Graphene

One- and Two-Dimensional Diffusion of Metal Atoms in Graphene**

Yanjie Gan, Litao Sun, and Florian Banhart*

Single-layer networks of graphitic carbon have attracted enormous attention in the past decade. Graphene in its real single-layer structure first became available in the cylindrically closed shape of single-walled carbon nanotubes (SWCNTs).[1,2] More recently, flat sheets of graphene have been isolated and characterized,[3,4] and it has been shown that graphene and single-walled nanotubes have unique and outstanding mechanical and electrical properties.[5,6] The presence of metal atoms in graphene layers has a major influence on their properties. Metal atoms also play a central role in the catalytic formation of graphitic structures such as nanotubes.[7] However, our knowledge about the interaction between metal and carbon atoms is mainly based on energy calculations and molecular dynamics.[7–11] Therefore, an experimental observation of the behavior of individual metal atoms in graphene layers is highly desirable. Individual heavy atoms on light substrates have already been observed in early transmission electron microscopy (TEM) studies.[12] Later it was shown by Tanaka et al.[13] that the migration of single heavy atoms can be studied in situ using high-resolution TEM techniques. The scattering of the electron beam at single atoms is low, but heavy atoms can be seen under favorable conditions.[14]

In the present work, individual Au or Pt atoms in layers consisting of one or two graphene planes have been monitored in real time at high temperature by high-resolution TEM. We obtain information about the location of metal atoms in graphene and the diffusion mechanisms. Activation energies for diffusion are obtained in a temperature range close to the temperature of the technically important metal-assisted CVD process.

The material was synthesized in an arc discharge [15,16] (see experimental section) and consisted of multi-walled nanotubes, onion-like graphitic nanoparticles, and some more or less isolated graphenic sheets. These sheets consisted of one or

a few graphene planes. The metals prevailed as nanometer-sized crystals of Au or Pt on the graphitic structures, small clusters of a few atoms sitting on the graphitic surfaces, or single atoms appearing as dark dots on the flat or curved layers. Owing to the large mass difference between carbon on the one hand and Au or Pt on the other hand, individual metal atoms in graphitic particles can be seen in TEM images.[17] However, because of the migration of metal atoms, a dynamical picture is obtained and the contrast of individual atoms varies from image to image. The number of monoatomic layers in the graphitic stacks can in most cases be determined even when the layers are in a plan-view orientation.[18] Since the edges are often bent or rolled up, the number of edge fringes in the image (inter-fringe distance 0.34 nm) should correspond to the number of layers.
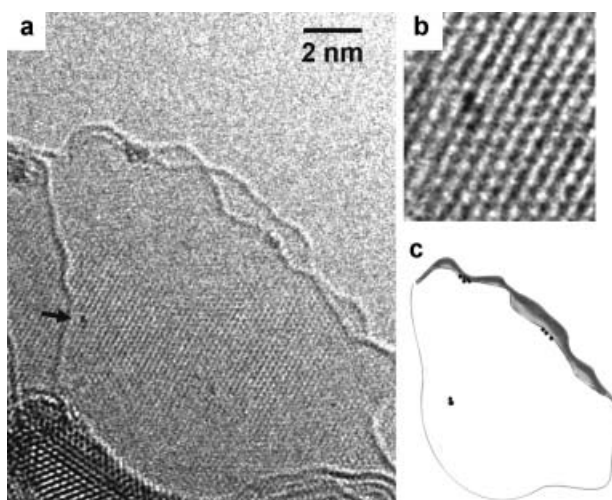
Figure 1 shows a monolayer of graphene with Pt atoms at 700 °C. The layer is slightly rolled at the edge (top), and the absence of graphitic fringes with interdistance of 0.34 nm shows that it is really a monoatomic layer. Although the layer is curved, the contrast of the hexagonal graphene lattice appears. Clustering of Pt atoms has led to the formation of Pt crystals as seen in the bottom of the image. Some Pt atoms are sitting at the edge of the layer (top). Of more interest is a cluster of about four Pt atoms that is located in the layer (arrowed). The inset shows a magnified view of this area. It can be seen that the position of the Pt atoms coincides well with the graphene lattice, that is, the Pt atoms appear localized on regular lattice sites of carbon atoms.

Figure 2a and b shows Pt atoms in a four-layer graphitic structure at 600 °C. The image in (b) was recorded approximately one minute after (a). Two Pt atoms (arrowed) join and form a cluster (a third Pt atom on the left hand side remains almost immobile). Such clusters of two or several Au or Pt atoms were often observed. They remained stable for certain periods but were seen to disperse after some time. It is apparent that an attractive force, though weak, acts between the metal atoms within the graphenic lattice.

Because we cannot determine from a plan-view image, such as Figure 1 or Figure 2a–b, whether the metal atoms are located in the graphene plane or just sitting on top of the layer, several images were recorded with the viewing direction along the layers, that is, where the layers are locally aligned parallel to the electron beam. This is the case at the periphery of curved layers. Examples are shown in Figure 2c and d. In Figure 2c a curved two-layer graphenic structure contains Au atoms. One atom is located at the periphery, which appears here as an edge in the projection because the viewing direction is locally parallel to the layer. The contrast of the Au atom is high (apparently the atom remained immobile during the exposure) and clearly overlaps with the contrast of the outermost graphene layers. Therefore a location of the Au atom on top of the layer can be clearly excluded. Another example is shown in Figure 2d for Au atoms in a multi-walled carbon nanotube (MWCNT). Although hundreds of such images were recorded, no example of a metal atom sitting clearly on top of the surface of a layer was found. If we have more than one graphene layer, possible interlayer positions of metal atoms (intercalation) have to be considered. Such a configuration cannot be excluded although no strong evidence

[*] Y. Gan, Prof. L. Sun
     Institut für Physikalische Chemie, Universität Mainz
     Mainz 55099 (Germany)
     Prof. L. Sun
     Present address: MEMS Ministry of Education
     Key Laboratory School of Electronic Science and Engineering
     Southeast University
     210096 Nanjing (P.R. China)
     Prof. F. Banhart
     Institut de Physique et Chimie des Matériaux
     UMR 7504, 23 rue du Loess, 67034 Strasbourg, (France)
     E-mail: banhart@ipcms.u-strasbg.fr

Figure 1. a) Plan-view of a monolayer of graphene with platinum atoms (arrowed) at 700 °C. The geometry is visualized in the drawing in (c). The open edge of the layer rolls up at the top. The edge is the line where some Pt atoms are sitting (inner fringe in the center of the image). A larger Pt crystal is visible on the bottom. b) An enlarged view of the group of in-plane Pt atoms (arrowed in (a)). The lattice contrast in (b) has been slightly enhanced by Fourier filtering.

was found. Even if the metal atoms are located perfectly in-plane, the appearance of an interlayer position may occur due to projection effects in curved structures. A slight off-layer position of metal atoms would be expected when the metal
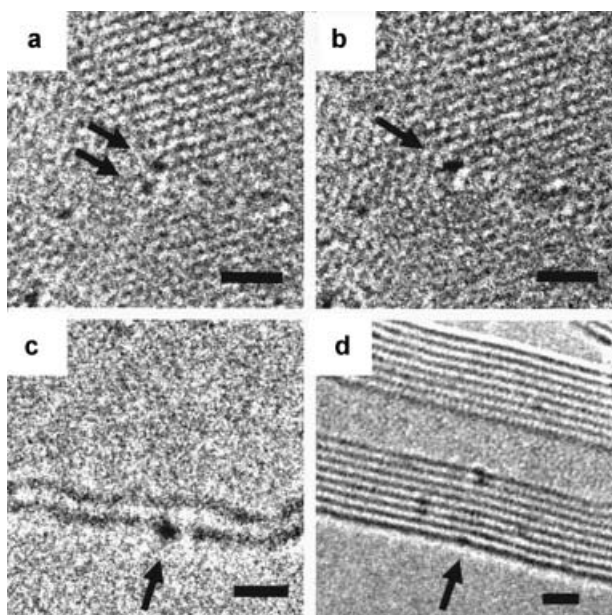
Figure 2. a, b) Platinum atoms in a four-layer graphitic sheet, seen in plan-view (viewing direction normal to the layer). The image (b) was recorded one minute after (a). Two Pt atoms (arrowed) merge and form a cluster. c, d) Gold atoms in curved layers seen in side-view (viewing direction parallel to the layer surface). (c) shows the rolled edge of a two-layer graphene sheet (the graphene sheet is on the top); (d) shows an MWCNT. The position of the Au atoms in the outermost layer is arrowed. No considerable off-layer position is detectable. The scale bar in all images is 1 nm. All images were recorded at a specimen temperature of 600 °C.

atoms occupy single vacancies in graphene because the metal–carbon bond is somewhat longer than a carbon–carbon bond.[11,19] Nevertheless, no clear indications for an off-layer position were seen in this study.

Figure 3 shows a sequence of plan-view images with the migration of Pt atoms in the plane of a graphenic layer at 600 °C. The brighter area is a hole in a two- or three-layer sheet, so we can assume that we observe the migration of Pt atoms in a single or two-layer structure. The temporary appearance of clusters is also visible. We can clearly see how individual Pt atoms change their position by diffusion. Atoms diffusing within the layer are labeled with "L". The hole in the layer gives us the possibility to study the tendency of metal atoms to stick to open edges of graphene layers (there is no bending at this edge because of van der Waals interactions between the layers). It is clearly observable that metal atoms prefer edge sites rather than in-plane positions. It is also visible how the atoms at the edge (labeled with "E") migrate along the edge. Here a small cluster of Pt atoms disperses when the atoms migrate towards the bottom of the edge.

Figure 4 shows the migration distance for a number of Au and Pt atoms (measured in the lateral direction, i.e., along the layer for two-dimensional (2D) diffusion) as a function of time at different temperatures. Owing to the statistical nature of diffusion and the difficulty of determining the jump distance precisely, there is considerable scatter in the data. Nevertheless, the data follow roughly the square-root law of diffusion.

The migration of Au or Pt atoms was also studied in MWCNTs attached to metal crystals. Figure 5a shows 2–4 Pt atoms in the layers of a nanotube at 600 °C (the exact number of atoms is difficult to determine because a migration of the atoms during the exposure of the image cannot be excluded in this example). In Figure 5b we see a nanotube whose right end is terminated by a Au crystal. Several Au atoms have migrated from the crystal into the layers of the nanotube. The migration of the atoms along the circumference of the tube cannot be determined unambiguously because of projection effects, but a diffusion in the axial direction can be quantified.

From the measured migration distances within certain time intervals we can derive values for the diffusion coefficients. For an atom migrating in a graphene plane over a mean distance $\bar{x}$ within a time interval t, the coefficient for 2D diffusion is given by

$$D = \frac{\bar{x}^2}{4t} \tag{1}$$

From the measurements of the in-plane diffusion we obtain a range of values $D = 6 \times 10^{-22}$–2×10^{-21} m^2 s^{-1} for Au and $D = 4 \times 10^{-22}$–1×10^{-21} m^2 s^{-1} for Pt, both at 600 °C. For Pt at 700 °C we obtain $D = 1$–7×10^{-21} m^2 s^{-1}.

The diffusion coefficient is related to the activation energy E_a for atom jumps by

$$D = g a^2 \nu_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{2}$$

where g is a geometrical factor slightly smaller than unity, a is the lattice constant, ν_0 an attempt frequency of the order of the Debye frequency, and k_B Boltzmann's constant. At the
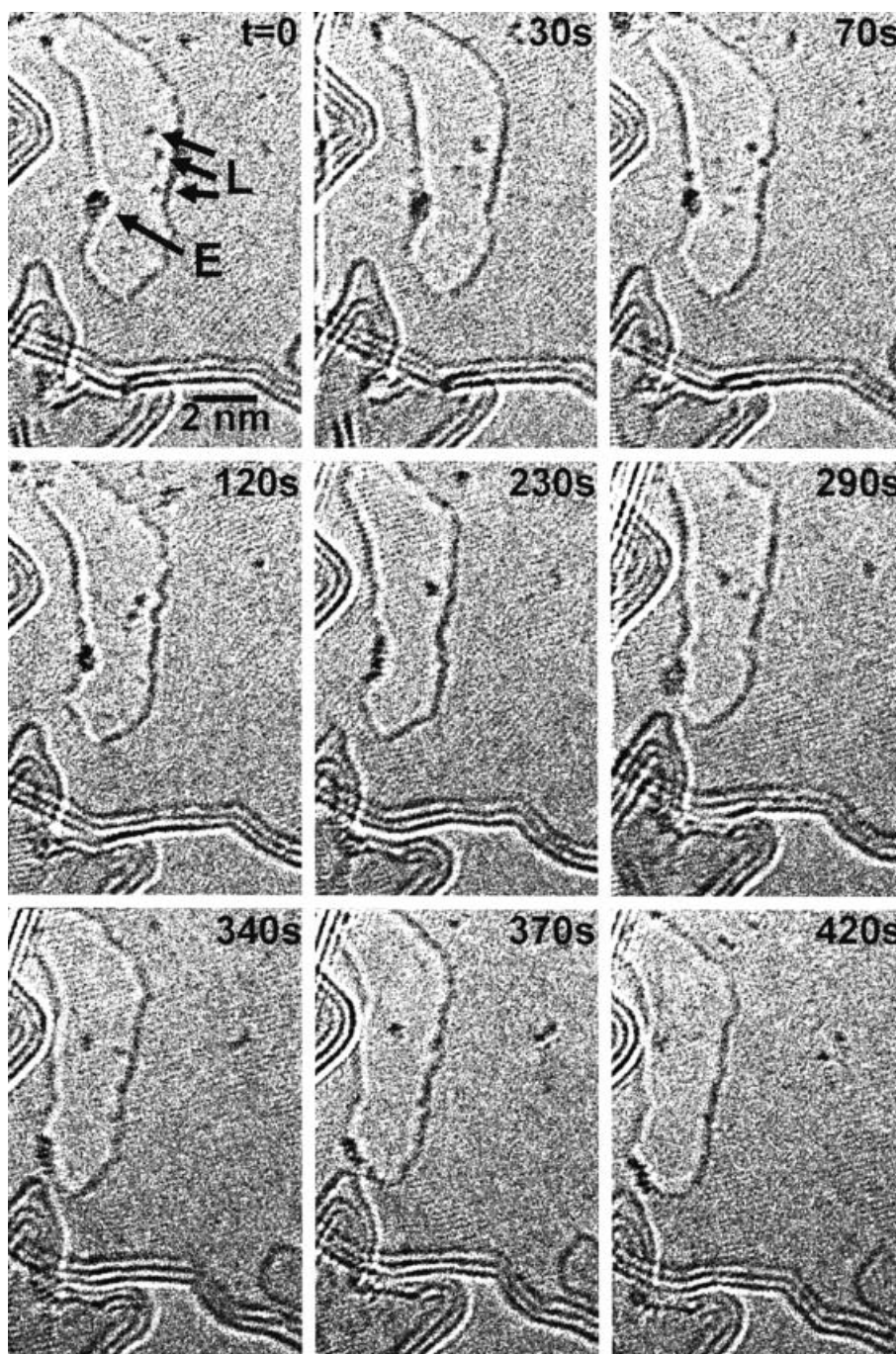
Figure 3. Series of images showing the diffusion of Pt atoms in graphene at 600 °C. Within the vertically elongated hole (the slightly brighter area) in a 2–3-layer graphene sheet we may have a 1–2 layer sheet where Pt atoms are diffusing two-dimensionally (marked with "L"). A cluster of Pt atoms sitting at the edge of the remaining layer (marked with "E") disperses, and the atoms migrate one-dimensionally along the edge of the graphene layer. The observation time is indicated in each image.

temperatures of our experiments we obtain an activation energy of $E_a \approx 2.5$ eV for both Au and Pt diffusing in the graphenic planes (uncertainties in the pre-exponential factor have only minor influence). For the diffusion of metal atoms along the axial direction in the layers of carbon nanotubes we obtain $D = 2$–4×10^{-20} m^2 s^{-1} for Pt (for Au no reliable data could be obtained), corresponding to an activation energy of $E_a \approx 2.3$ eV. It appears that the diffusion of metal atoms in the

curved layers of nanotubes is slightly faster than in planar graphene.

The preferential residence of metal atoms at the edges of graphenic sheets as observed in these experiments (cf. Figures 1 and 3) suggests a more stable configuration at the edges. In Figure 3 we see a chain of Pt atoms moving along the edge. The migration as seen here would correspond to a diffusion coefficient of approximately 3×10^{-21}–1×10^{-20} m^2 s^{-1} that
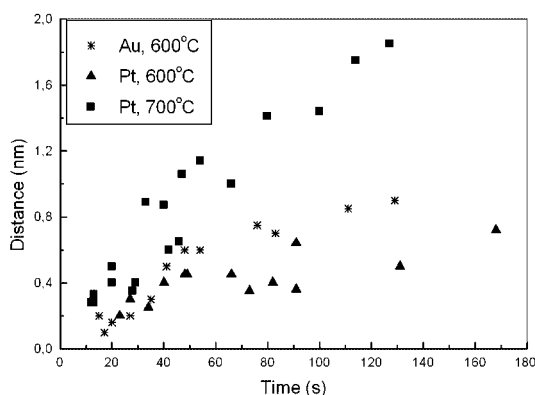
Figure 4. Migration length measured from micrographs for Au and Pt atoms at 600 °C and for Pt atoms at 700 °C.
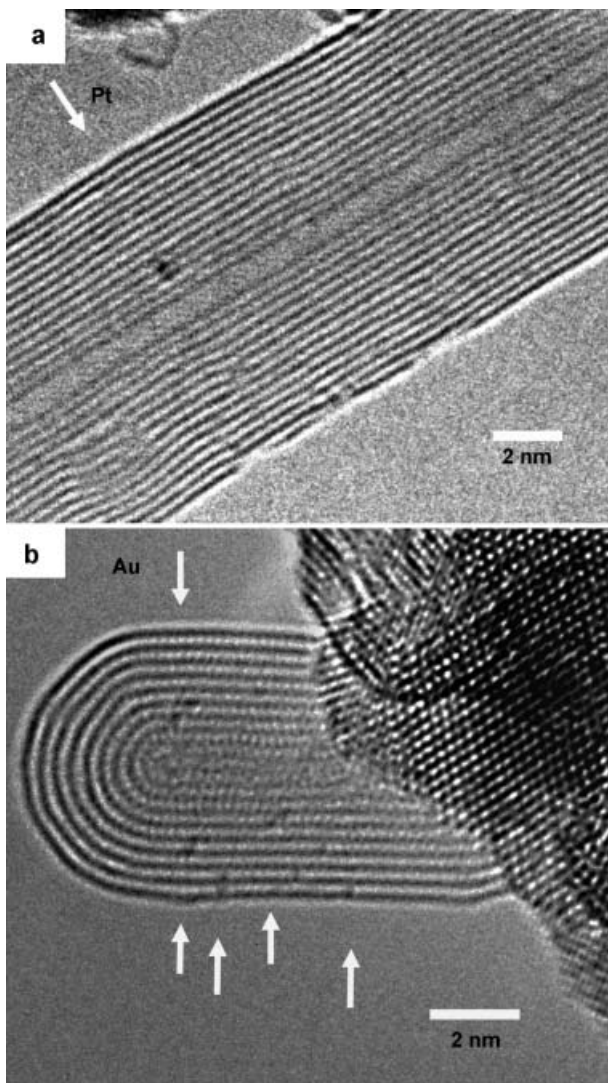
Figure 5. a) Platinum and b) gold atoms in MWCNTs. Some metal atoms are arrowed. The nanotube in (b) is attached to a Au crystal.

gives an activation energy of 2.3 eV for the 1D diffusion of Pt atoms at an open graphene edge. Similar values have already been obtained in a theoretical study.[11] Surprisingly, there is only a minor difference, if at all, between the 2D diffusivities of metal atoms within the graphene layer and the 1D diffusivity along its edge. A saturation of the open edges by hydrogen is possible and could lead to a lower diffusivity of metal atoms because hydrogen atoms have to be displaced during the diffusion.

The rather high activation energies of 2.2–2.5 eV point to a strong covalent bonding between metal and carbon atoms within the graphenic network.[11] If we compare this value with the activation energy for site exchange of carbon atoms (self-diffusion) that is given by the vacancy migration energy in graphene ($1.2 \, eV^{[20]}$) the migration of metal atoms in the network is orders of magnitude slower than the migration of carbon atoms. We can clearly exclude a surface migration mechanism that would need much lower activation energies, for example, in the range of 0.14 eV[11] (theoretical value for Pt) to 0.28 eV[21] (experimental value for Au). Although the measurement of the migration distances in this study are not very precise and influenced by the statistics of diffusion, we can exclude an activation energy of smaller than 2 eV because the atoms would migrate much too fast to be visible in TEM images. Of course, an additional mechanism of faster diffusion (such as surface diffusion) could also occur, but is not detectable by TEM. The upper limit of detectability would be a value of 2.8 eV in which the atoms would remain immobile within the observation times of our study.

In the absence of vacancies, there are no interstitial sites for foreign atoms in a monolayer of graphene. Hence, we have to assume that the metal atoms reside on voids in the layer that might be either single or multiple vacancies. The observation that metal atoms are not in detectable off-plane positions indicates that the metal atoms reside in double or triple vacancies. On the other hand, the location of metal atoms appears to be on regular lattice positions (Figure 1), indicating single vacancy occupation. In any case, diffusion should occur by site exchange of a carbon and a metal atom. With a formation energy of more than 7 eV, even single vacancies are practically absent in thermal equilibrium at the temperatures of this experiment. The replacement mechanism appears therefore reasonable in a wide temperature range and may also play a role in the catalytic growth of carbon nanotubes.[8] The small difference between the diffusivities of Au and Pt is surprising because it is known that the C–Au interaction is weaker than the C–Pt interaction.[10] The slightly smaller activation energy of metal diffusion in the layers of nanotubes might be because of a lower vacancy formation energy and a higher vacancy diffusivity in curved graphenic structures.

We also have to consider the influence of the unavoidable electron irradiation in this experiment. Irradiation-induced displacements of carbon atoms lead to vacancies in the graphitic layers.[22] We can estimate the vacancy formation rate [23] by assuming a displacement threshold of 15 eV and a beam current density of 30 A cm^{-2} and obtain an order of one displacement of every carbon atom in 180 s. Since the migration barrier for vacancies and interstitials in graphitic structures is quite low (e.g., in SWCNTs $E_a = 1.2$ eV for

vacancies and $E_a = 0.3–0.8\,eV$ for interstitials [20,24]), we can assume rapid defect annealing in the graphenic layers. A larger defect concentration can be achieved by irradiation with a higher electron dose but the reconstruction after vacancy formation is rapid and would lead to strong and clearly visible curvature effects (warping and cage-like structures). Unlike carbon atoms, the heavy metal atoms can hardly be displaced by knocks from the electrons. Therefore, electron irradiation should have only minor influence on the migration of metal atoms although a certain contribution of radiation-enhanced diffusion, which is a sub-threshold effect,[25] should be taken into account.

To conclude, the direct observation of the behavior of Au and Pt atoms in graphenic structures allows us to determine the position of the atoms and their diffusivities. Metal atoms replace carbon atoms and are located in single or multiple vacancies. Metal atoms with considerable off-plane positions can be excluded. A small attractive interaction between the metal atoms leads to a tendency of clustering but the clusters are not stable. The activation energy for the in-plane migration of both Au and Pt atoms in graphene is around 2.5 eV, indicating covalent bonding between metal and carbon atoms. Linear diffusion of metal atoms along the open edge of a graphene layer occurs with only slightly lower activation energy. The diffusion of metal atoms in curved graphenic layers of nanotubes is slightly faster than in planar graphene. Slow surface diffusion can be excluded.

The knowledge of the bonding between metal and carbon atoms and of the location and diffusivity of metal atoms in graphene layers allows us to refine models of catalytic growth of carbon nanotubes and other nanostructures. But foreign atoms in graphene layers are also of importance for future applications of graphene in devices. Doping of graphene or single-walled nanotubes with impurities is expected to have a tremendous effect on their electrical properties.[26] In this context, it is necessary to know how impurities could diffuse into and within graphenic structures. Electrical contacts between a nanotube or graphene layer and a metal will certainly be an element in devices. The present study shows quantitatively how metal atoms diffuse into the graphenic structure at such a contact at elevated temperatures and under what conditions "contamination" of graphene by metals can occur.

Experimental Section

Powders of gold or platinum were mixed with graphite powder and filled into holes in graphite anodes of an electric arc discharge apparatus.[15,16] An arc (40 V, 55 A) was operated for 5–10 s in a helium atmosphere (330 mbar). The deposit on the cathodes was dispersed and sonicated in ethanol and collected on standard Cu or Mo grids for electron microscopy studies. The specimens were held at temperatures of 600 or 700 °C in a heating stage during electron microscopy observation. An elevated specimen temperature was chosen to speed up the migration of metal atoms and to anneal radiation damage in the graphene layers that may occur under the electron beam. A field emission electron microscope (FEI Tecnai F-30) with an acceleration voltage of 300 kV was used. Images with lattice resolution were recorded with a slow-scan CCD camera. Every 10–30 s still images with an exposure time of 0.3 s were taken. The contrast of the microscopy images was enhanced by image processing to improve the visibility of the metal atoms.

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