Enhanced Water Vapor Barrier Property of Poly(chloro-p-xylylene) Film by Formation of Dense Surface Cross-linking Layer via Hyperthermal Hydrogen treatment

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Supporting information

1. The working principle of Hyperthermal Hydrogen Induced Cross-linking (HHIC) technology

Hyperthermal Hydrogen Induced Cross-linking is a method capable of selectively breaking C-H bonds without breaking other bonds using hyperthermal molecular hydrogen. In this method, a hydrogen plasma is generated by an electron cyclotron resonance (ECR) microwave and protons are extracted from the hydrogen plasma with an electric field to accelerate them to an appropriate kinetic energy. The protons enter into a drift zone to collide with molecular hydrogen in gas phase. The cascades of collisions produce a high flux density of 10^{16} cm^{-2} of hyperthermal molecular hydrogen, which is many times higher than the flux of protons extracted from usual hydrogen plasma. The nominal flux ratio of hyperthermal molecular hydrogen to proton is controlled by the hydrogen pressure in the drift zone, and by the length of the drift zone. The extraction energy of the protons is shared by these hyperthermal molecules so that average energy (10-20 eV) of the hyperthermal molecular hydrogen is controlled by extraction energy of the protons and the nominal flux ratio. Besides, other charged species such as H^+, H^-, and electrons can be repelled by two grids above

the sample with an appropriate voltage bias, a process which avoids undesirable electrical damage and side-reactions. Since the hyperthermal molecular hydrogen projectiles do not carry any electrical charge, the flux of hyperthermal hydrogen can be used to engineer surface of both electrical insulating products and conductive products. When this method of generating a high flux of hyperthermal molecular hydrogen is applied to bombard organic molecules with desirable chemical functionalities on a substrate, the C-H bonds are cleaved preferentially due to the kinematic selectivity of energy deposition from the hyperthermal hydrogen projectiles to the hydrogen atoms in the precursor molecules. The induced cross-linking reactions produce a stable molecular layer having a controllable degree of cross-linking and retaining the desirable chemical functionalities of the precursor molecules. HHIC is thus a versatile research tools for surface engineering of polymeric materials.

2. Chemical selectivity of hyperthermal hydrogen for C-H bond cleavage

According to the hard sphere binary collision model, the maximum energy transfer between two colliding species (proton and hydrogen molecule) is determined by the two masses with the formula $4M_1M_2/(M_1+M_2)^2$.

The formula for the kinetic energy transferred from an incident hard-sphere particle of mass M_1, having initial energy E_1, to a target particle of mass M_2, initially at rest ($E_2 = 0$), during an absolutely elastic head-on collision, is the following:

$$\varepsilon = \frac{E_2^*}{E_1} = \frac{4M_1M_2}{(M_1+M_2)^2},$$

where the E_2* represents the kinetic energy after collision. According to this formula, for H_2 projectiles, $\varepsilon = 0.89$ in a H_2/H collision and $\varepsilon = 0.49$ in a H_2/C collision. Consequently, since the energy transfer is more efficient for H_2 collisions with H, than for those with C, there is in principle a window of opportunity to preferentially cleave C-H bonds without breaking C-C bonds.

By contrast, if Helium projectiles are used, $\varepsilon = 0.64$ in a He/H collision and $\varepsilon = 0.75$ in a He/C collision. Since the latter figure is bigger than the former, the possibility to do HHIC with helium is hindered in principle as C-C bonds get broken

on average more often than C-H bonds.

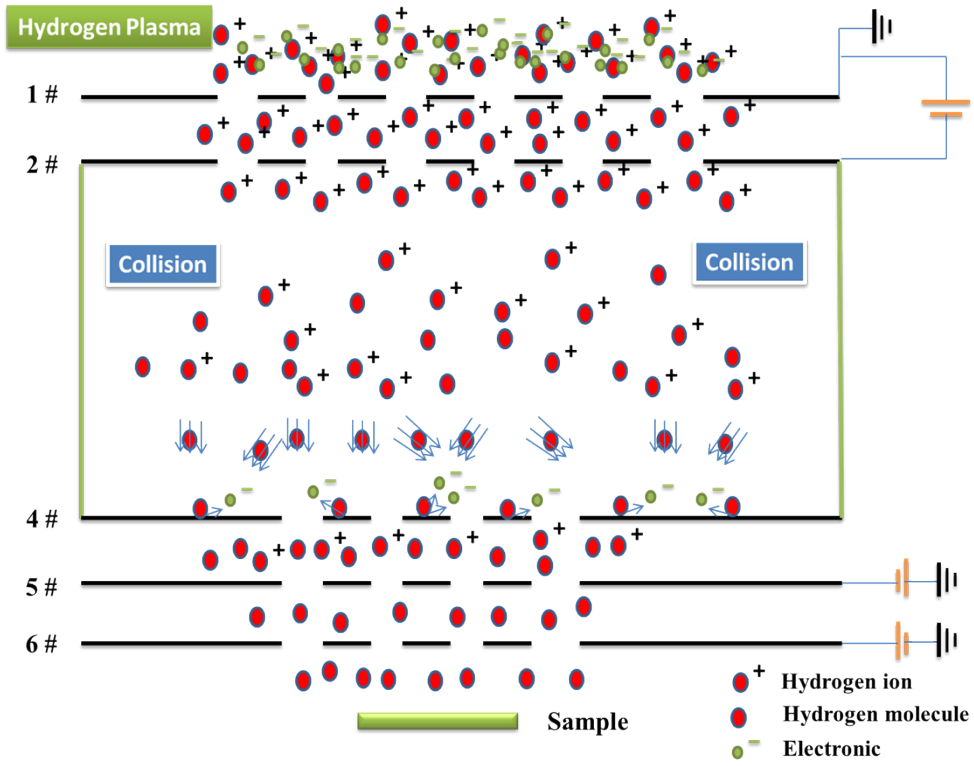

Figure 1S Schematic diagram illustrating the HHIC working principle.

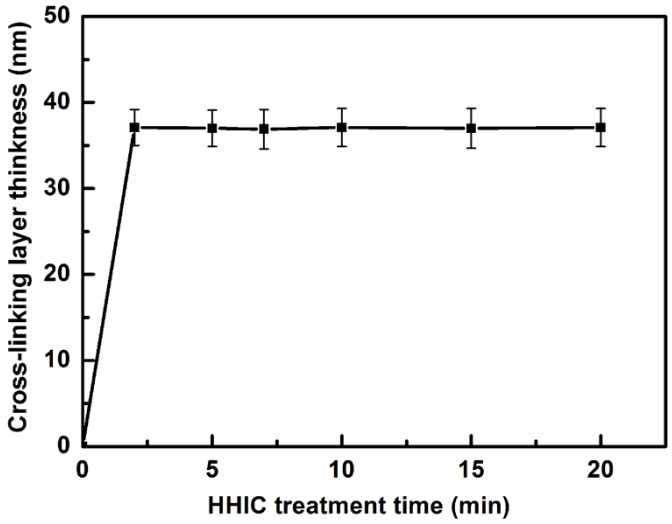

Figure 2S Cross-linking layer thickness of PPXC film with various HHIC treatment time.