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Author(s)	Takahashi, Keisuke; Wang, Yongming; Chiba, Shotaro et al.
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Correspondence and requests for materials should be addressed to K.T. (keisuke.takahashi@eng.hokudai.ac.jp)

* Creative Research Institution, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan.

Low temperature hydrogenation of iron nanoparticles on graphene

Keisuke Takahashi, Yongming Wang*, Shotaro Chiba, Yuki Nakagawa, Shigehito Isobe* & Somei Ohnuki

Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8278, Japan.

Hydrogenation of iron nanoparticles was performed both computationally and experimentally where previously chemically-bonded iron hydride is considered to be unachievable under ordinary conditions. Density functional theory (DFT) calculations predict that hydrogenated iron nanoparticles are stabilized on a single-layer graphene/Cu substrate. Experimentally, iron nanoparticles were deposited onto a graphene/Cu substrate by vacuum deposition. Hydrogenation was done at 1atm of hydrogen gas and under liquid nitrogen. Mass spectrometry peak confirmed the hydrogen release from hydrogenated iron nanoparticles while a scanning transmission electron microscopy is used in order to link a geometrical shape of iron hydride nanoparticles between experimental and theoretical treatments. The hydrogenated iron nanoparticles were successfully synthesized where hydrogenated iron nanoparticles are stable under ordinary conditions.

Synthesis of iron hydrides is challenging due to the extreme conditions under which they generally exist[1,2]. Thus far, iron hydrides have been reported to exist within the atmospheres of stars such as the Sun and red dwarfs in a gas state as FeH and FeH_2 molecules and within the earth's core in a bulk state, requiring very low temperatures such as −243°C or high pressure such as 3.5 GPa[2–9]. Iron hydride molecules have been synthesized by evaporating the iron source within a hydrogen-argon gas mixture at −263°C[10–12]. Theoretical studies predict that small iron nanoparticles have the ability to be hydrogenated in a gas phase[13,14]. However, synthesis and deposition of hydrogenated iron nanoparticles on a surface has not yet been achieved under ordinary conditions. Here we theoretically screened for optimal substrates that support iron hydrides by using density functional theory (DFT) and experimentally tested hydrogenation of iron nanoparticles on the most optimal substrate, single layer graphene/Cu. DFT calculations indicate that a single layer graphene preserved the hydrogenation properties of iron clusters. Iron nanoparticles were then experimentally deposited on a single-layer graphene/Cu subtrate via vaccuum deposition where transmission electron microscopy (TEM) revealed that iron nanoparticles formed planar shapes on graphene/Cu. Hydrogenation of the iron nanoparticles was performed with 1 atm of hydrogen gas and hydrogenated under liquid nitrogen. Mass spectrometry captured the peak of hydrogen release from the hydrogenated iron particles. Hydrogenated iron nanoparticles were successfully synthesized on the single layer graphene/Cu substrate which is stable under ordinary conditions.

Graphene is a two dimensional crystal which has shown remarkable electronic and mechanical properties, yet it still has undiscovered effects[15,16]. Graphene is commonly synthesized on a Cu substrate by chemical vapor deposition as a Cu substrate is proven to have advantages for commercial applications due to industrial scalability and efficient production[17–19]. Recent research has discovered that graphene is also considered to be an effective substrate for supporting nanoparticles[20,21]. The properties of nanoparticles are strongly dependent on their size and structure[22–24]. In particular, small gas-phase iron nanoparticles are calculated to have the capacity to absorb large amounts of hydrogen and are known to have large magnetic moments where the magnetic moment can be controlled upon hydrogenation[13]. However, the properties of nanoparticles can be affected by the surface upon the depositon of nanoparticles, making it imperative to find a way to preserve the desired properties of the nanoparticles without interferance from other nanoparticles or surfaces. Therefore, optimal surface planes for iron nanoparticle were computationally explored.

Computational Result

Density functional theory (DFT) calculations were performed within a real space grid of the projector augmented wave method[25,26]. The exchange-correlation of the vdW-DF is implemented[27]. Linear combination of atomic orbitals mode with GPAW is used. Grid spacing is set to 0.20 Å and 4×4×1 special k points of the Brillouin zone sampling is used for surface calculations where the 15Å of vacuum was applied to the z-axis for surface calculations.

DFT calculations were applied in order to find the surface planes that can preserve the hydrogenation properties of Fe clusters. A FeH cluster was deposited on the surface planes of commonly-used substrates including Al_2O_3, SiO_2, MgO, and a single layer graphene sheet. Calculations indicated that the hydrogenation properties of the FeH cluster are preserved most on a single layer graphene compared to the other surfaces where the properties of the FeH cluster are strongly affected by the surface. However, a single layer graphene sheet must be deposited on a substrate in order to hold a single graphene sheet during the experiment. A Cu substrate was chosen as it is widely used as a supporting substrate for graphene synthesis[18,19]. In particular, the binding energy and the distance between single layer graphene and Cu are calculated to be −0.15 eV and 3.60 Å, respectively. The single layer graphene is weakly bonding with the Cu substrate through physisorption, and as a result the properties of the single layer graphene are not affected by the Cu substrate.

An atomic model of the FeH cluster on a single layer graphene/Cu(111) is shown in Figure 1. Calculations indicate that the FeH cluster is weakly bonded with graphene/Cu(111) where the binding energy is calculated to be −1.15 eV. The binding energy of H on Fe/graphene/Cu(111) is calculated to be 0.51 eV. The magnetic moments of the Fe atom within FeH on a single layer graphene/Cu(111) and the Fe atom within a gas-phase FeH cluster are both calculated to be 3.00 μ_B. The bond length of a gas-phase FeH is calculated to be 1.56 Å where the FeH cluster on a single layer graphene/Cu(111) is calculated to be 1.60 Å. The electronic structure of the FeH cluster on the single layer graphene/Cu(111) suggests that it may be possible to hydrogenate the iron nanoparticles on a single layer graphene/Cu substrate.

Further DFT calculations were applied in order to understand the geometrical shape of bare Fe clusters on graphene/Cu. Calculations show that Fe_4 cluster forms a regular tetrahedron structure on graphene/Cu(111) as shown in Figure 1 (c) while previous theoretical work reports that the ground state structure of gas phase Fe_4 has a tetragonal disphenoid structure[13]. The Fe_7 cluster shown in Figure 1 (d) has a hexagonal shape while gas-phase Fe_7 has a pentagon structure[13]. The theoretical data suggests that small iron clusters grow towards regular planar shapes. Bare Fe clusters on graphene was previously observed by transmission electron microscopy where Fe clusters form regular planar shapes from a top view against a two dimensional graphene plane, confirming the planar-forming behavior of the bare Fe clusters[28]. DFT calculations were further performed in order to understand the geometrical shape of the hydrogenated Fe_4 and Fe_7 clusters on graphene/Cu(111) as shown in Figure 1 (e) and (f). Calculations show that the structures of Fe_4 and Fe_7 are elongated by hydrogenation while the geometrical shape still remains same as bare Fe_4 and Fe_7.

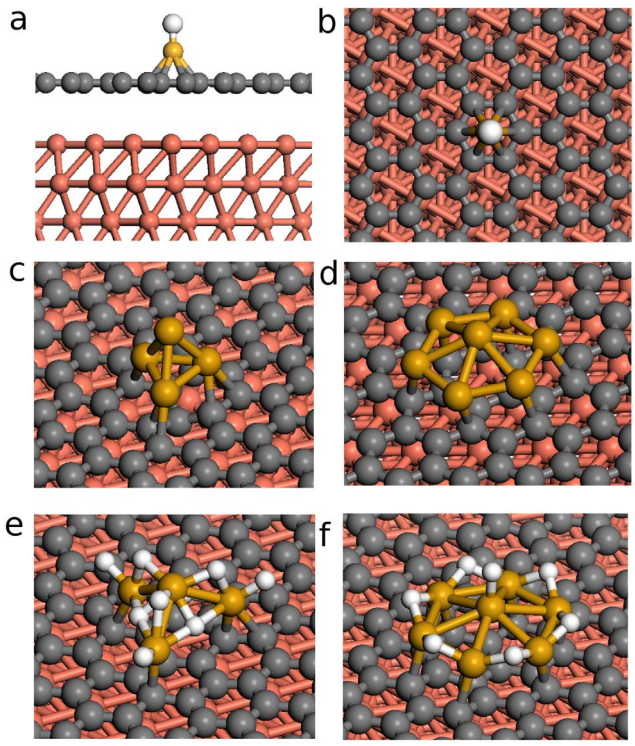


Figure 1 | Atomic model of FeH cluster on graphene/Cu(111), a) side view and b) top view. (c) Fe_4 and (d) Fe_7 clusters on graphene/Cu(111). Hydrogenated (e) Fe_4 and (f) Fe_7 clusters on graphene/Cu(111). Atomic color codes: Fe, ochre; H, white; C, gray; Cu; red.

Experimental Result

Experimentally, a single layer graphene sheet was grown on a Cu surface by chemical vapor deposition where a single layer of graphene was confirmed by Raman spectroscopy. Fe nanoparticles were deposited by using vacuum deposition. Fe nanoparticles on graphene/Cu is then observed by using STEM (FEI, Tecnai Osiris) 1 atm of pressure of hydrogen gas was then applied to the Fe nanoparticles on graphene/Cu, followed by hydrogenation of Fe nanoparticles under liquid nitrogen (−196°C) for 3 hours. The dehydrogenation of hydrogenated Fe nanoparticles were analyzed by mass spectrometry.

Deposited Fe nanoparticles on the graphene/Cu sample were observed by using a STEM as shown in Figure 2 (a). Figure 2 (a) provides that small Fe nanoparticles are spread over the graphene/Cu substrate where dark areas are confirmed to be Fe by energy dispersive X-ray spectrometry (EDS) shown in Figure 2 (b). Thus, Fe nanoparticles were successfully deposited by vacuum deposition. Figure 2 (a) also shows that the sizes of the Fe nanoparticles range from 1 nm to 3 nm. In particular, each Fe nanoparticle has the possibility to form planar shapes as DFT calculations suggest Fe clusters form a planar shape on graphene shown in Figure 1 (c) and (d).

Further DFT calculations were performed in order to fill the size of nanoparticles between the calculation and experiment. Figure 2 (c) and (d) shows the Fe_{25} and $Fe_{25}H_{16}$ on graphene/Cu(111), respectively. The size of Fe_{25} and $Fe_{25}H_{16}$ on graphene/Cu(111) is calculated to be 1.12 nm and 1.15 nm, respectively. The structure of Fe_{25} on graphene/Cu(111) shown in Figure 2 (c) have triangle like structure which similar structure is seen in Figure 1 (a). Figure 2 (d) shows that Fe_{25} can be hydrogenated on graphene/Cu(111) where the structure is slightly elongated upon hydrogenation.

Dehydrogenation of the hydrogenated Fe nanoparticles on a graphene/Cu sample was investigated by using mass spectrometry in order to confirm if the Fe nanoparticles were hydrogenated. Two type of samples were prepared: i) hydrogenated Fe on graphene/Cu, and ii) hydrogenated graphene/Cu for comparison where hydrogenation for both samples was performed under the same conditions. Both hydrogenated samples were taken from the sample holder after hydrogenation and switched to a new sample holder under an argon-filled glovebox. Sample holders with each sample were then vacuumed for 1 hour in order to remove gas impurities.

Each sample was then inserted into a furnace which was preheated to 400°C. Figure 3 indicates that hydrogen gas is released from the hydrogenated Fe on the graphene/Cu sample (Figure 3 i) at 110 seconds, whereas the hydrogen release was not observed in the hydrogenated graphene/Cu case (Figure 3 ii). This confirmed that hydrogen is released from the Fe nanoparticles. Note that the temperature of sample holder indicates 190°C at the peak of hydrogen release, 110 seconds.

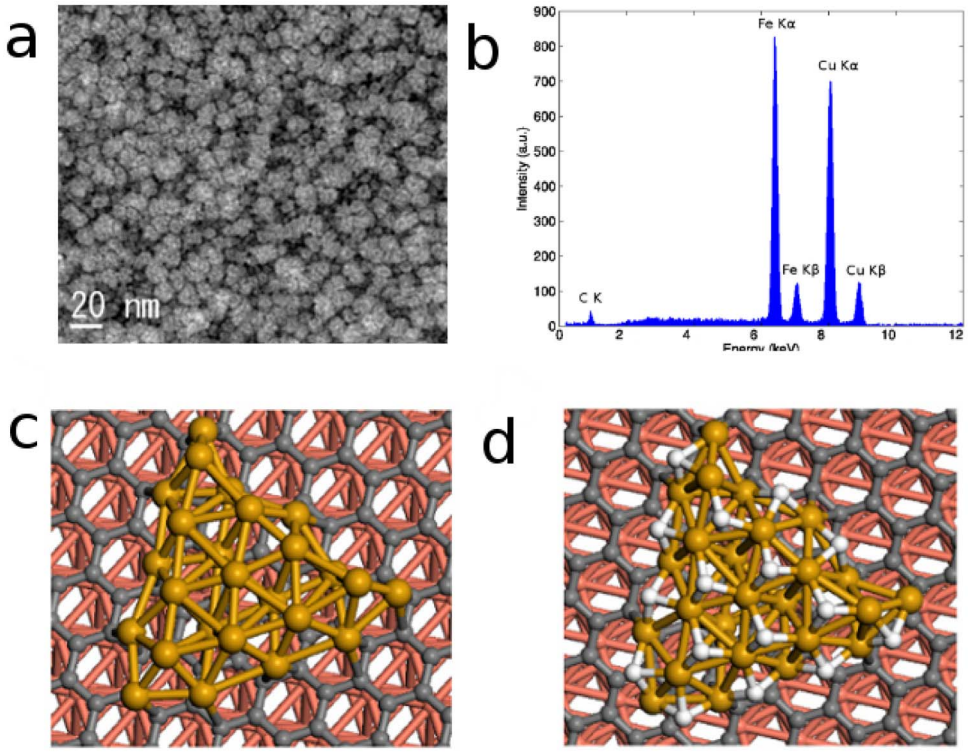


Figure 2 | (a) STEM images of Fe nanoparticles on graphene/Cu and (b) corresponding EDS analysis. Calculated atomic models of (c) Fe_{25} graphene/Cu(111) and (d)$Fe_{25}H_{16}$ on graphene/Cu(111). Atomic color codes: Fe, ochre; H, white; C, gray; Cu; red.

Conclusion

In conclusion, hydrogenation of Fe nanoparticles was explored from both computational and experimental approaches. DFT calculations revealed that hydrogenation properties of iron nanoparticles were well preserved on a single layer graphene/Cu substrate. Iron nanoparticles were then experimentally deposited on the graphene/Cu substrate by using a vacuum deposition. Low temperature hydrogenation of iron nanoparticles on the graphene/Cu substrate successfully created hydrogenated iron nanoparticles on graphene/Cu which is stable under ordinary conditions.

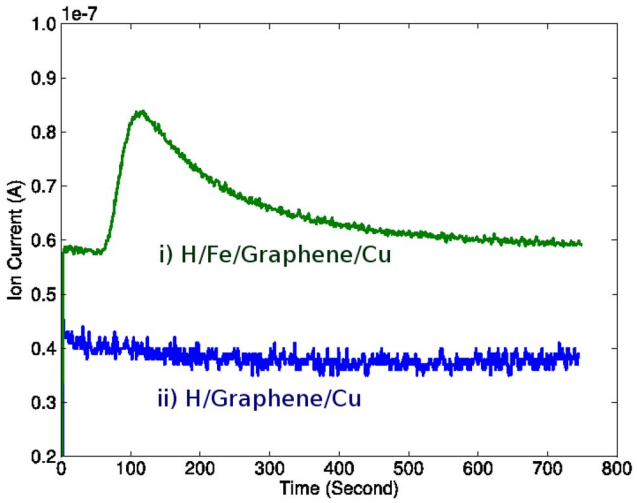


Figure 3 | **Dehydrogenation as characterized by mass spectrometry where it is set to detect only hydrogen gas.** Dehydrogenation was performed at 400°C. i) Hydrogenated Fe on graphene/Cu and ii) hydrogenated graphene/Cu.

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Author contributions

K.T. coordinated the project, designed, ran and analyzed the density functional theory calculation and experiment, and wrote paper. Y.W. designed and ran the TEM and sample preparation. S.C. and Y.N. ran the sample preparation and mass spectrometry analysis. S.I. organized the discussions, and S.O. sponsored the project. All authors discussed about the results and commented on the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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