

# Controlled Hydrogenation of Graphene Films Grown on a Modified Pt(111) Substrate

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Hydrogen is the most abundant energy carrier and hydrogen-based fuel cells are one of the effective devices that utilize this chemical energy by converting it to electrical energy. A key step in the development of a reliable hydrogen-based technology is to overcome two barriers. (i) The storage of hydrogen and (ii) its transportation. Recently, several studies on graphene have highlighted the potential of carbon based materials for hydrogen storage. However, C-H bond is very strong and viable utilization of stored hydrogen from graphene remains a problem [1]. In the last years, the modification of C-H bond on graphene and properties of graphene-metal contact [2,3] [4].

Graphene grown on single crystal metal surfaces offers ideal frameworks to investigate atomic level interactions in detail. Hydrogenating the surface of graphene also changes the interaction between graphene and the surface of the metal substrate. Thus, hydrogenation capacity of graphene might depend on the substrate of choice. Besides, modification of the parent substrate might play an important role. It is now well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces [5]. The modification effect is especially important when the admetal coverage is in the submonolayer to monolayer regime.

In our study, an ultra-high vacuum system with a base pressure of  $4 \times 10^{-10}$  mbar has been employed. Setting the substrate temperature to 800K, dosing benzene to the chamber and finally flashing the temperature up to 1000K lead to the formation a monolayer graphene on the substrate. An atomic hydrogen source has been employed for providing the atomic hydrogens in the preparation of hydrogenated graphene. Pt/3d/Pt(111) were prepared by physical vapor deposition of 3d metals onto the surface, followed by subsequent annealing to drive the 3d admetal atoms into subsurface positions [6].

We show that the electronic and therefore the chemical properties the graphene films grown on Pt(111) single crystalline substrates can be modified by embedding and intercalation of a monolayer of transition metals (Ni, Fe, Co, V) in Pt(111) subsurface. The temperature programmed desorption (TPD) of hydrogen investigations show that these subsurface alloys enable us to manipulate desorption activation energies of hydrogen from graphene. Our results show that between all 3d metals which have been studied in our investigation, cobalt is the most effective one at reducing the C-H bond strength. Pt/Co/Pt(111) subsurface alloy reduces the hydrogen desorption activation energy by weakening C-H bond energy in graphene from  $\sim 111$  kJ/mol to  $\sim 57$  kJ/mol.

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