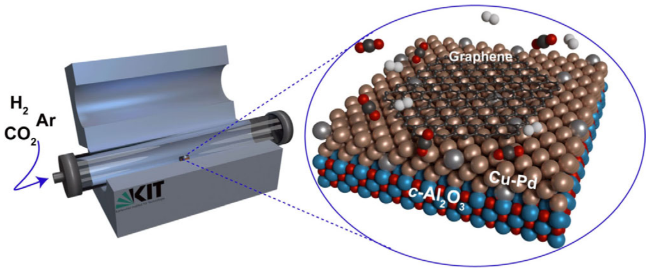

Figure 1. Growth of Graphene from CO_2. Representation of the synthesis of graphene from CO_2, H_2, and Ar. The left side shows the gases employed during the growth process and the APCVD reactor. On the right, a view of the Cu–Pd alloy sputtered on *c*-Al_2O_3 is shown with the grown graphene on top. Color code: Cu, brown; Pd, grey; Al, blue; O, red; H, white; and C, black.

Results and Discussion

Cu and Pd metals were chosen to fabricate a series of metallic substrates owing to their advantageous properties in the activation of CO_2[13] or graphene growth.[14] The main goal was to find the right metal, or combination of metals, that can act as a catalytic agent and substrate in the direct capture and conversion of CO_2 into graphene. The metallic substrates were prepared by sputtering Cu or/and Pd metals on a 5×5 mm 0001-sapphire (*c*-Al_2O_3) chip. Four substrates were studied exhibiting the following compositions: (i) Substrate 1 (Sub1) was prepared by sputtering 900 nm of Cu on *c*-Al_2O_3. On the top of the deposited Cu film, four islands of Pd (1 mm^2 each) with a thickness of 150 nm were deposited (Figure 2 a). (ii) Substrate 2 (Sub2) consisted of 900 nm of Cu on the *c*-Al_2O_3 substrate (Figure 2 b). (iii) Substrate 3 (Sub3) comprised a 900 nm layer of Pd on *c*-Al_2O_3 (Figure 2 c). (iv) Substrate 4 (Sub4) was prepared by sputtering half side of *c*-Al_2O_3 with 900 nm of Cu and on the other half with 900 nm of Pd separated by 1 mm, to avoid direct contact (Figure 2 d).

The purpose of Sub1 was to study the relation between Cu and Pd in the conversion of CO_2 into graphene. Furthermore, Sub1 allowed us to establish whether both metals, Cu and Pd, are required to be in contact to convert CO_2 to graphene. Sub2 and Sub3 were prepared to investigate whether the CO_2 conversion is achieved only by a single metal, whereas Sub4 was designed to test if one metal (i.e., Pd) could act alone as the catalytic agent, while the other (i.e., Cu) acts as a substrate for the graphene growth or vice versa.

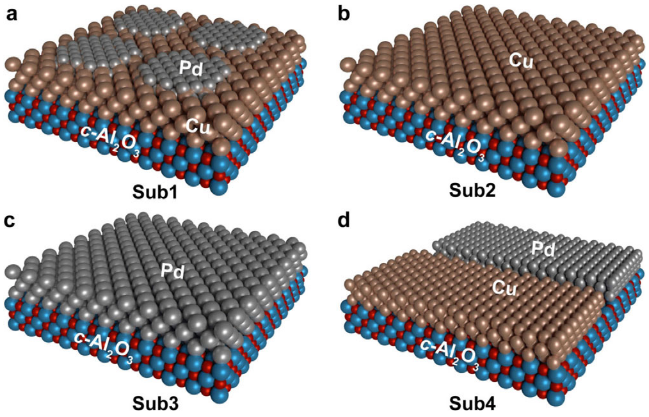

Figure 2. Metallic Substrates. View of the substrates used to investigate the growth of graphene from CO_2: (a) Sub1: Cu sputtered on *c*-Al_2O_3 with four islands of Pd sputtered over Cu; (b) Sub2: Cu sputtered on *c*-Al_2O_3; (c) Sub3: Pd sputtered on *c*-Al_2O_3; (d) Sub4: half of the *c*-Al_2O_3 substrate with Cu and the other half with Pd sputtered on *c*-Al_2O_3. Color code as in Figure 1.

The study of graphene growth, utilizing CO_2 as carbon source, was carried out in an APCVD reactor employing a procedure involving 4 steps as follows: (i) the substrate was positioned in a quartz tube and placed in the heat zone of the CVD furnace, which is later heated to 1000 °C; (ii) the substrate was annealed in the presence of a mixture of Ar and H_2 (1.4:1) for 30 min; (iii) the growth process was conducted in a mixture of Ar, H_2, and CO_2 with an 8:5:3.5 ratio at 1000 °C for 40 min; and (iv) the metallic substrate was allowed to cool down to room temperature (Figure S1 in the Supporting Information).

After the growth procedure, all substrates were initially characterized by Raman spectroscopy, being the most employed technique for the characterization of graphene.[14,15] Raman studies revealed that solely Sub1 exhibited the characteristic bands of graphene, that is, D (≈1347 cm^{-1}), G (≈1582 cm^{-1}), and 2D (≈2689 cm^{-1}) bands (vide infra), whereas for Sub2, Sub3, and Sub4 no signal corresponding to any carbon species was found (Figure S2). Note that the synthesis of graphene was achieved only in Sub1, in which both metals, Cu and Pd, are in direct contact. Raman mapping analysis of different areas of Sub1 corroborates the presence of graphene along the substrate, as confirmed by the characteristic D, G, and 2D bands of graphene (Figure 3 a). Moreover, we examined the

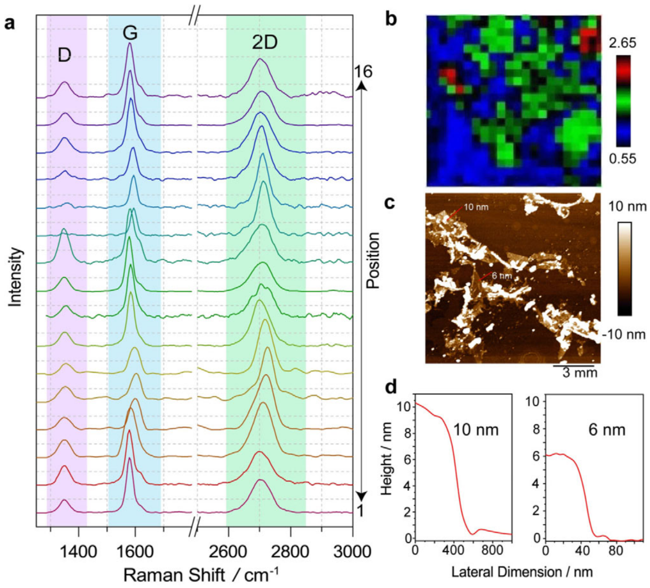

Figure 3. Characterization of Graphene obtained on Sub1. (a) Raman spectra of 16 different positions of graphene grown on Sub1. The colored bands show the D (pink), G (pale blue), and 2D (pale green) characteristics of graphene; (b) Raman mapping shows the I_{2D}/I_G ratio of graphene films; (c) AFM image of the graphene transferred to a Si substrate; (d) height profile of the graphene on Si substrate along the lines shown in Figure 3 c, exhibiting thickness from 6 and 10 nm.

ratio of the 2D and G peak (I_{2D}/I_G) obtained in the Raman mapping, where the I_{2D}/I_G ratio is indicative of the number of layers of graphene (Figure 3 b); that is, large I_{2D}/I_G ratios indicate the presence of mono- to few-layer graphene, whereas lower values indicate multi-layer graphene formation.[16] By evaluating this parameter, values ranging from 0.55 to 2.65 were found, thus, confirming the formation of regions of multi-layer graphene. The thickness of the obtained graphene was further probed by atomic force microscopy (AFM). For this purpose, the graphene from Sub1 was first transferred onto a Si substrate and characterized (Figure 3 c). AFM height profiles indicated the formation of graphene sheets with thicknesses ranging from 6 to 10 nm, denoting a number of graphene layers between 17 to 28 layers (Figure 3 d).

Note that the high temperature employed (1000 °C) triggered a diffusion process of the Pd islands into Cu, leading to a more homogeneous Cu–Pd mixture. The different intensity of the Raman peaks can be attributed to height irregularities of the graphene film, owing to the de-wetting of the metals at high temperatures, as observed in the optical and scanning electron microscopy (SEM) images (Figure S3 a, b). A similar type of structure was observed in graphene growth employing Cu films deposited on dielectric surfaces.[17] We also probed the concentration of Cu–Pd of Sub1 via energy dispersive X-ray spectroscopy (EDS), resulting in a concentration 93 and 7 at % of Cu and Pd, respectively.

To exclude the presence of contaminants being responsible for the formation of graphene, blank experiments were performed. For this, Sub1 was subjected to the same procedure previously described, without the inclusion of the CO_2 as a carbon source. Raman analysis after this procedure, revealed no graphene formation, confirming that the source of carbon in our approach is CO_2 (Figure S4).

Although the experiments with Sub1 demonstrated that both metals in the Cu–Pd mixture promoted the conversion of CO_2 into graphene, there is an emerging question concerning the optimal composition involved in the process. In Sub1, it was found that a concentration of 93 at % of Cu yielded the formation of graphene. To study the effect of other Cu–Pd ratios on the catalytic conversion of CO_2 to graphene, additional experiments were devised with the main goal of determining whether any Cu–Pd ratio was suitable for the one-step process. For this purpose, two new substrates exhibiting different Cu–Pd composition were prepared. The new substrates were obtained by co-sputtering different quantities of Cu and Pd on a 5 × 5 mm c-Al_2O_3 chip. The composition of the substrates is enlisted as follows: Substrate 5 (Sub5) was prepared by the deposition of an initial layer of Cu (900 nm of Cu sputtered on c-Al_2O_3) followed by a co-sputtering Cu and Pd on the top of the prepared Cu film (Figure 4 a). Substrate 6 (Sub6) was prepared by co-sputtering Cu and Pd directly on the c-Al_2O_3 substrate. Upon annealing, it is expected that the Pd atoms diffuse into the copper structure, leading to a more homogeneous Cu–Pd alloy. Moreover, owing to the preparation procedure, Sub5 is anticipated to contain a higher Cu concentration than Sub6.

Employing these substrates (i.e., Sub5 and Sub6), the growth of graphene was performed maintaining the previously described conditions (vide supra). Analysis of Sub5 by Raman spectroscopy after the growing step with CO_2 revealed the characteristic D, G, and 2D bands of graphene (Figure 4 c). Figure 4 b shows the optical image of the area of Sub5 where the

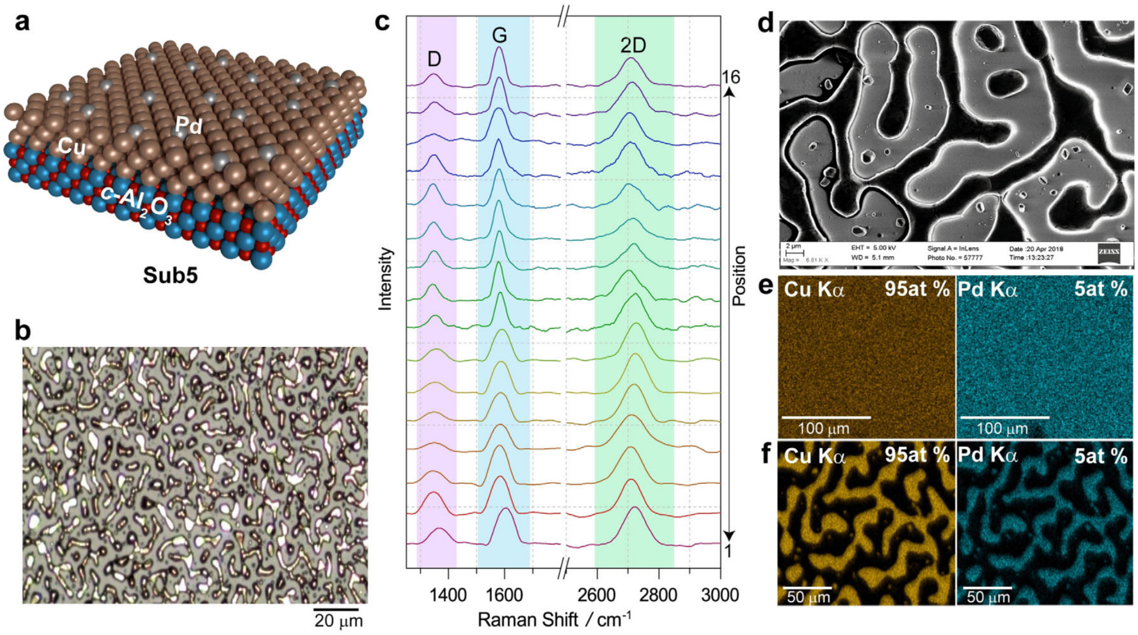

Figure 4. Characterization of graphene obtained on Sub5. (a) Representation of Sub5. Cu–Pd film alloy deposited on c-Al_2O_3 substrate; (b) optical image of the area employed to perform the Raman mapping; (c) Raman mapping of Sub5 showing the D (pink), G pale blue), and 2D (pale green) bands; (d) SEM image of Sub5; (e) EDS of Sub5 before the growth procedure revealing a Cu and Pd concentration of 95 and 5 at %, respectively; and (f) EDS of Sub5 showing the fingerprint of the metals diffusion after growing step.

Raman analysis was performed. Additionally, SEM and optical microscopy images revealed that Sub5 exhibits a similar dewetting pattern as observed in Sub1 (Figure 4b,d,f). Furthermore, EDS was employed to quantify the exact Cu–Pd composition of Sub5 before and after the graphene growth step (Figure 4e,f). As expected, we find a high average Cu concentration (95 at%) in Sub5.

In contrast, we find no graphene formation in Sub6, as revealed by Raman spectroscopy. Interestingly, the EDS analysis of Sub6 showed a lower average quantity of Cu (77 at%) compared to Sub5. Subsequent experiments, employing 96, 85, and 82 at% contents of Cu show that graphene growth is only operable when the Cu concentration of the metallic alloy remains higher than 82 at%, whereas lower quantities of Cu in the alloy suppress the growth of the graphene (see Figure S5). Note that at 96 at% of Cu the graphene growth is achievable, although Raman analysis indicates a very limited graphene formation (Figure S5a).

The quality and structural aspects, such as the number of layers and crystallinity, of the graphene films obtained in Sub5, were determined by transmission electron microscopy (TEM). For this experiment, the graphene from Sub5 was transferred onto a holey carbon grid. After the transference to the grid, Raman experiments were conducted to confirm the presence of the graphene films. Figure 5a corresponds to the Raman spectrum of the transferred film on the grid, which exhibited the characteristic peaks of graphene (D, G, and 2D). TEM experiments of the films revealed the formation of crystalline graphene layers. A low magnification image of the multiple layers of graphene is presented in Figure 5b, with an inset displaying the selected area electron diffraction (SAED) pattern from the framed area in red. The SAED pattern shows two sets of diffraction spots corresponding to the {100} and {110} planes in a single crystalline area of the graphitic carbon. Moreover, the expectedly strong reflections from the {002} planes are absent, which indicates a dominant in-plane growth of graphene and high crystallinity of the film. At the folded-up edges of the film visible in Figure 5c, the stacking of the layers of graphene can be clearly seen at higher magnification in Figure 5d. The inset on the upper left side shows the local fast Fourier transform (FFT) from the red box region with the characteristic stacking of graphene with an average {002}interlayer distance of 0.357 nm.[18] Additionally, the inset at the upper-right of Figure 5d displays a local FFT from the blue section, which exhibits a diffraction pattern that does not have any {002} reflections corresponding to the in-plane growth of the graphene obtained. An intensity profile from the stacked region (Figure S6) revealed from 10 to 20 graphene layers, in agreement with the results obtained from the AFM height profile of the transferred graphene grown on Sub1. From the TEM analysis, we can also confirm the direct formation of multiple layers of graphene from CO_2.

Undoubtedly, our experiments show the direct formation of multi-layer graphene from CO_2, employing a Cu–Pd alloy film, which acts as both catalyst and substrate. Other studies have shown that the relatively strong carbon–metal (C–M) interac-

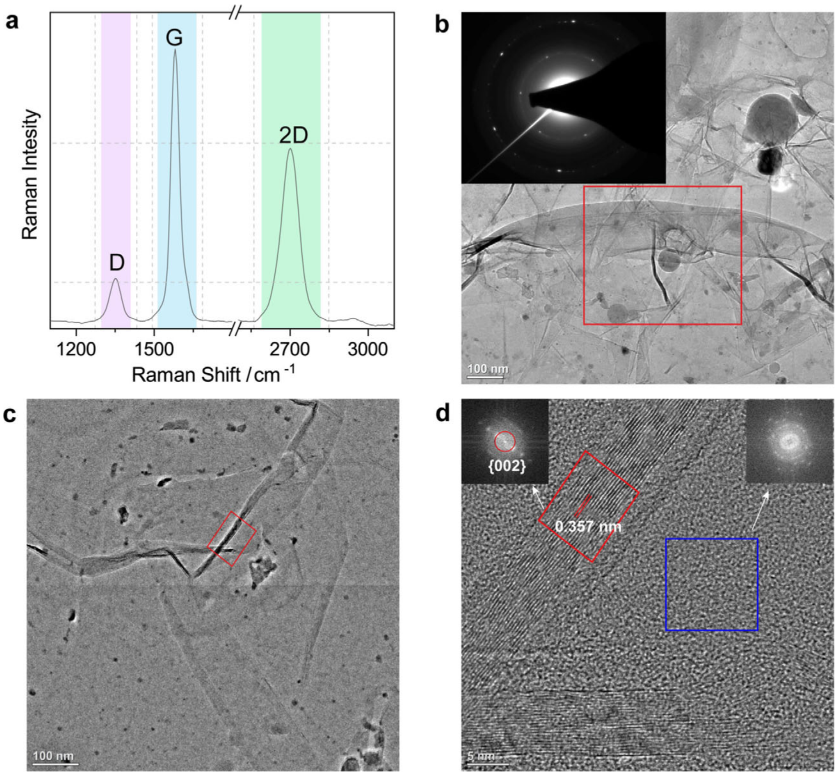

Figure 5. TEM Characterization of graphene obtained in Sub5. (a) Raman of the graphene on the TEM grid; (b) low magnification TEM image and SAED diffraction pattern (inset) of the graphene revealing a high crystallinity; (c) low resolution image of the staking of graphene layers; (d) high resolution TEM image showing the graphene interlayer of 0.357 nm. The inset at the upper-left corner shows the local FFT of the {002} reflections of the staking of graphene (red square). The upper-left inset (corresponds to the blue square) shows no reflection from the staking of graphene.

tion between CO_2 and Cu–Pd metals enhance the efficiency for the reduction and conversion of CO_2 into more reactive chemical species.[19,20] In addition, it was determined that the Cu–Pd phase is important for the capture and conversion of CO_2.[19] By examining Cu–Pd phase diagrams, it is expected that at our working temperatures the face centred cubic (FCC) phase prevails,[21] thus a homogeneous substrate is expected to be involved in the growing process.[22] Furthermore, reports employing electrochemical procedures have shown that mixing Cu with noble metals (e.g., Pd, Pt, and Au) can create efficient systems for the reduction of CO_2 into more reactive species.[19,22–24] Considering the reported studies, a possible mechanism for the capture, reduction, and conversion of CO_2 to graphene could be the concerted interaction of the CO_2 molecule with the Cu–Pd surface as follows: (i) the carbon of the CO_2 interacts with the Cu–Pd metal substrate, debilitating one of the oxygen bonds of the CO_2; (ii) H_2 reacts with the labile oxygen of the CO_2 leading to the formation of H_2O and generation of CO[25] or other molecules, such as methane,[26] methanol,[13] and others;[19] and (iii) the precursors obtained are rapidly converted to graphene. In fact, although other small hydrocarbons can also be produced, it was suggested that by mixing Cu (with a high ΔH_{CO}) and Pd (with lower ΔH_{CO}) can lead to better evolution of CO. The reaction given for the whole process can be described as:[27]

$$CO_2 + 2\,H_2 \rightarrow C + 2\,H_2O \qquad \Delta_R H_f = -90\,\text{kJ}\,\text{mol}^{-1}$$

Furthermore, it is important to stress that the formation of graphene was just observed in alloys with a Cu content higher than 82 at%, whereas lower concentrations of Cu (i.e., larger of Pd) inhibited the formation of graphene. Some reports have proposed that Cu promotes a larger CO_2 absorption and desorption at the Pd reactive site, whereas larger quantities of Pd preclude the reduction of CO_2.[19] This is a result of the strong affinity between Pd and CO, which binds strongly to Pd, making the Pd sites inaccessible to further CO_2 reduction steps.[25] Studies to corroborate our hypothesis are the aim of future work.

Conclusions

In this study, we present a feasible one-step method for the conversion of gaseous CO_2 to graphitic material, employing Cu–Pd alloy films at high temperatures. We show that the metallic substrates act as both heterogeneous catalyst and substrate. Characterization techniques, such as Raman and AFM, evidenced the formation of multilayer graphene on the metallic substrates. Moreover, TEM analysis confirmed the graphitic nature of the material obtained. Interestingly, the conversion of CO_2 to graphitic material is only achieved when the metallic substrate has a Cu content above 82 at%. Unfortunately, owing to the high working temperature and the nature of the bimetallic alloy, the de-wetting of the metals was observed, which led to the non-homogenous growth of graphene, thus not the best quality was achieved. Nevertheless, by overcoming this problem it would be possible to achieve a better quality of graphene from CO_2 in this one-step approach.

Experimental Section

Substrate preparation: Cu and Pd metal substrates were synthesized by direct current magnetron sputtering at a working pressure of 5×10^{-3} mbar (1 bar $=10^5$ Pa). The base pressure of the magnetron sputtering chamber was $\approx10^{-8}$ mbar. The power to the Cu and Pd targets was maintained at 110 and 20 W, respectively. The deposition was performed constantly for 45 min at room temperature. The target–substrate distance was fixed at approximately 11.5 cm. Six different samples were then sputtered; *c*-Al_2O_3 substrates (5×5 mm^2) were used for four different samples. Sub1: 150 nm of Pd was deposited in situ on top of the Cu thin film (900 nm thickness) as islands of 1 mm^2 each with 150 nm thickness. Sub2: 900 nm of Cu sputtered on the top of sapphire. Sub3: 900 nm of Pd was sputtered on the top of *c*-Al_2O_3. Sub4: one half of Cu (900 nm) and one half of Pd (900 nm) sputtered on the top of sapphire ($\approx$1 µm of thickness). Sub5 preparation consisted of the deposition of 900 nm of Cu on the *c*-Al_2O_3 substrate and followed by the deposition of Cu and Pd metals simultaneously above the 900 nm of Cu previously deposited ($\approx$1 µm of thickness). Sub6 was prepared by depositing Cu and Pd metal targets simultaneously for 45 min, directly on the *c*-Al_2O_3 substrate ($\approx$900 nm of thickness). The composition of sputtered Cu and Pd was obtained by EDS yielding a content of 95 at% Cu and 5 at% Pd in Sub5. On the other hand, Sub6 exhibits a composition of 77 at% Cu and 23 at% Pd.

Graphene growth: The growth of graphene was performed employing APCVD reactor, in which the substrate was placed into a quartz tube in the heat zone of the furnace. Three main gases were used with a purity of Ar (99.9999%), CO_2 (99.995%), and H_2 (99.9999%). Graphene was synthesized employing a 4 step ramp, which consisted of: (i) the substrate is heated up to 1000 °C with a rate of 30 °C min^{-1}; (ii) the annealing procedure starts soon after the temperature reached 1000 °C by passing through a mixture of Ar (70 sccm) and H_2 (50.5 sccm) for 30 min; (iii) afterwards, the synthesis of graphene initiated by introducing the stream of CO_2 (25.9 sccm) into the CVD reactor, the H_2 was held constant and the stream of Ar was increased to 83.5 sccm. The mixture of gases was allowed to react for 40 min at 1000 °C; (iv) finally, the system was cooled down slowly under a stream of Ar (70 sccm).

Transfer of graphene to Si: Graphene was transferred to a Si substrate via wet transference. The substrate was coated with 4% poly(methyl methacrylate) (PMMA) solution and subsequently dipped in a solution of $(NH_4)_2S_2O_8$ 0.1 M. After 3 h, the PMMA/graphene was collected and washed with distilled water several times to eliminate any remaining salt. The PMMA/graphene was placed on a silicon wafer and afterwards the PMMA was removed with hot acetone. Subsequently, the graphene on the top of Si was dipped for 5 min in diluted aqua regia ($2\,H_2O$:$2\,HNO_3$:1 HCl).

TEM sample preparation: TEM samples were prepared by dropping isopropanol on a holey carbon-coated Mo grid placed on the top of the metallic substrate with the graphene. Afterwards, the Mo grid attached to the metallic substrate was dipped into diluted aqua regia to etch the metals. The carbon film was washed with distilled water. Afterwards, the carbon film containing the grown-graphene was carefully collected with a 200-mesh Cu TEM grid.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide · chemical vapor deposition · copper · graphene · palladium

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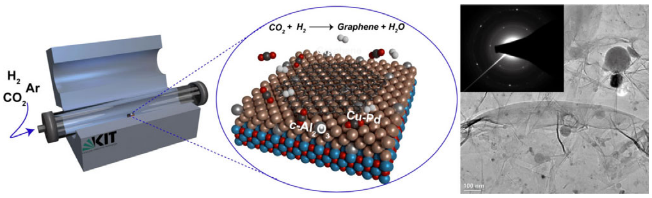

Green graphene: Herein we report the direct conversion of CO_2 gas to graphene. We achieve this one-step process through a combination of the reductive power of hydrogen and the catalytic properties of a Cu–Pd alloy.

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Direct Conversion of CO_2 to Multi-Layer Graphene using Cu–Pd Alloys