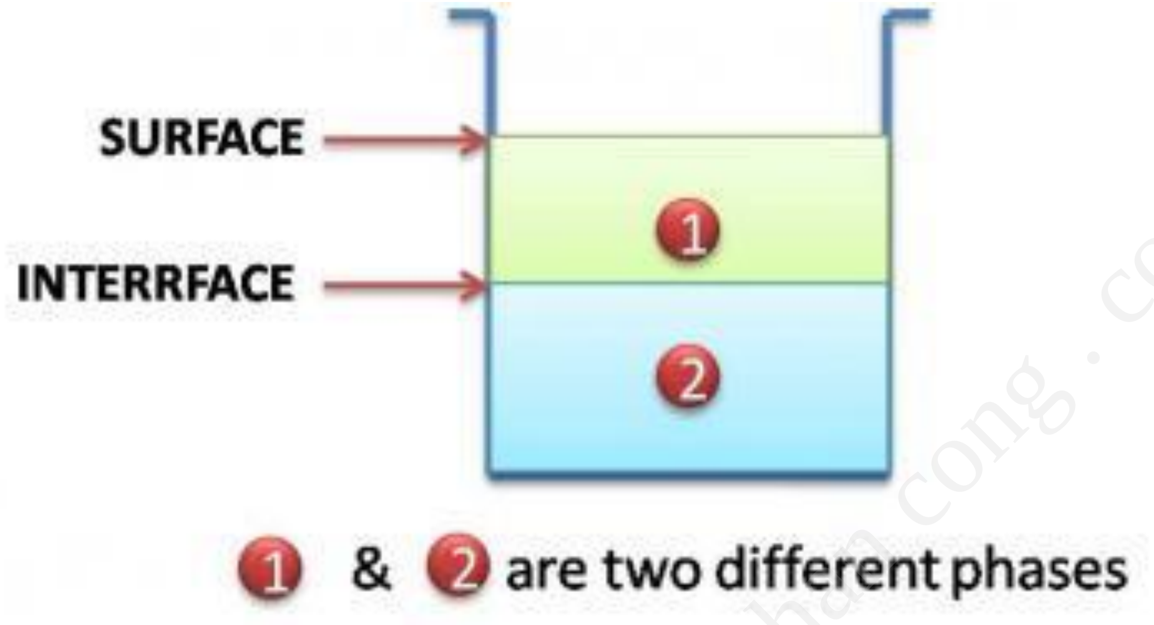
Chương 4. Biến tính bề mặt vật liệu với lớp mỏng các phân tử hữu cơ (T6)

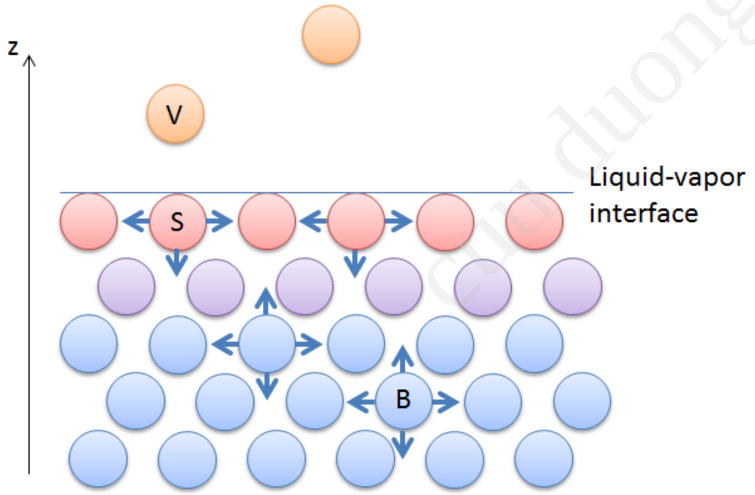
4.1. Biến tính bằng lớp mỏng hữu cơ kích thước nano mét

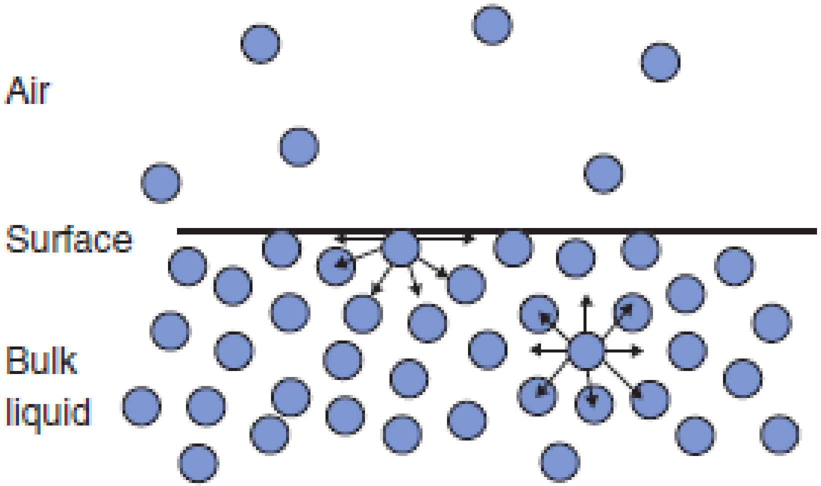
4.2. Biến tính bằng lớp mỏng hữu cơ đa lớp

4.3. Một số tính chất bề mặt của vật liệu biến tính bằng lớp mỏng hữu cơ

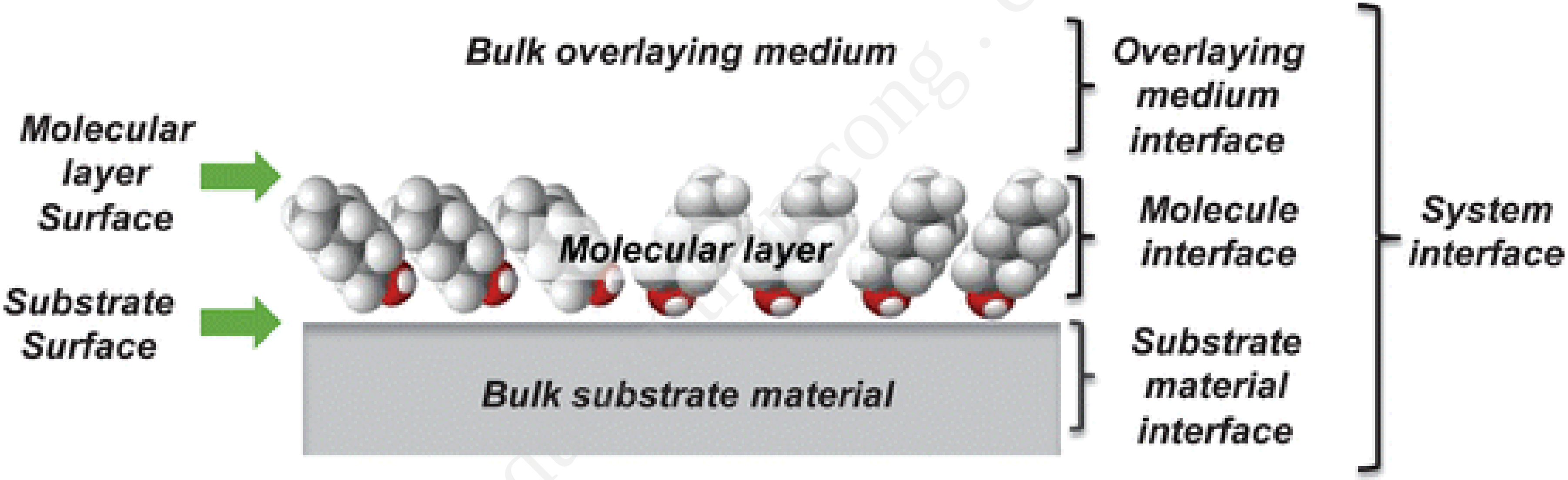
surface and interface



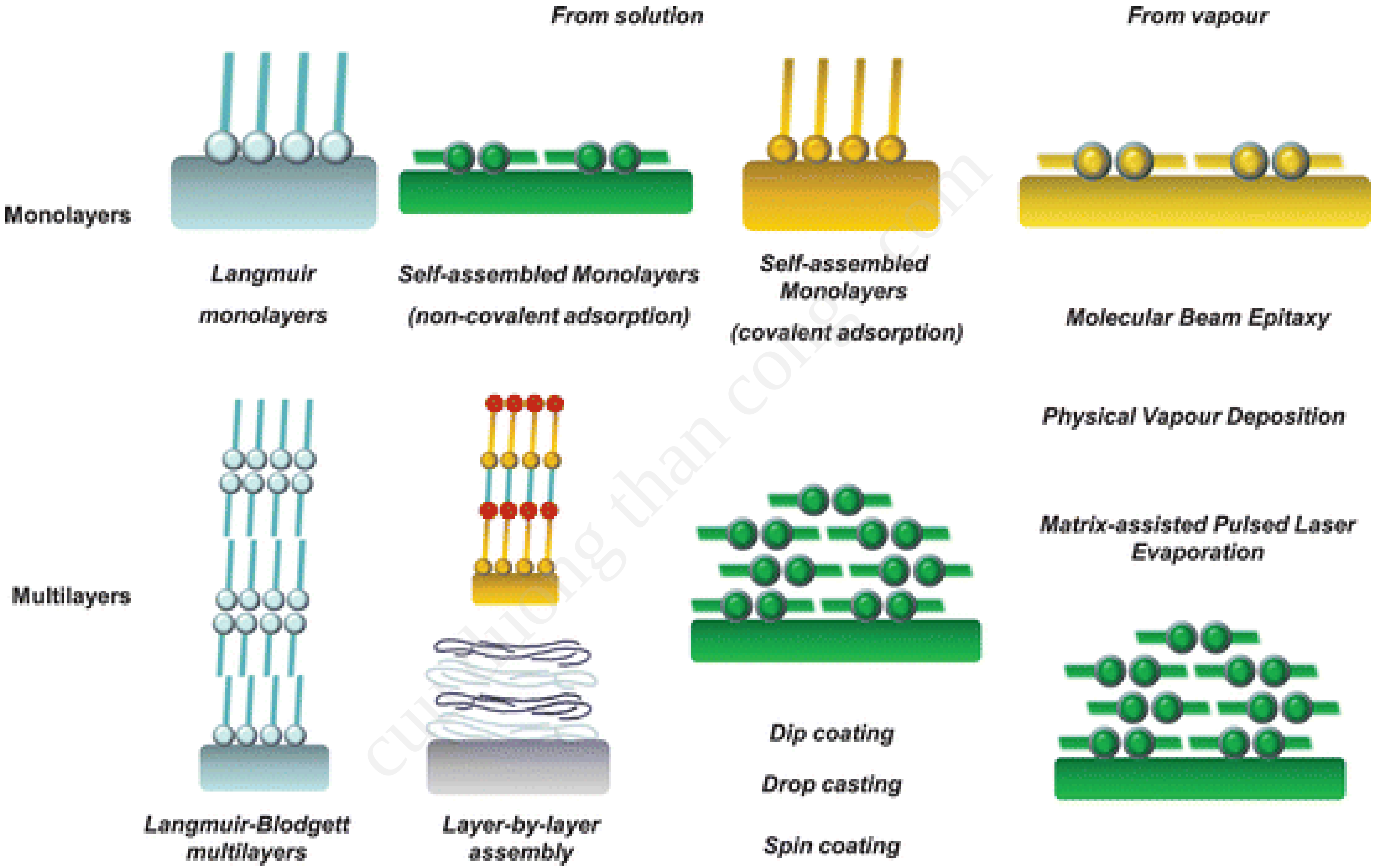




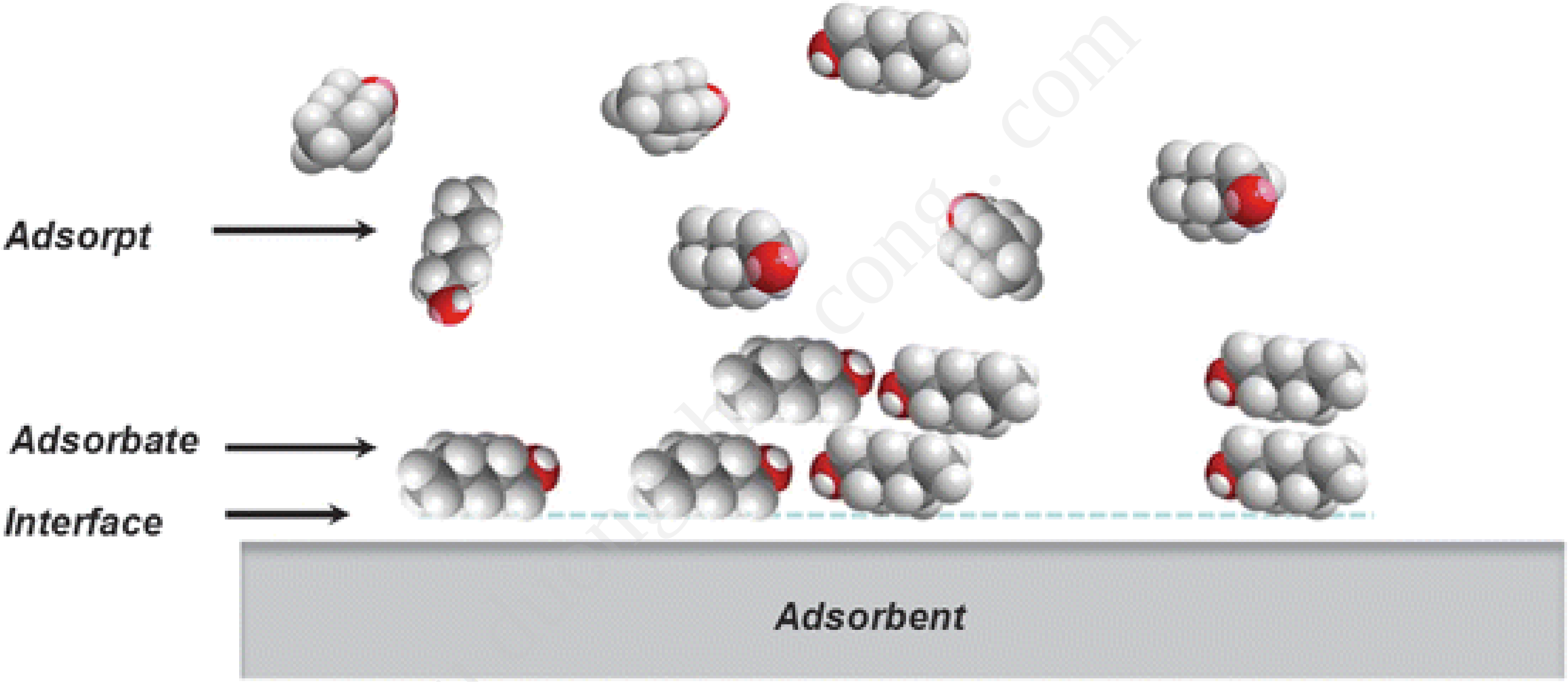
Surfaces for Supramolecular Systems



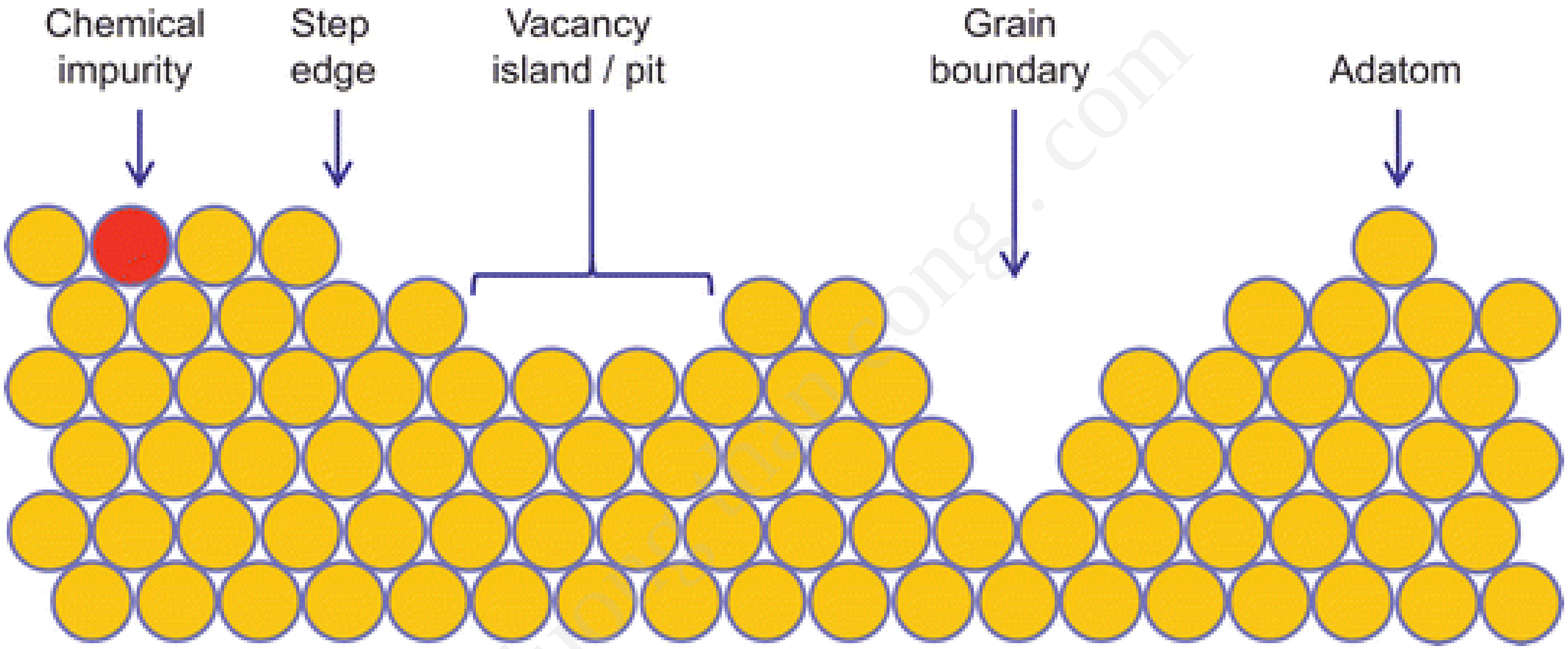
The concepts of surface and interface, of each material and the system.



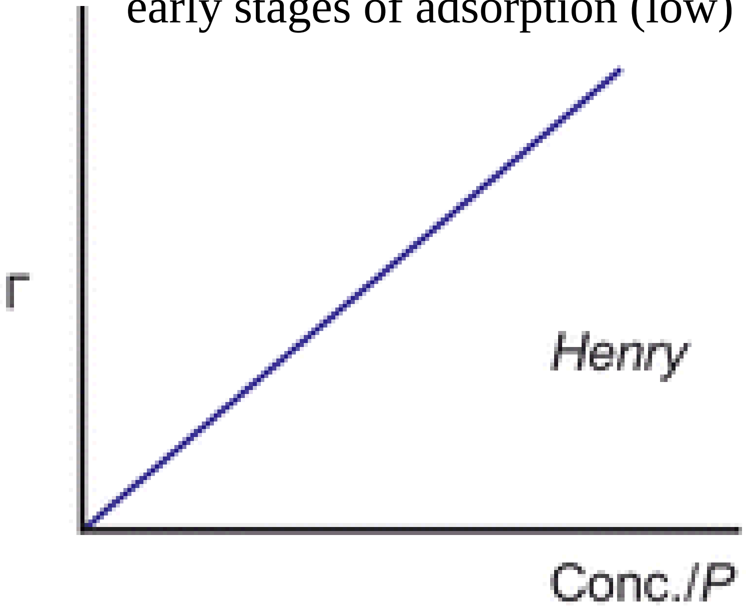
Some routes to the formation of layers of molecules on surfaces



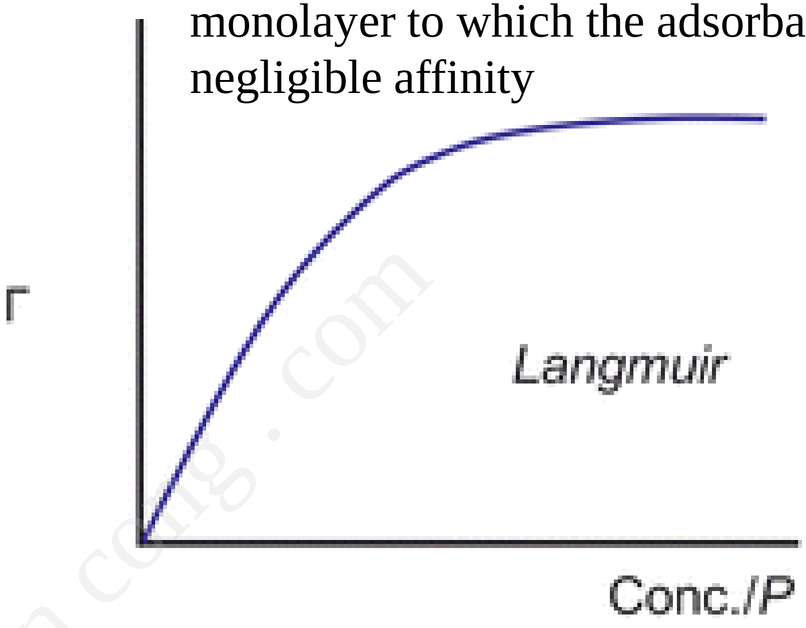
Adsorption and the definition of the components in the system



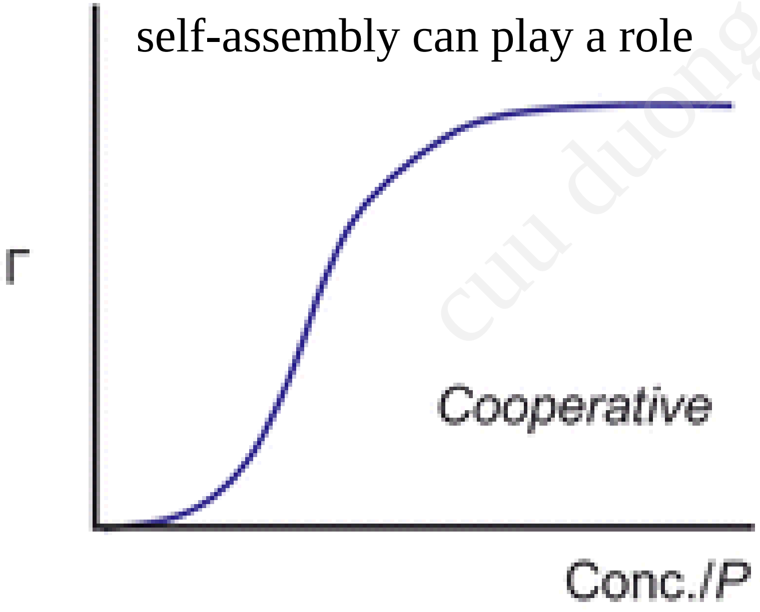
Some common surface defects on flat surfaces early stages of adsorption (low)



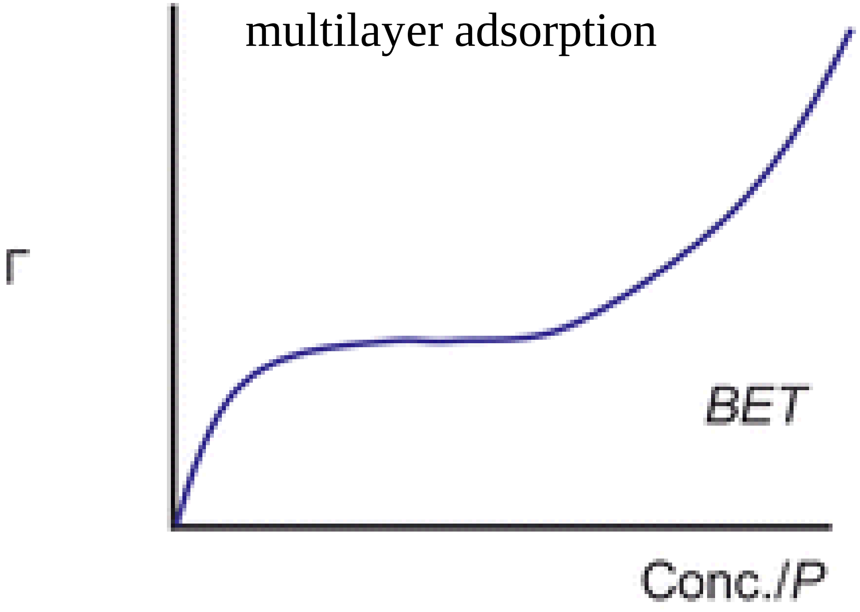
monolayer to which the adsorbate has negligible affinity

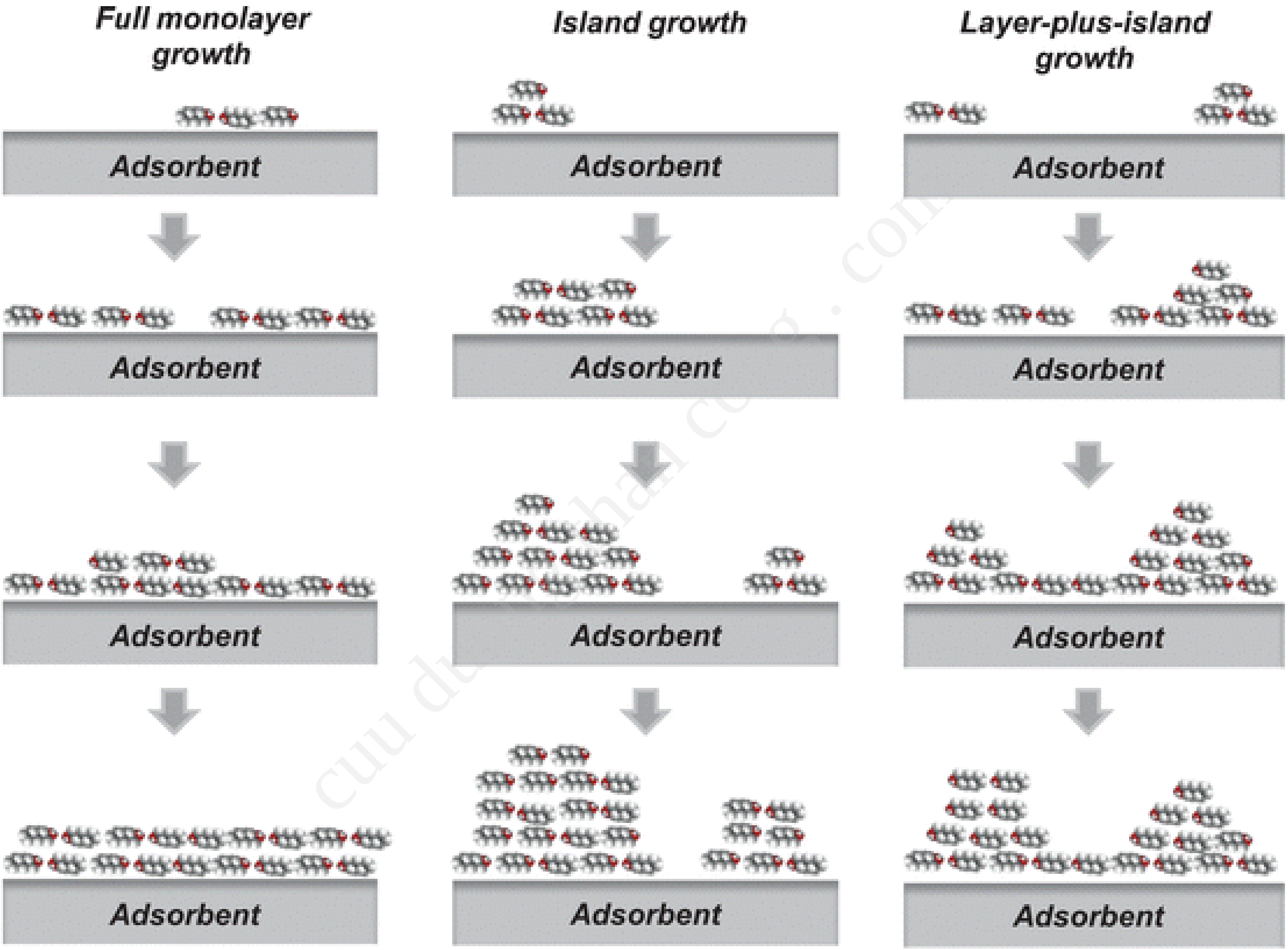


self-assembly can play a role



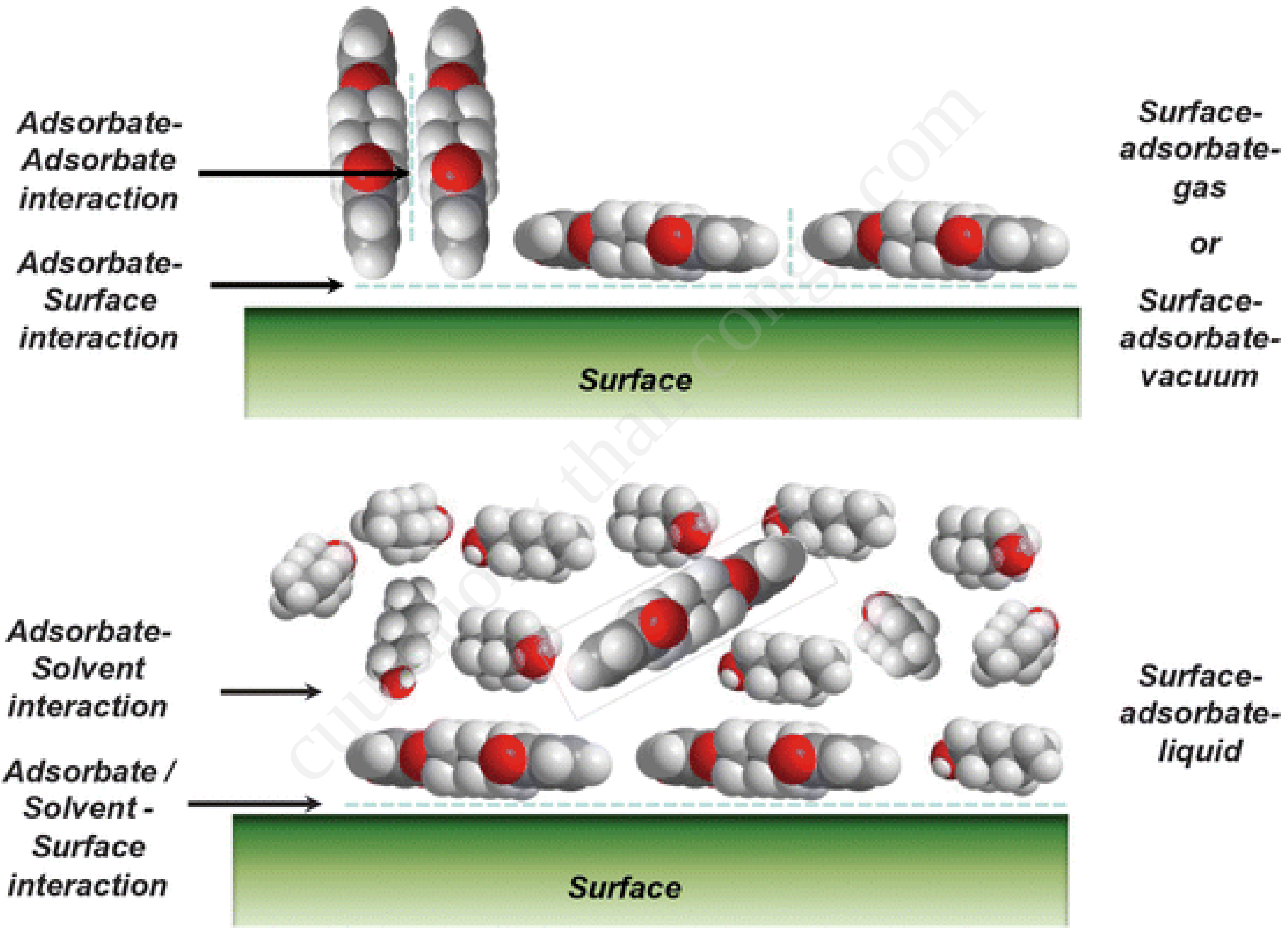
multilayer adsorption





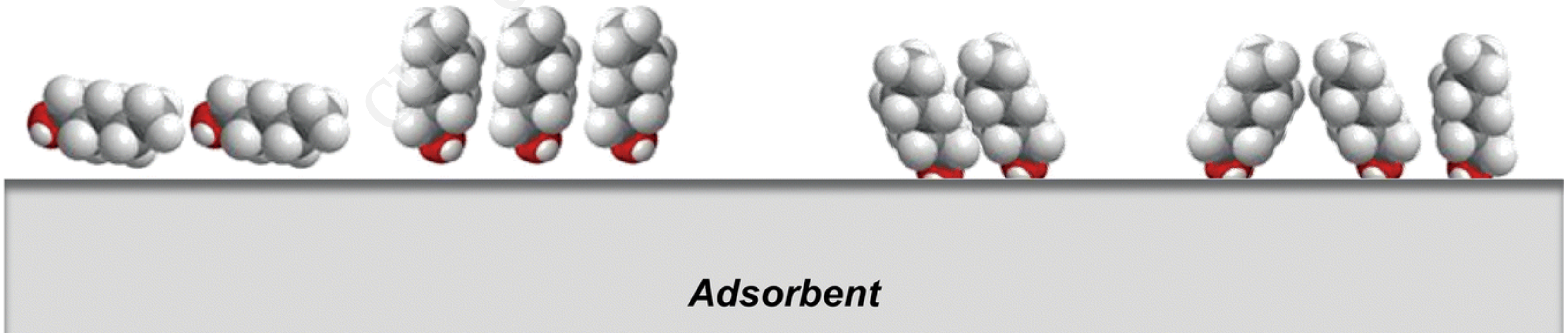
Three contrasting situations for layer formation on an adsorbent when an adsorpt attaches to it.

strong adsorbate–adsorbate interaction (compared with adsorbate–adsorbent) can lead to a perpendicular arrangement of the molecules



surface–adsorbate interaction dominates, then the molecules will lay coplanar to the surface

Physisorption	***Chemisorption***
Weak adsorbate-adsorbent bond	Strong adsorbate-adsorbent bond
Close to equilibrium	Far from equilibrium
Reversible	Not reversible
Desorption-re-adsorption possible	Adsorbate linked to surface
On-surface diffusion at low coverage	No diffusion once attached
Adsorbate orientation often specific and usually parallel to surface	Adsorbate orientation variable and usually quasi-perpendicular to surface
Partial layer relatively labile	Partial layer stable
Often all-or-nothing layers (cooperativity) with quite large domains	Full layers possible with relatively small domains

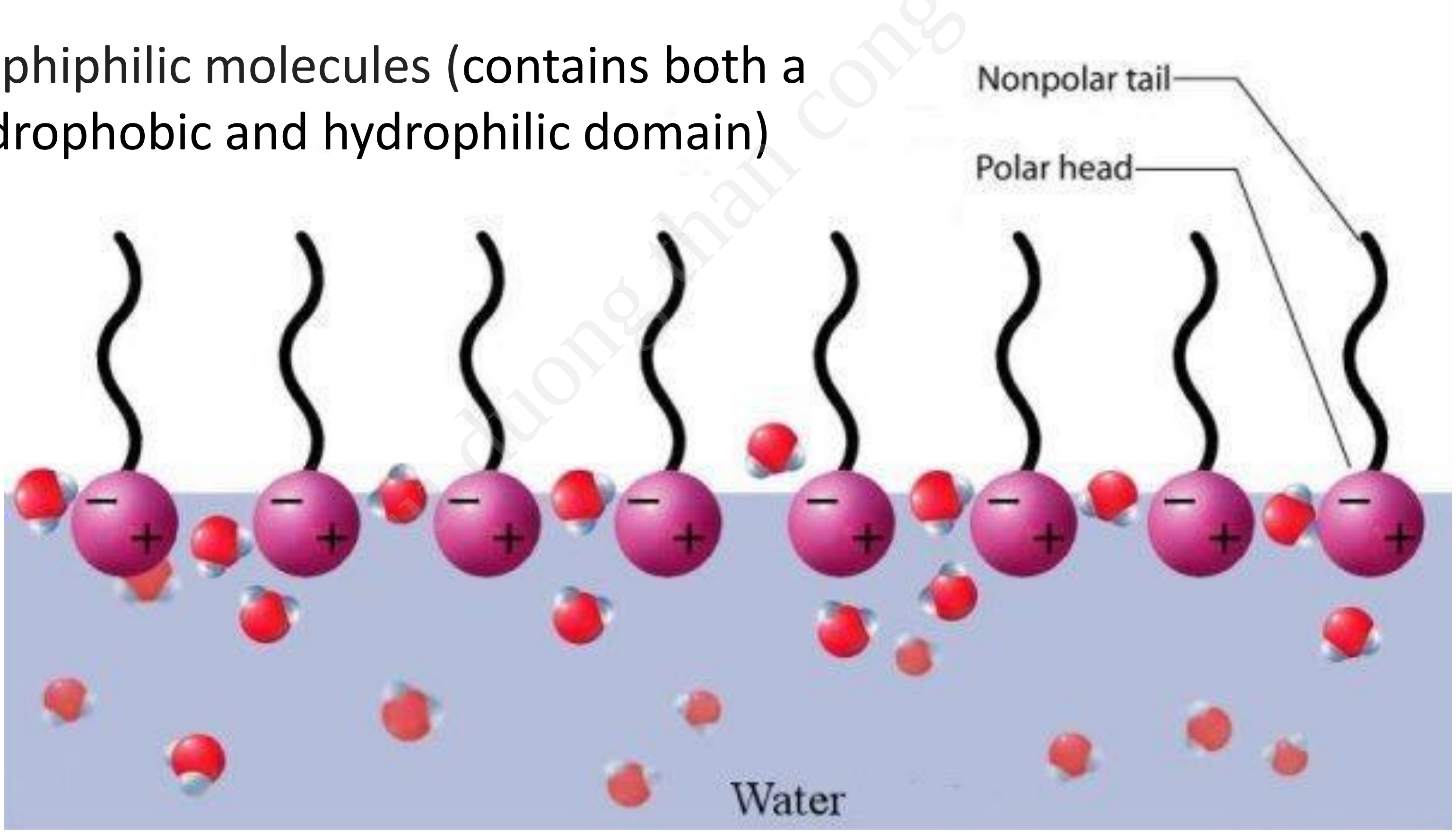


Some general characteristics of physisorbed and chemisorbed monolayers.

Dr. Irving Langmuir (1917): Single water-surface monolayers could be transferred to solid substrates

Dr. Katharine Blodgett (1935): several of these single monolayer films could be stacked on top of one another to make multilayer films

amphiphilic molecules (contains both a hydrophobic and hydrophilic domain)



Langmuir-Blodgett Layers (LB layers)

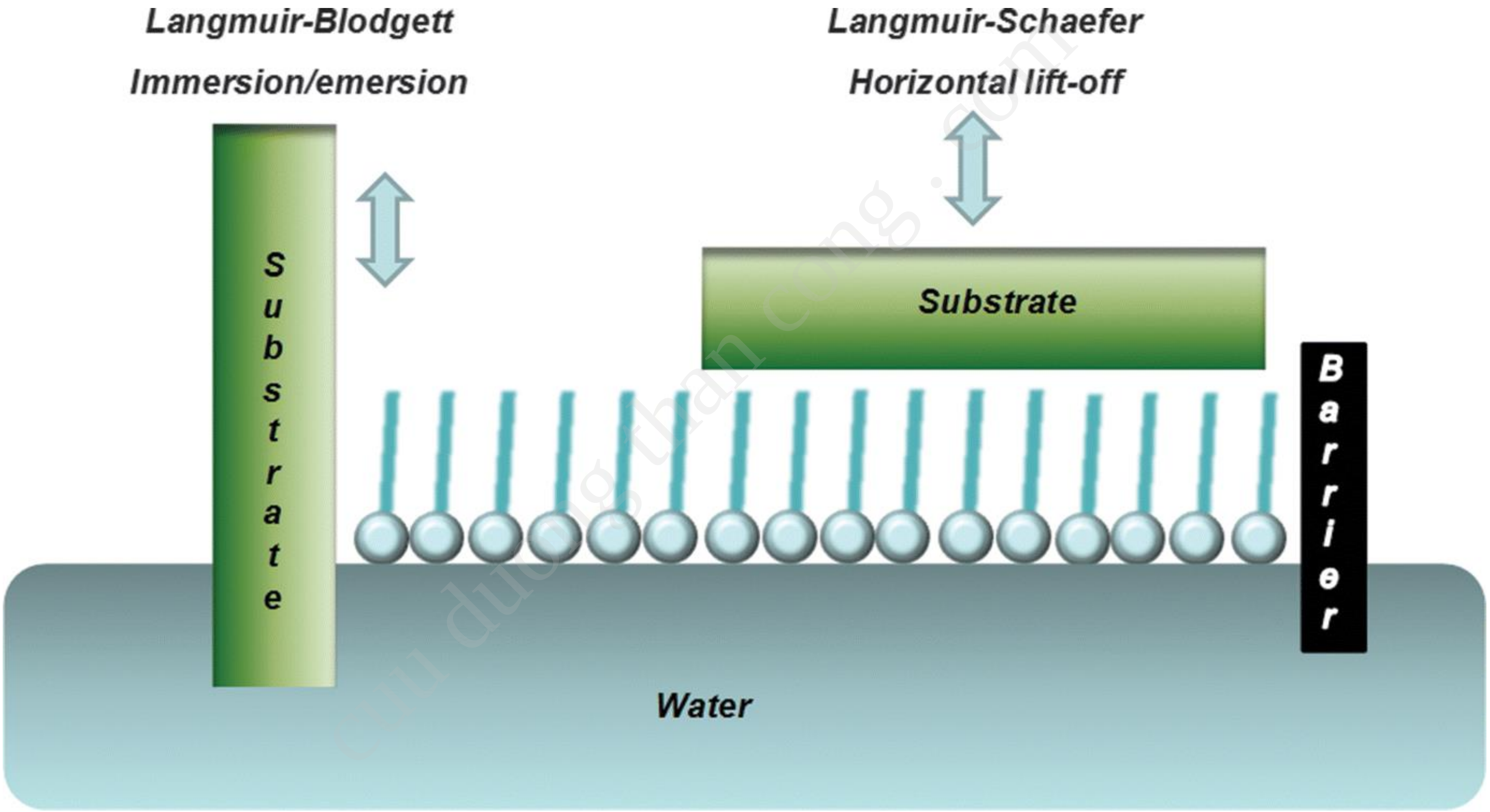
Early in the 20th century, Irving Langmuir and Katherine Blodgett founded the science of Langmuir-Blodgett films by examining the transfer of Langmuir monolayers onto substrates.

Irving Langmuir (1881 – 1957)
American chemist and
physicist, 1932 Nobel Prize in
Chemistry in surface chemistry

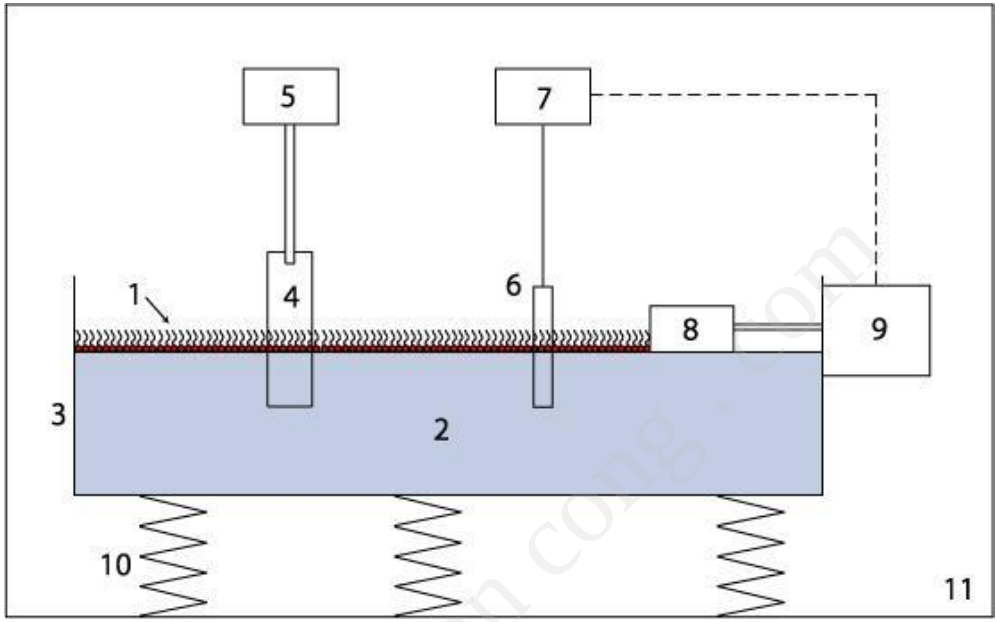
General Electric

Katharine Burr Blodgett (1898 –1979)
American scientific researcher
Film structure and method of preparation
US 2220860 A

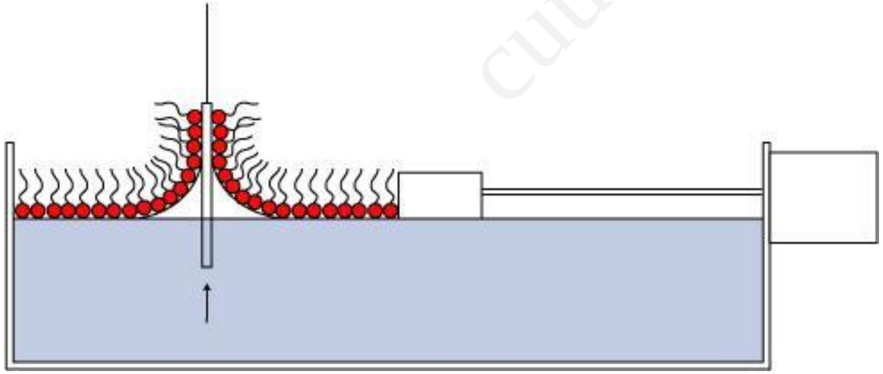
Assembly at the Surface of Liquids



The methods used to transfer Langmuir layers onto solid substrates, by dipping the solid substrate into the trough (the Langmuir–Blodgett method) or by contacting the solid parallel to the air–water interface (Langmuir–Schaefer, or horizontal lift-off method).

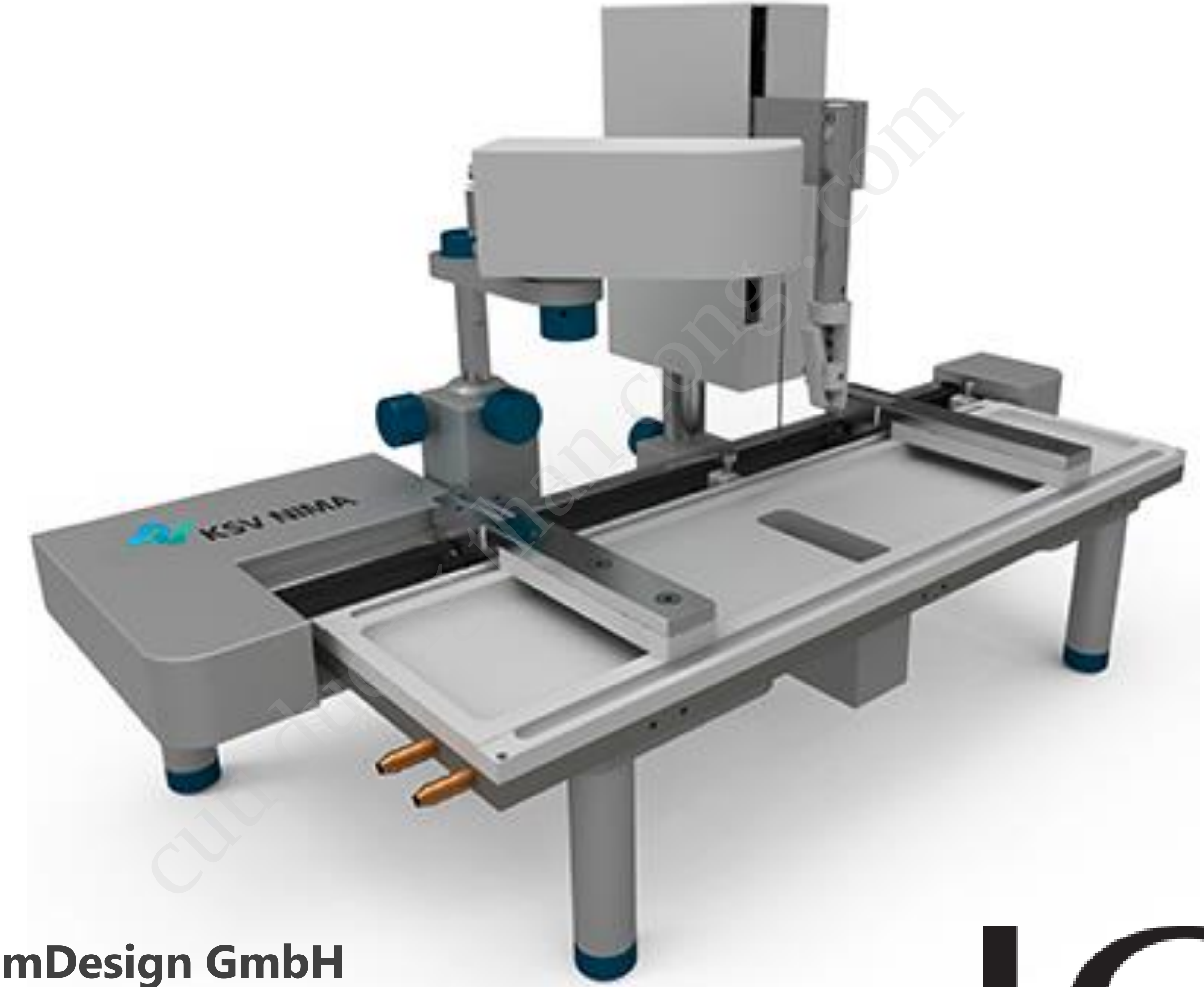


A schematic of a Langmuir Blodgett trough: 1. Amphiphile monolayer 2. Liquid subphase 3. LB Trough 4. Solid substrate 5. Dipping mechanism 6. Wilhelmy Plate 7. Electrobalance 8. Barrier 9. Barrier Mechanism 10. Vibration reduction system 11. Clean room enclosure



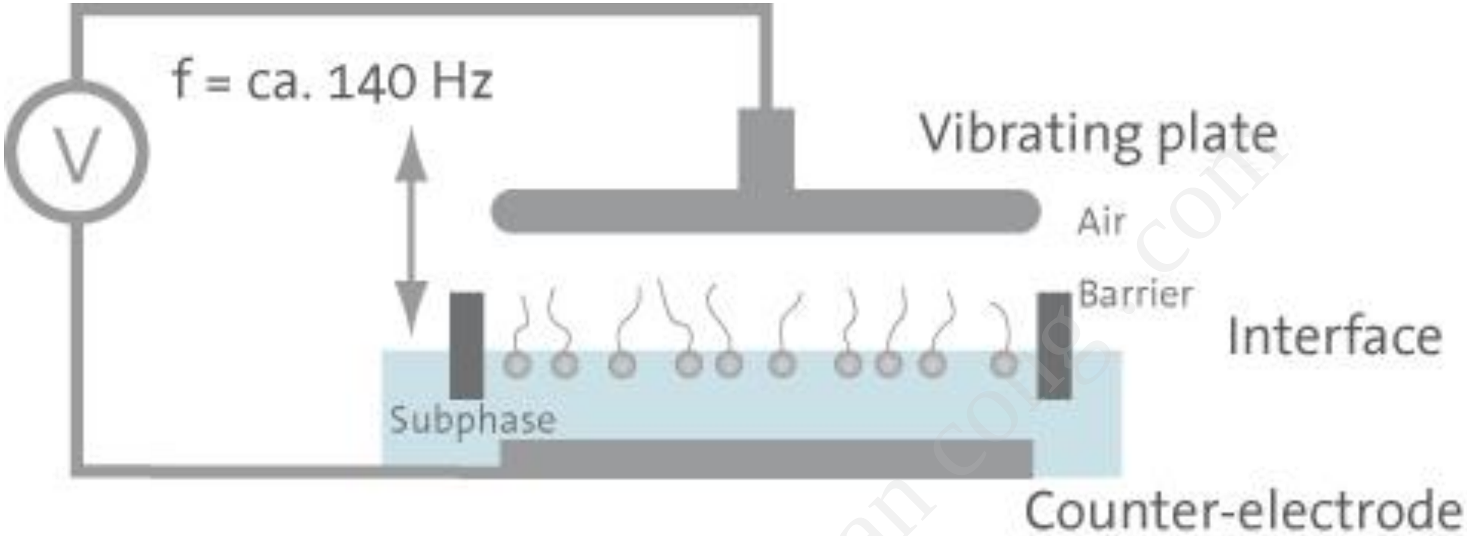
monolayer transfer onto a substrate after film compression. The substrate is moving from bottom to top and is hydrophilically coated since the polar head groups are adhering to the surface

Langmuir and Langmuir-Blodgett troughs



LOT-QuantumDesign GmbH
Im Tiefen See 58
64293 Darmstadt
Germany

LOT QuantumDesign



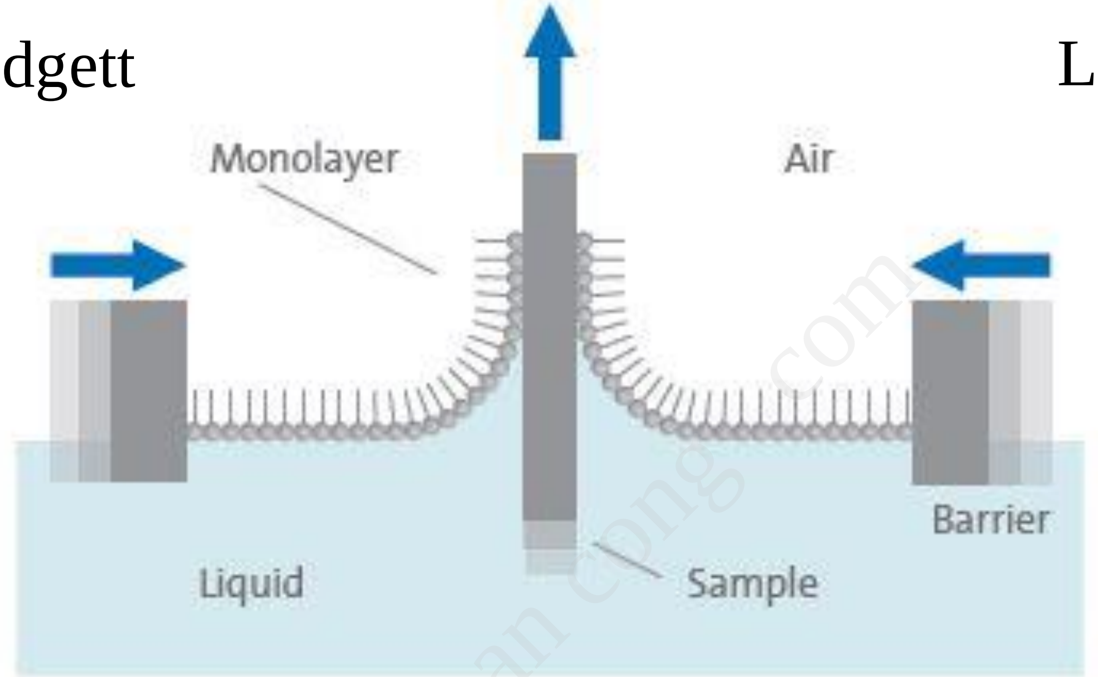
$\Delta V = \mu_n / \varepsilon \cdot \varepsilon_0 \cdot A$

with

ε = subphase permitivity (e.g. here water)
ε_0 = air permitivity
A = area per molecule
μ_n = vertical component of the dipole moment

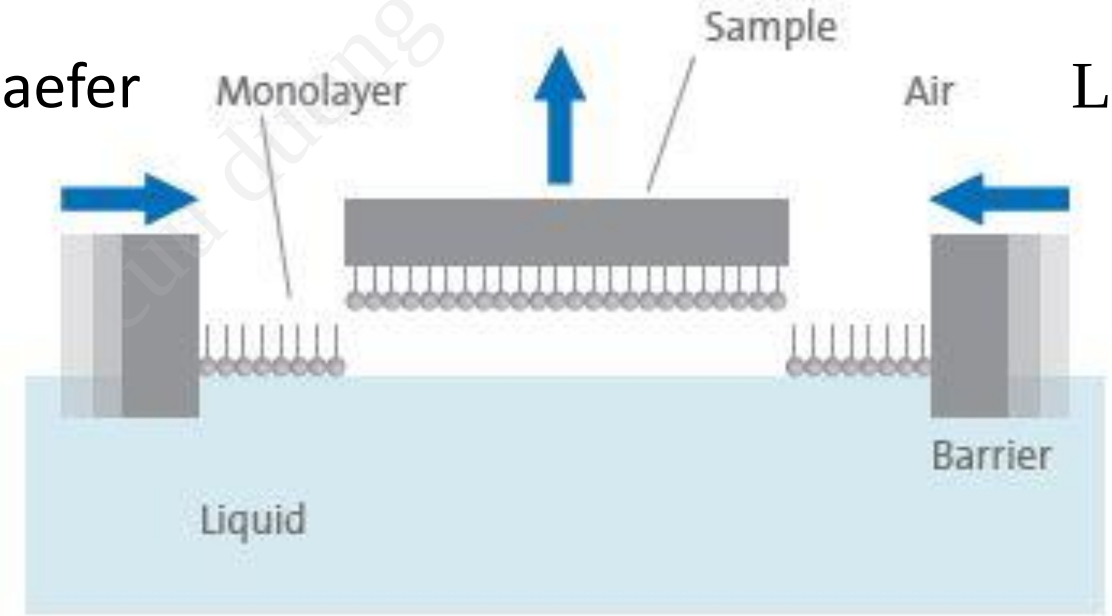
Langmuir–Blodgett method

LB method

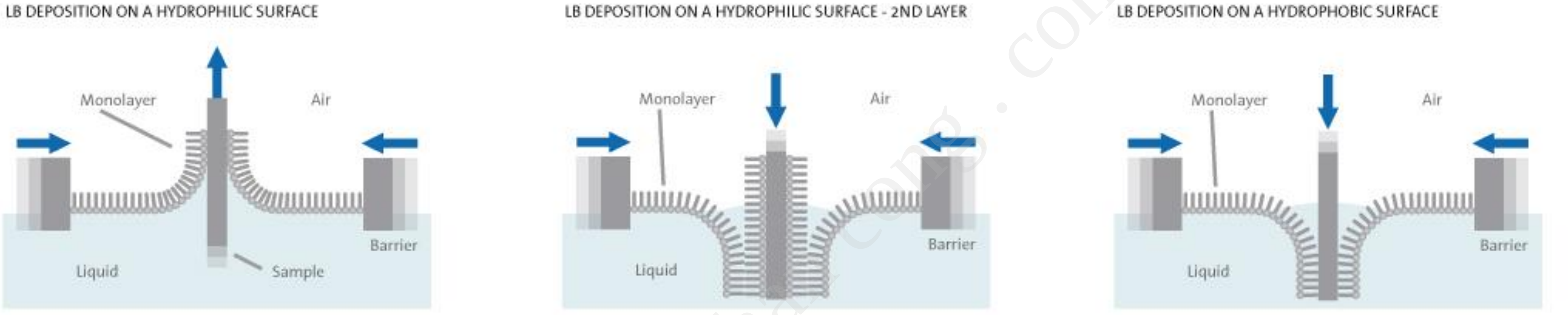


Langmuir–Schaefer method

LS method

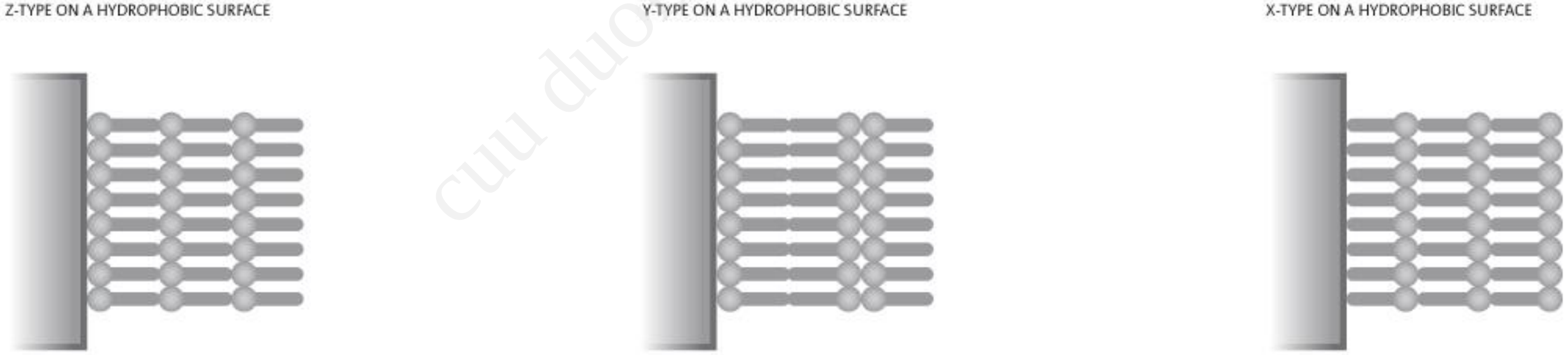


The density, thickness and homogeneity properties of the monolayers are preserved when transferring the Langmuir film. This gives the possibility to make organized multilayer structures with varying layer compositions.


LB DEPOSITION ON A HYDROPHILIC SURFACE

LB DEPOSITION ON A HYDROPHILIC SURFACE - 2ND LAYER

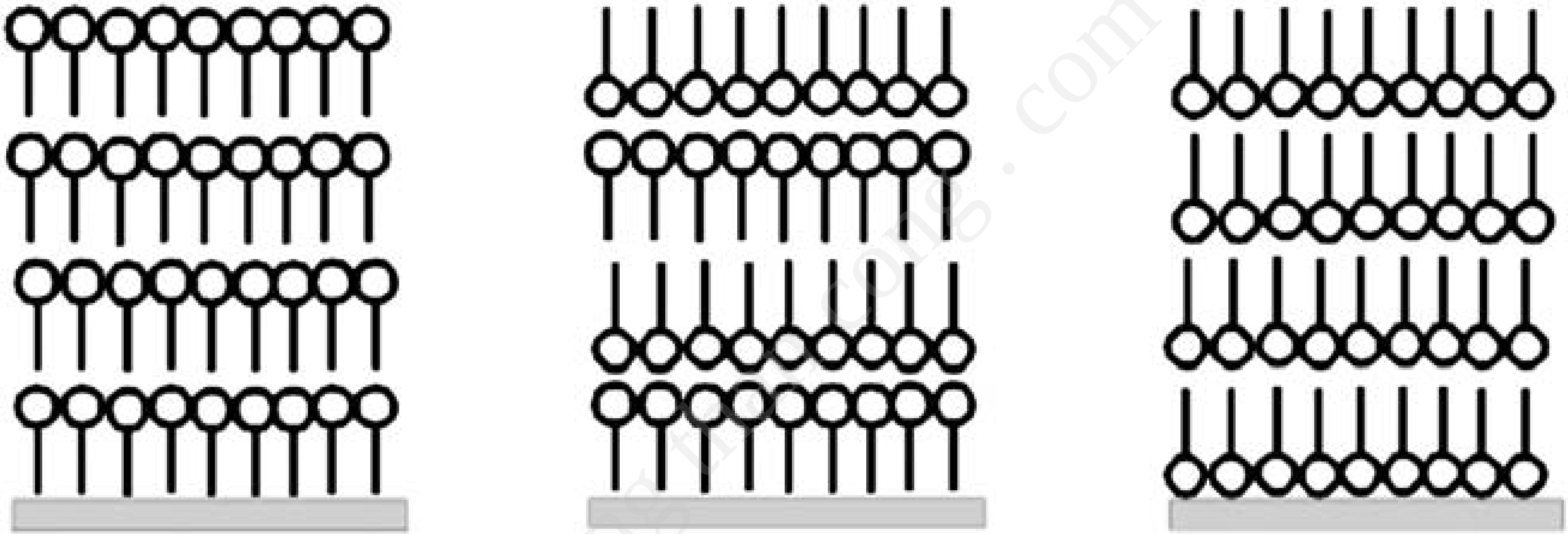
LB DEPOSITION ON A HYDROPHOBIC SURFACE


Z-TYPE ON A HYDROPHOBIC SURFACE

Y-TYPE ON A HYDROPHOBIC SURFACE

X-TYPE ON A HYDROPHOBIC SURFACE

Various LB deposition possibilities on hydrophobic and hydrophilic substrates.

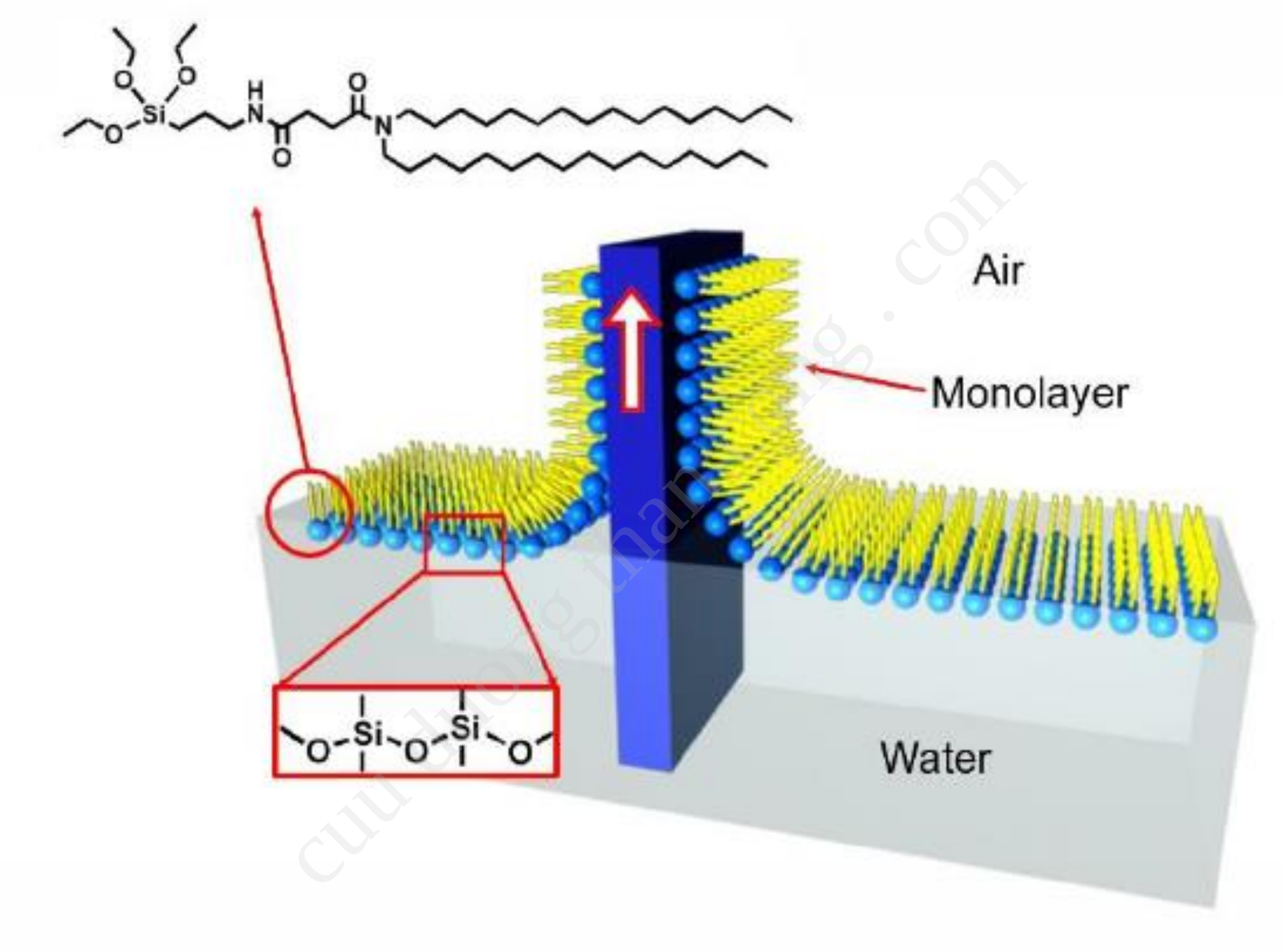


X-type

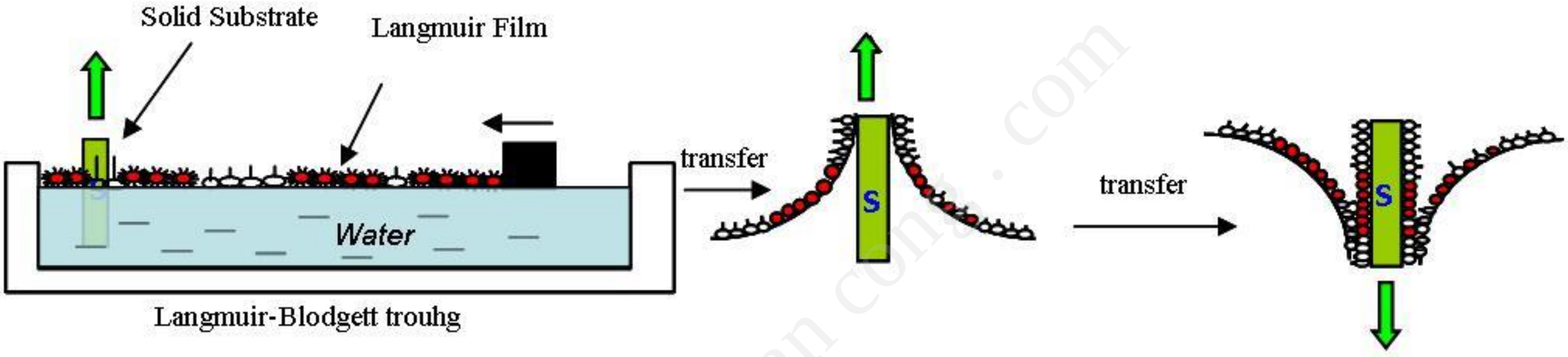
Y-type

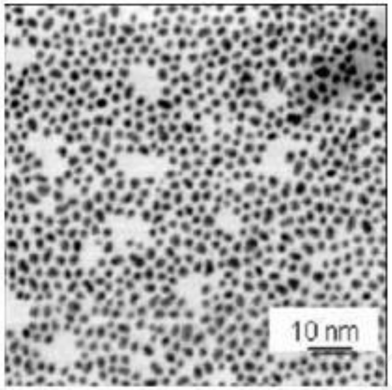
Z-type

Deposition types of LB multilayers

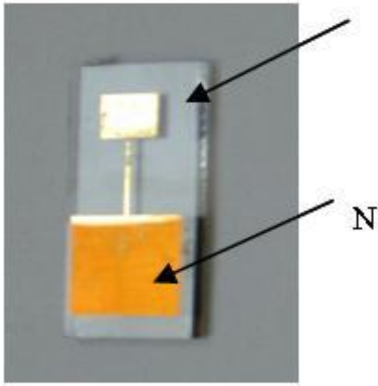


Langmuir-Blodgett film of silica-layer-baring monolayer at the air-water interface

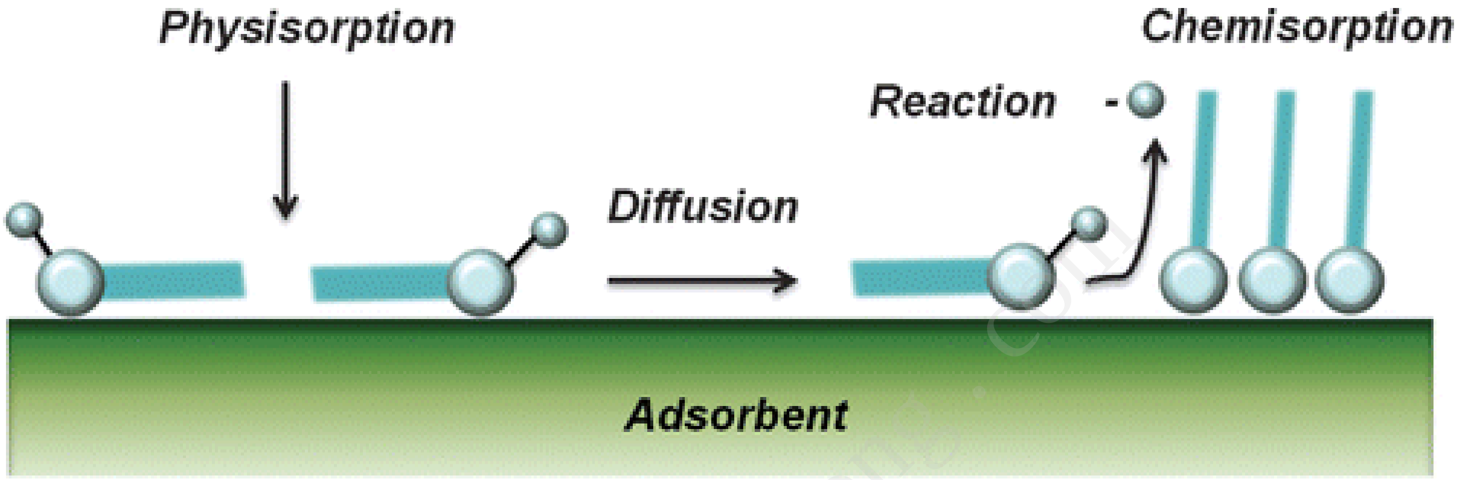




Nanoparticules
Monolayer



Langmuir-Blodgett films based on crown modified platinum nanoparticles



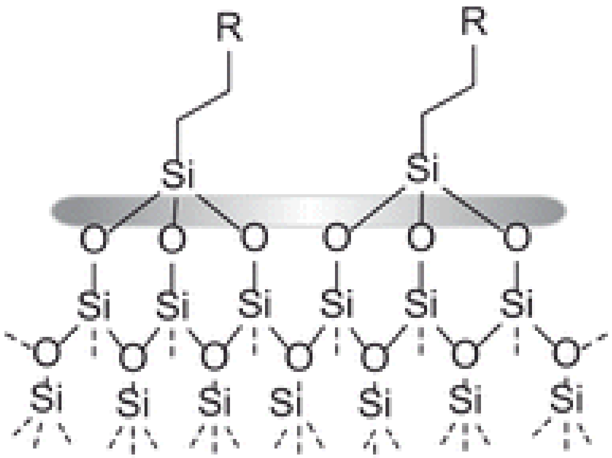
The processes leading to chemisorption.

- The first step is usually considered to be physisorption where the molecule adheres to the surface but is able to diffuse in the plane to a degree determined by the substrate temperature.

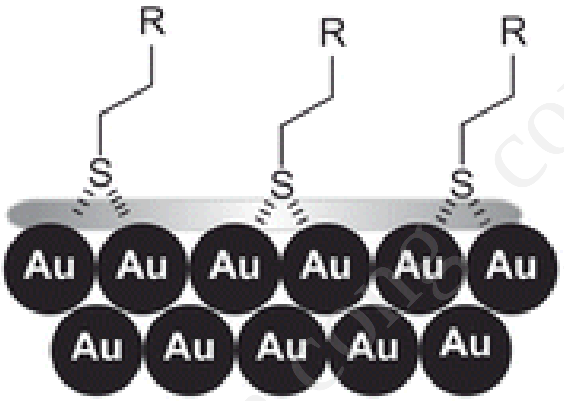
- The most frequent cases of chemisorbed molecules are those involving the bonding of organic molecules to metals, inorganic semiconductors or their oxides, and they are the basis of the development of a variety of self-assembled monolayers.

- The bonding is typically fully covalent, between oxygen or carbon atoms of the adsorbate and the surface atoms most commonly, or is essentially covalent through coordination between heteroatoms and inorganic surface atoms.

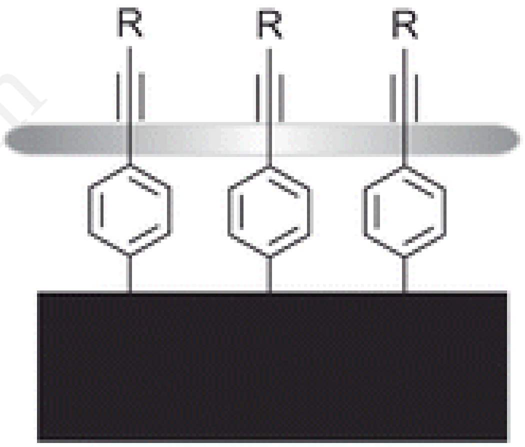
Layers Anchored with Covalent Bonds



Silicon oxide



Gold

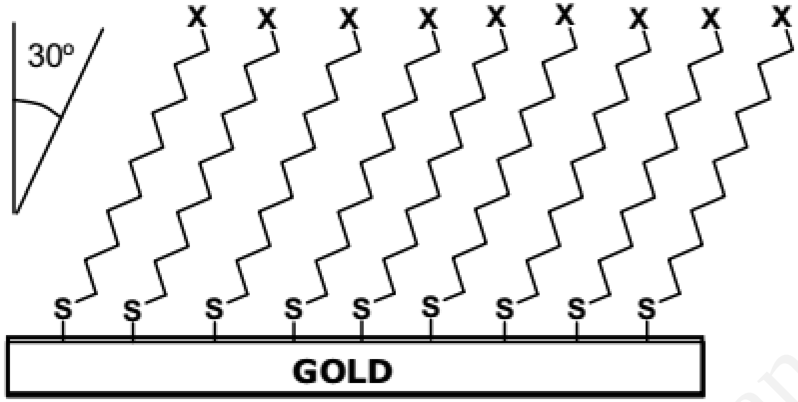


Organic or inorganic substrate

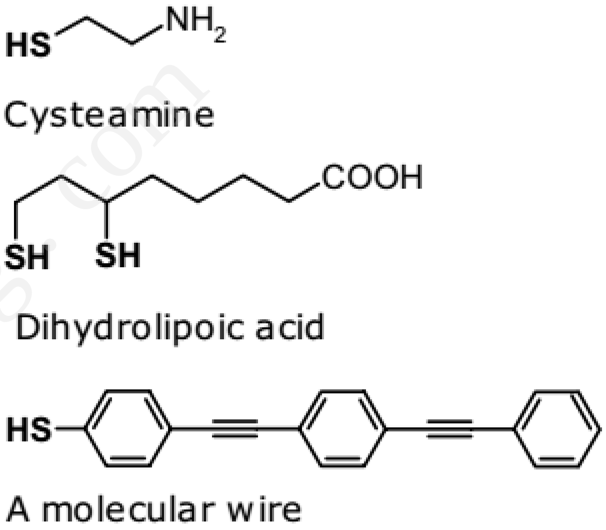
- Chemisorbed monolayers of organic compounds to the surfaces of oxides (silicon oxide), metals (for thiolates on gold) and organic surfaces where the term “grafting” is used frequently. The grey shaded region indicates the covalent bonds that are created during chemisorption.

- Electrochemical reduction of aromatic diazonium reagents leading a covalently bonded layer, anchored by a carbon-carbon bond. This scheme can also be applied to modify many other surfaces, including metals and semiconductors.

Metal Supports



The conformation of an alkanethiol layer at a gold surface (X functional group)



Common thiol reagents for functionalization of a gold surface by sulfur chemisorption.

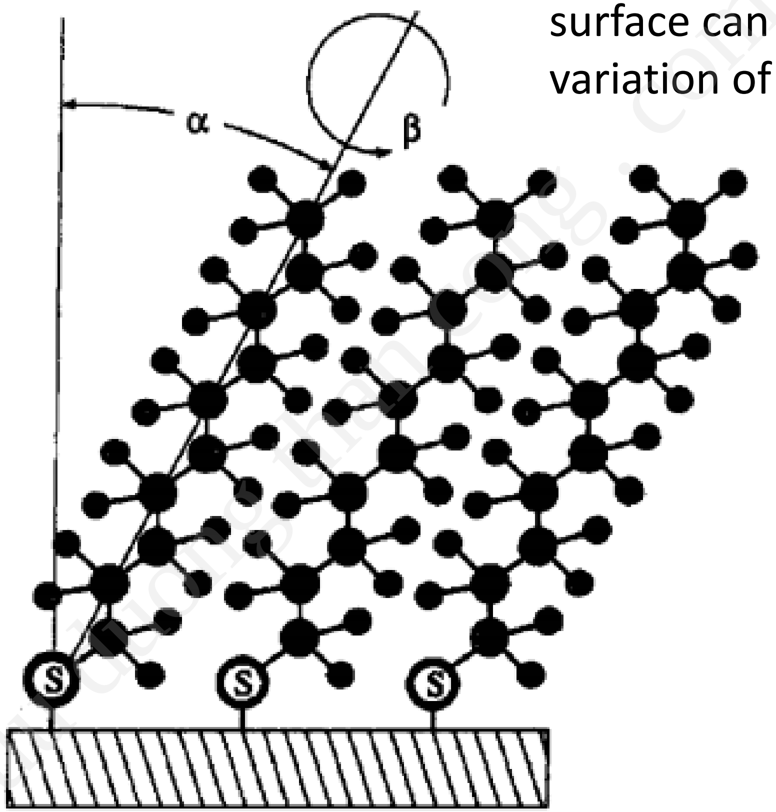
1/ Treatment of the metal surface to contain a high density of surface groups such as oxides or hydroxyl groups that will serve to form a bond with the modifying layer

2/ Direct reaction of the metal surface with a chemical agent (diazonium salts).

Self-assembled monolayer (SAM)

The chemistry and function of the surface can be controlled simply by variation of the tail group

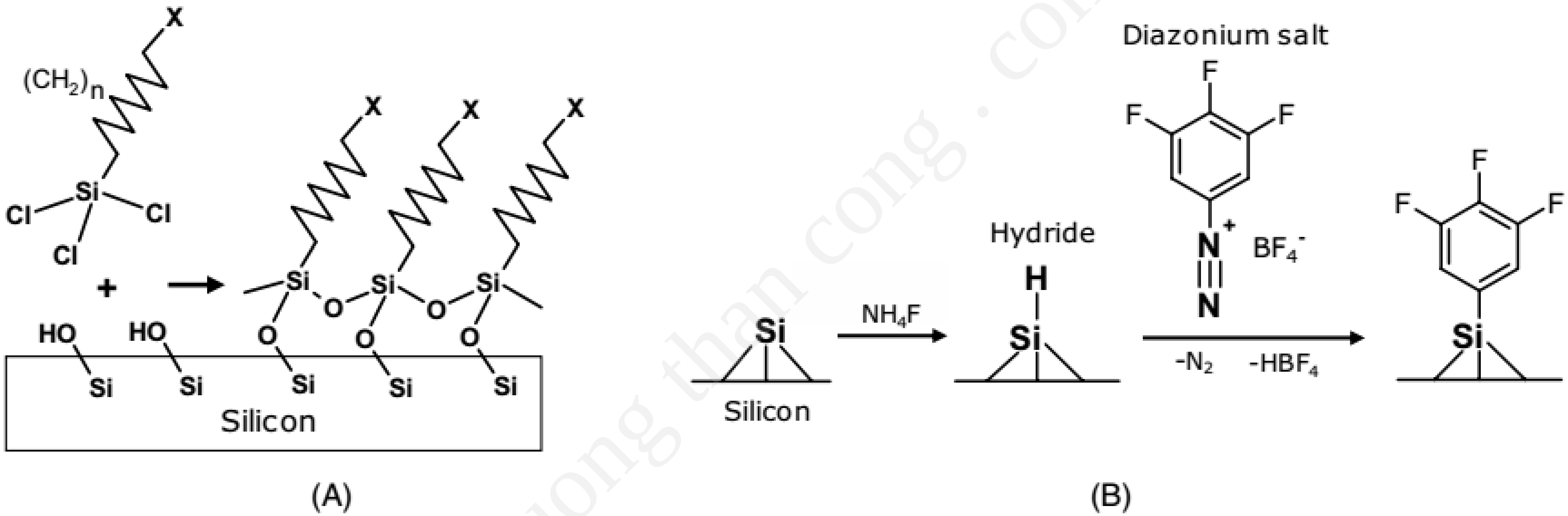
Noble metals
Semiconductors
Metal oxides



$7.7. 10^{-10}$ mol/cm^2

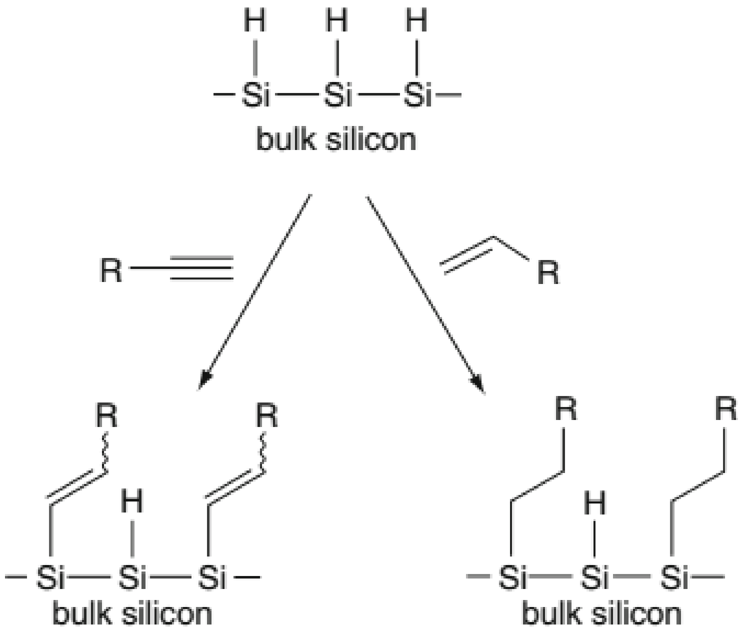
Schematic of a SAM composed of alkanethiolates chemisorbed at Au. The tilt (α) and twist (β) angles are shown here to define the precise orientation of the molecules on the surface

Semiconductor Supports

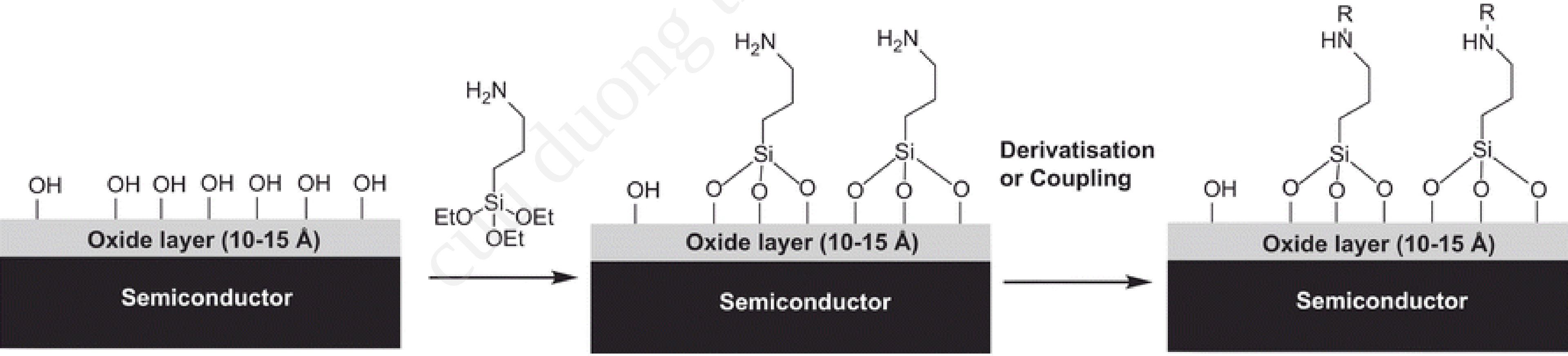


(a) Modification of silicon surface by trichlorosilanes. X can be an amino group that is suitable for subsequent crosslinking.

(b) Silicon surface modification by self-assembly of diazonium salts.



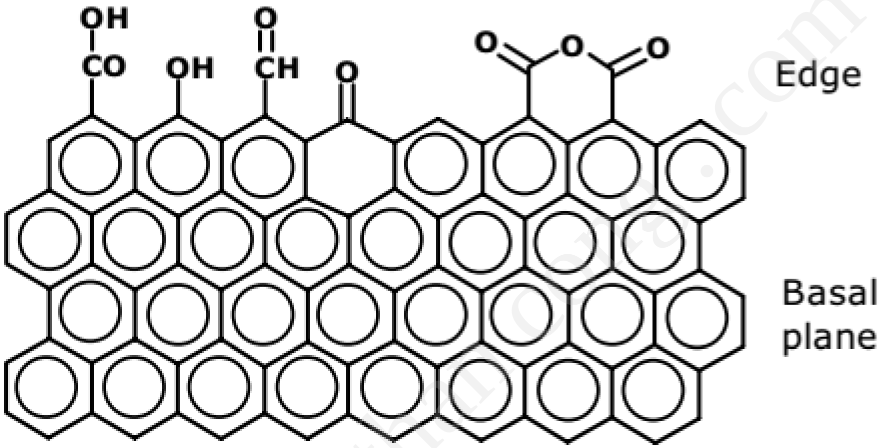
Covalent modification of Si: using either an alkyne (left) or alkene (right), a covalent bond results between the Si surface atoms and the modifying layer. These reactions can be activated with heat, light, or an added radical initiator

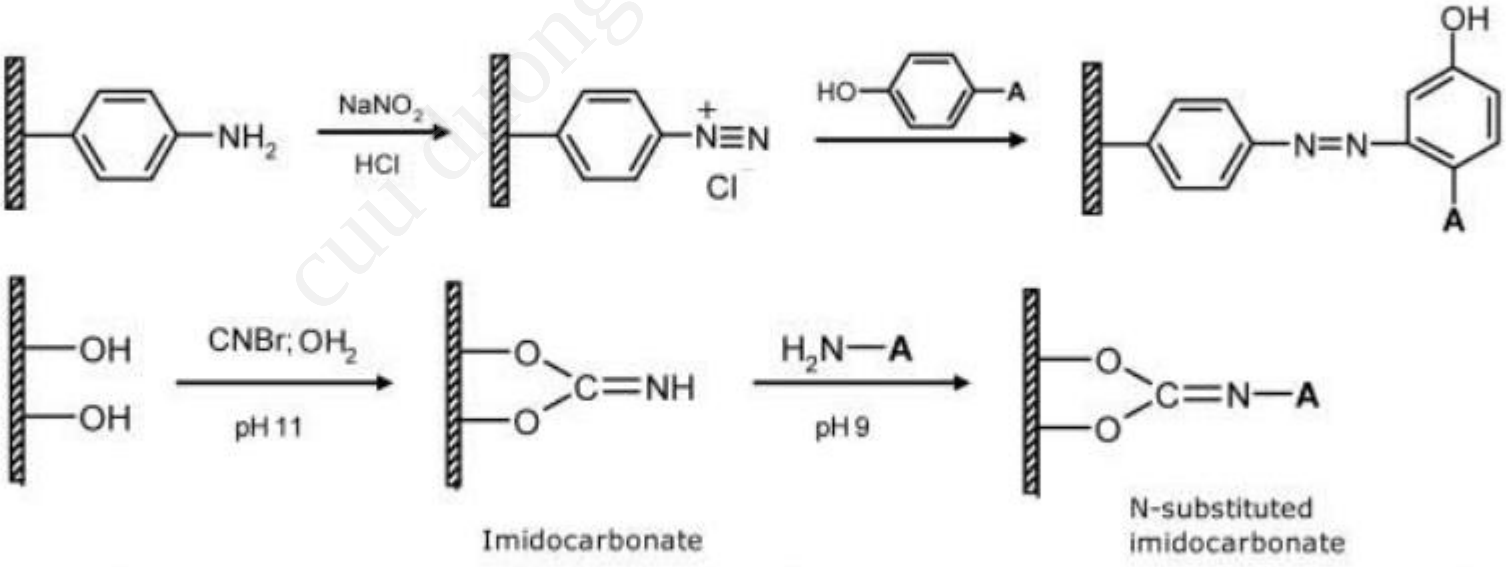


The chemical steps leading to the functionalisation of semiconductor surfaces by chemisorption of a siloxane followed by covalent modification.

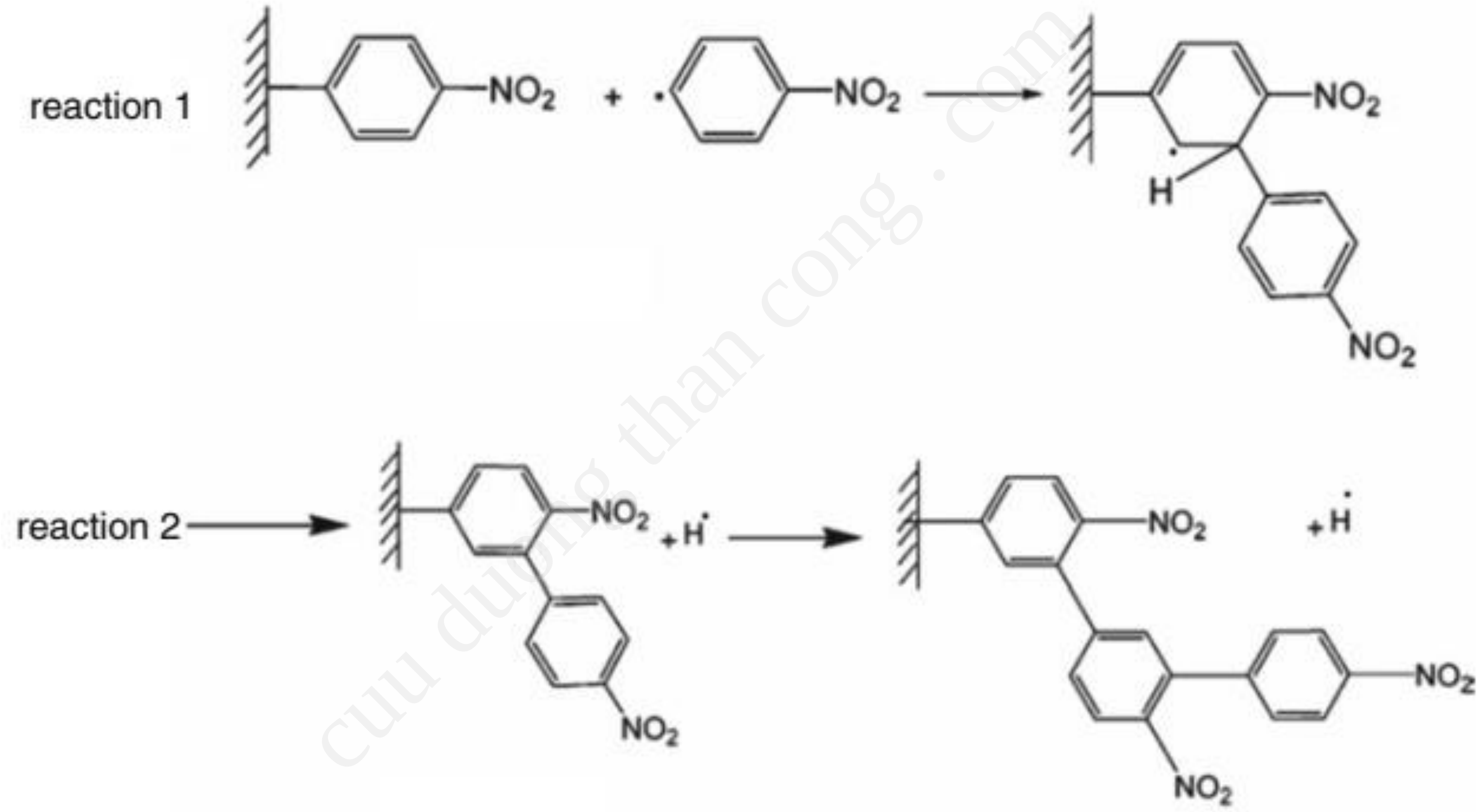
Carbon Material Supports

Graphite structure





Multilayer Surface Modification



1 nm to >100 nm

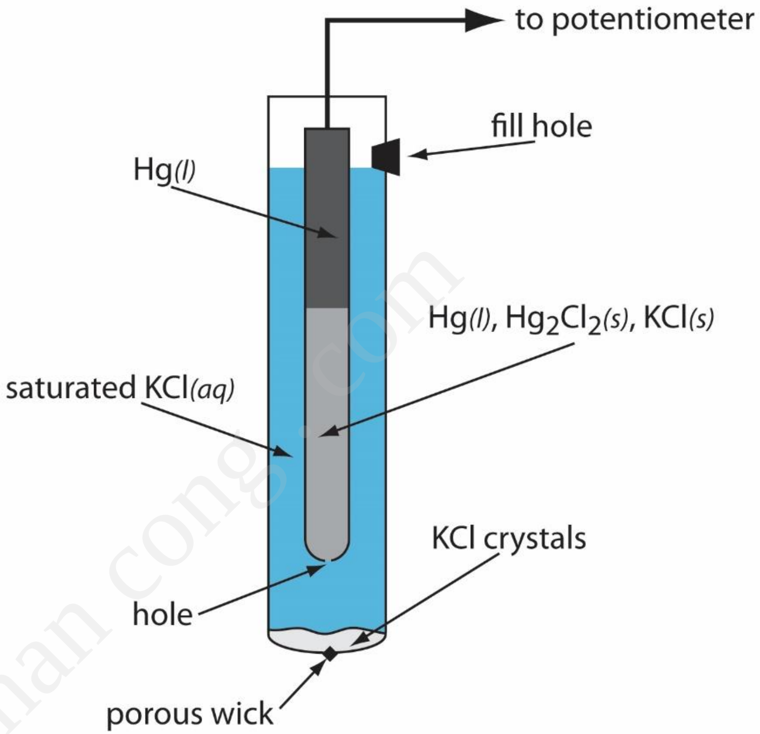
Electropolymerization

Electrochemical cell


Purge tube
Reference electrode
Working electrode
Counter electrode
Teflon cap for SVC-2
Adaptor
012668


012669


GAMRY
Ag/AgCl


to potentiometer
fill hole
Hg(l)
Hg(l), Hg_2Cl_2(s), KCl(s)
saturated KCl(aq)
KCl crystals
hole
porous wick

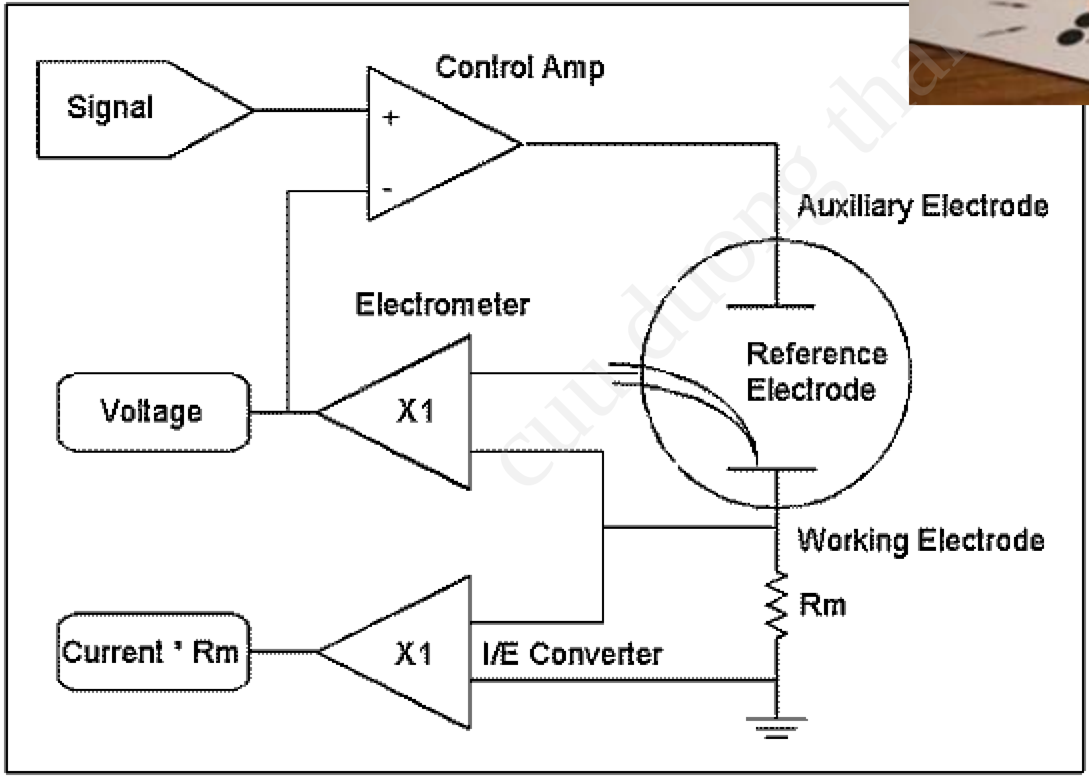
Platinum Electrodes

CE

Pt Plate 6x8 mm, Glass body:
Shaft: 12 mm Ø x 110 mm L,
Cable: 1M included

Pt Wire 1mm Ø, Glass body:
Shaft: 12 mm Ø x 110 mm L,
Cable: 1M included

Platinum Gauze Electrode	Platinum Gauze Electrode & Gold Gauze Electrode	
 ● **Part No. : PGE** • for bulk electrolysis experiment • 50mmH * 39mm dia. * 50mmL wire	 ● **Part No. : 002250** • Pt gauze electrode • 80mesh, 35*25mm	 ● **Part No. : 002251** • Au gauze electrode • 100mesh, 35*25mm



Potentiostat
Galvanostat

Single Channel Potentiostat/Galvanostat, WPG Series

Standard Type, WPG100

High Power Type, WPG100HP

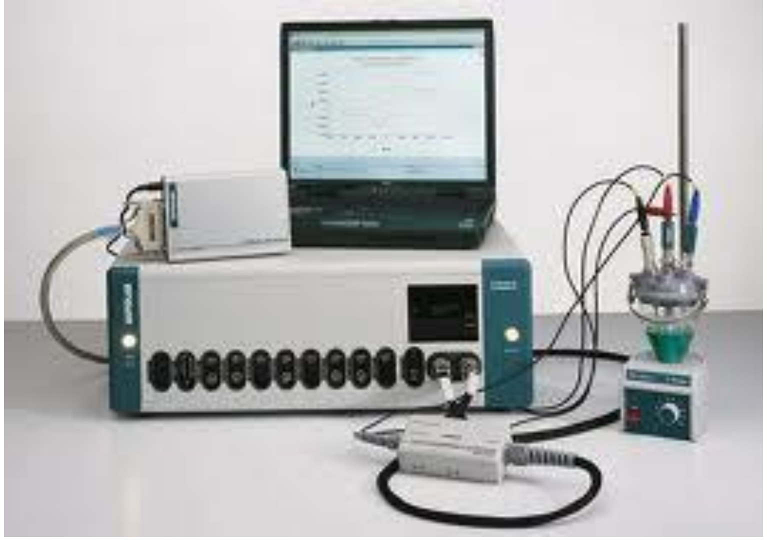
Multi-Channel Potentiostat/Galvanostat, WMPG Series

Standard Type, WMPG1000S

Low Current Type, WMPG1000L

High Power Type, WMPG1000HP

Mid Power Type, WMPG1000M2




AUTOLAB
249
249

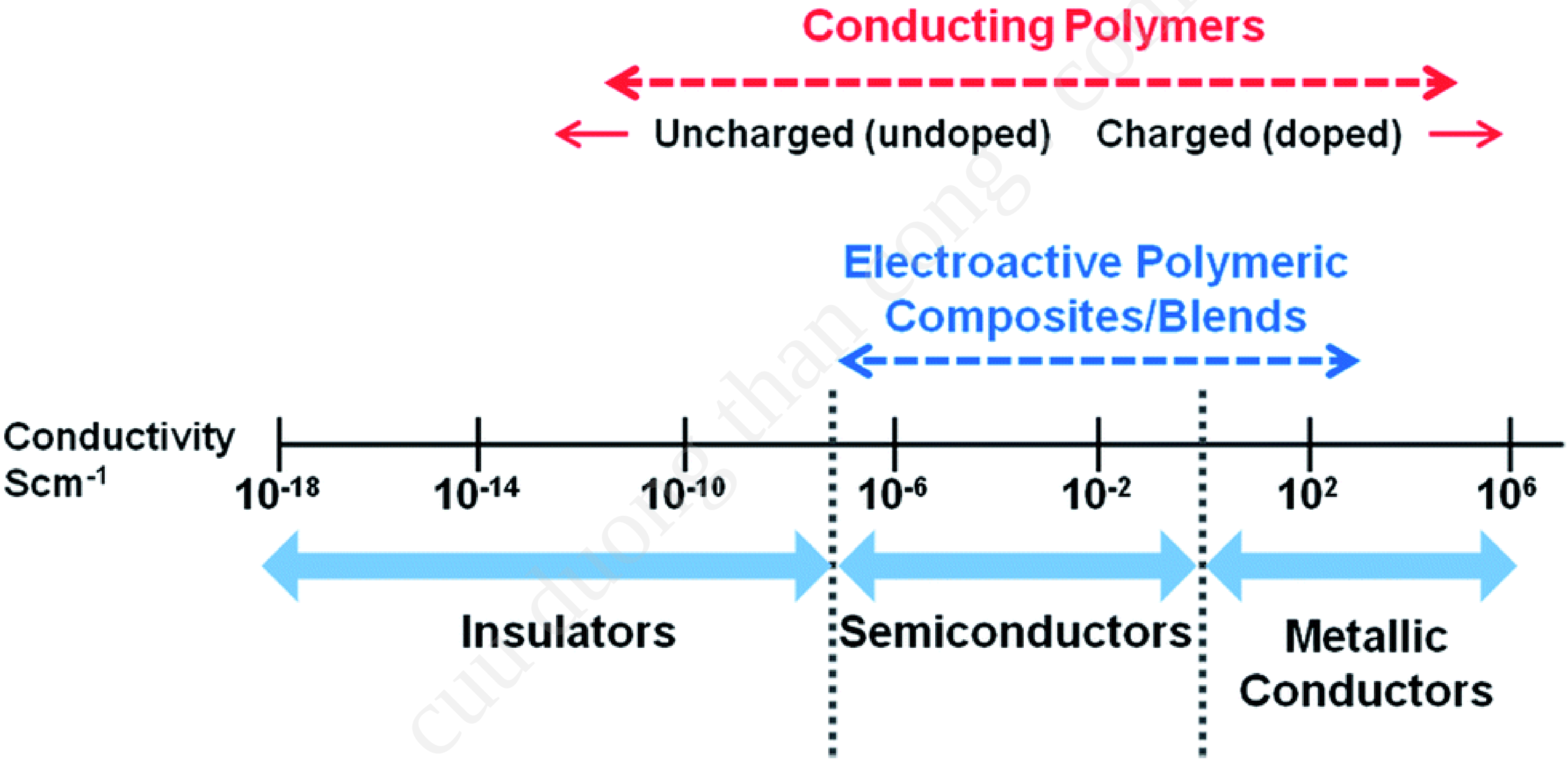

AUTOLAB
DELL


SP-200


SP-150


VSP-300


Test Box-1
VMP3
Fraunhofer
ENAS



Conducting Polymers

Uncharged (undoped) Charged (doped)

Electroactive Polymeric Composites/Blends

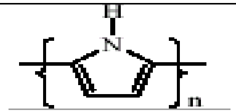
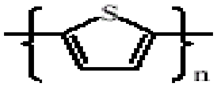
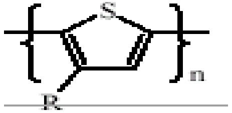
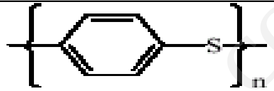
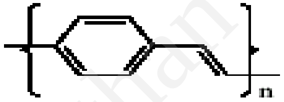
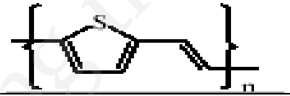
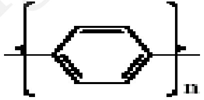
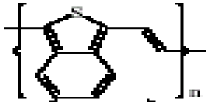
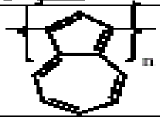
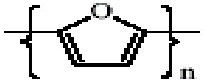
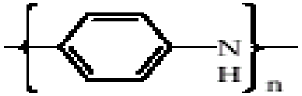
Conductivity Scm^{-1}

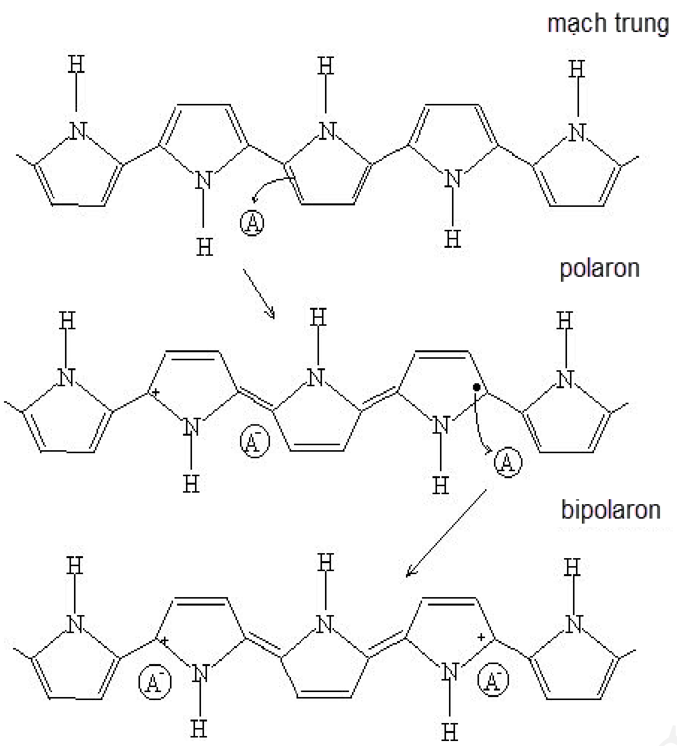
10^{-18} 10^{-14} 10^{-10} 10^{-6} 10^{-2} 10^{2} 10^{6}

Insulators

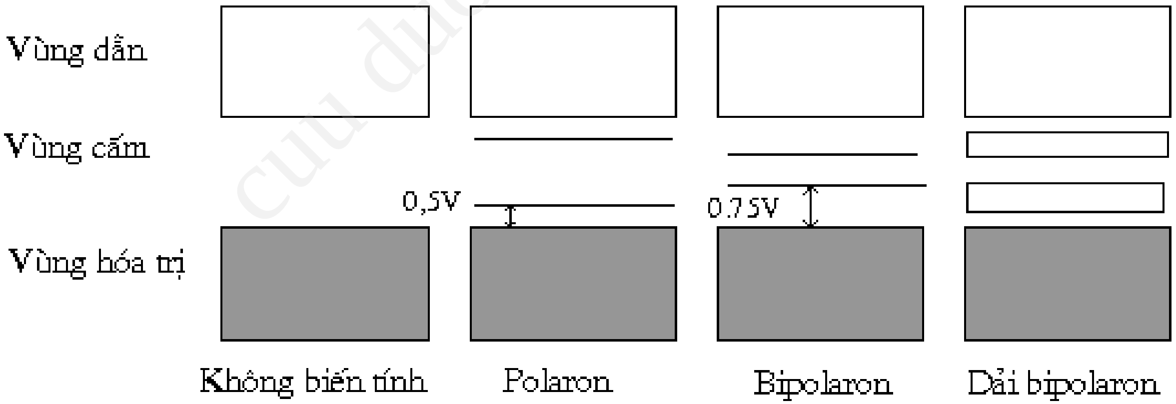
Semiconductors

Metallic Conductors

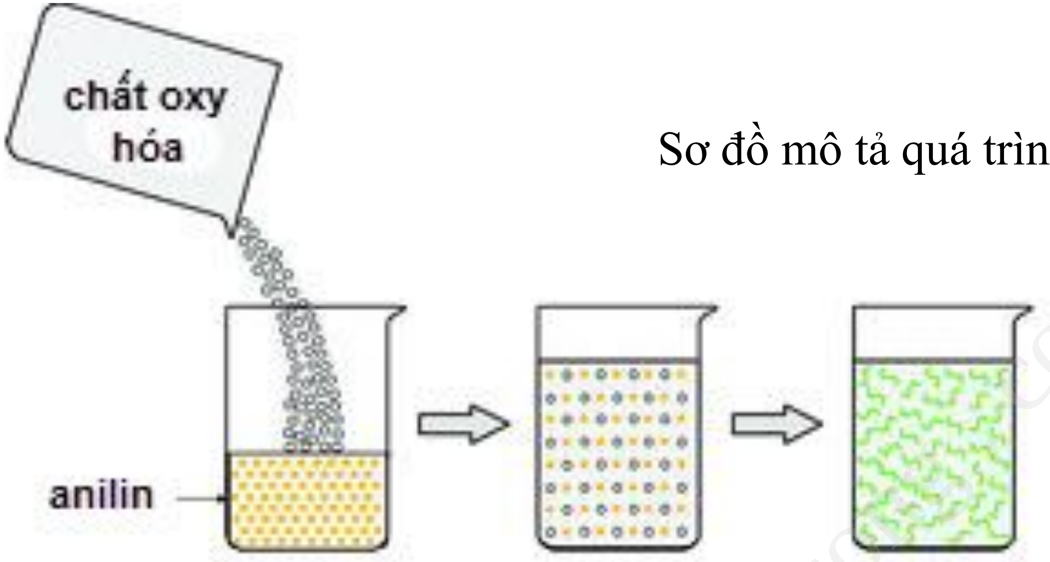
Polyme	Cấu trúc hóa học	Vật liệu pha tạp	Độ dẫn ($S\ cm^{-1}$)
Polyacetylen	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5	10.000
Polypyrrol (PPy)		BF_4^-, ClO_4^-	500-7.500
Polythiophen		BF_4^-, ClO_4^-	100
Poly(3-alkylthiophen)		BF_4^-, ClO_4^-	1.000-10.000
Polyphenylenesulfid		AsF_5	500
Polyphylenevinylen		AsF_5	10.000
Polythienylenevinylen		AsF_5	2.700
Polyphenylen		AsF_5, Li, Na	1.000
Polyisothianaphthen		BF_4^-, ClO_4^-	50
Polyazulen		BF_4^-, ClO_4^-	1
Polyfuran		BF_4^-, ClO_4^-	100
Polyanilin (PANi)		HCl	200



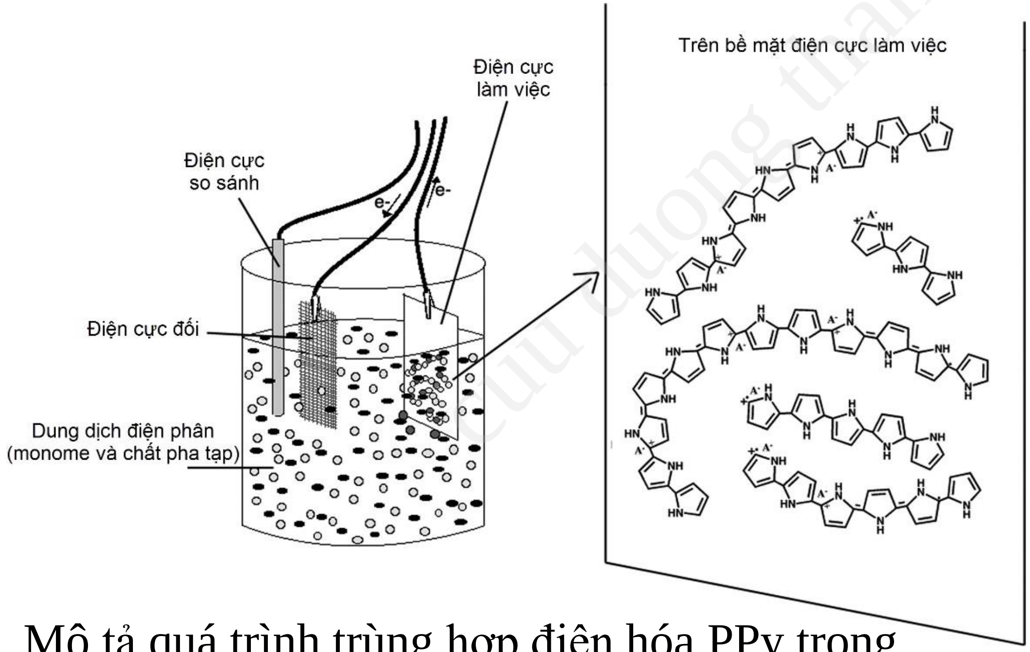
Trạng thái polaron và bipolaron của PPy



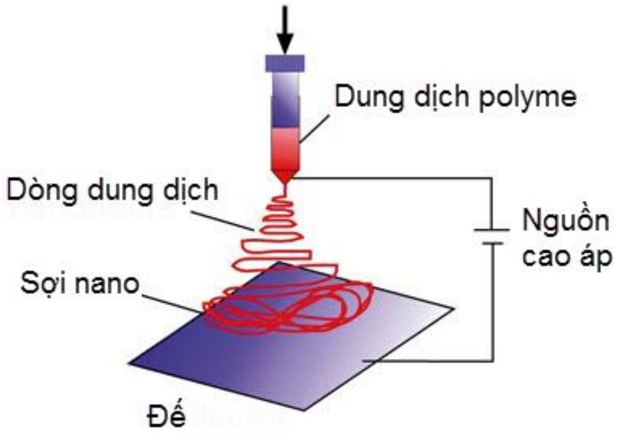
Sơ đồ vùng năng lượng của polyme dẫn điện trước và sau khi bị oxy hóa



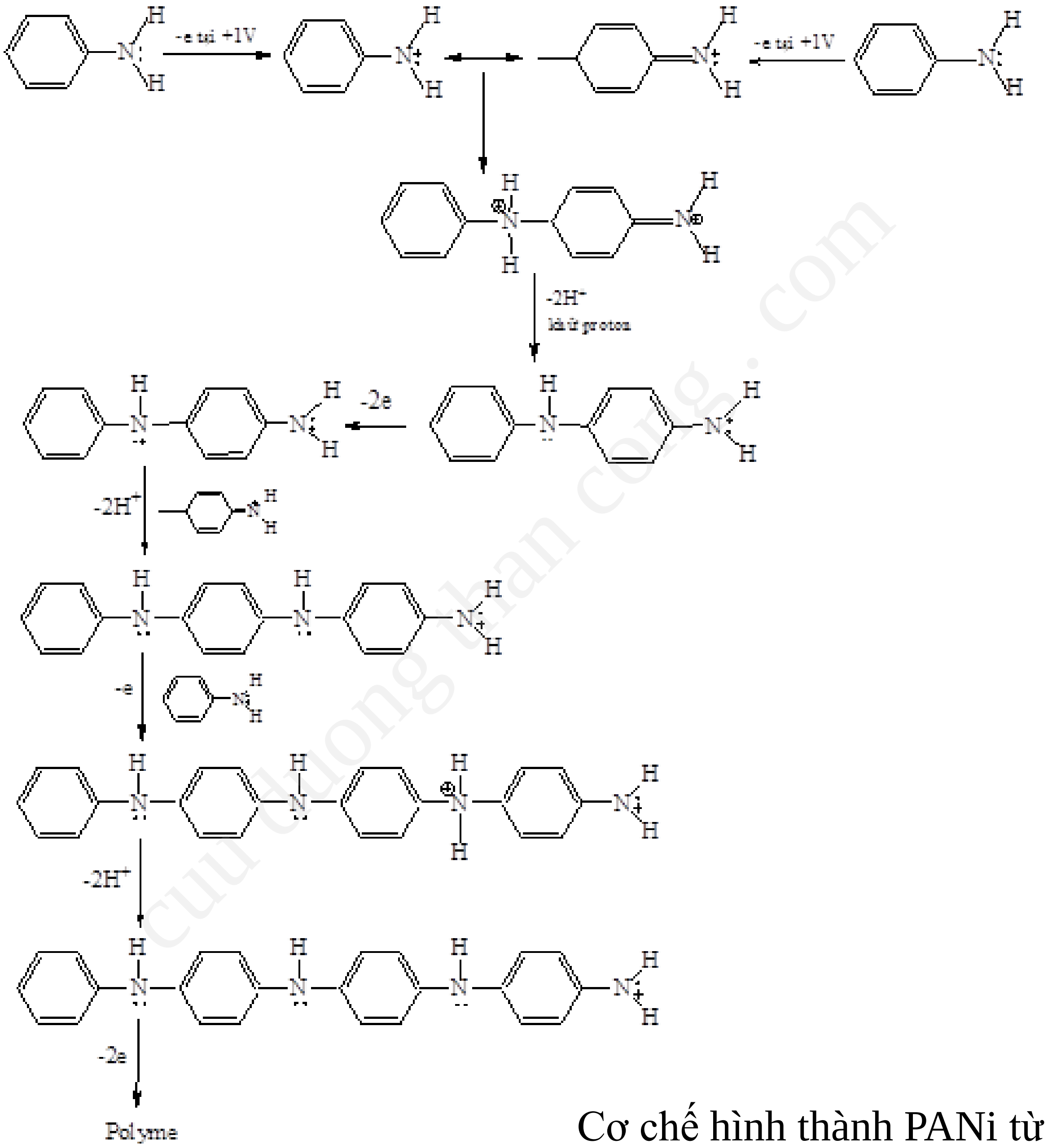
Sơ đồ mô tả quá trình tổng hợp hóa học PANi



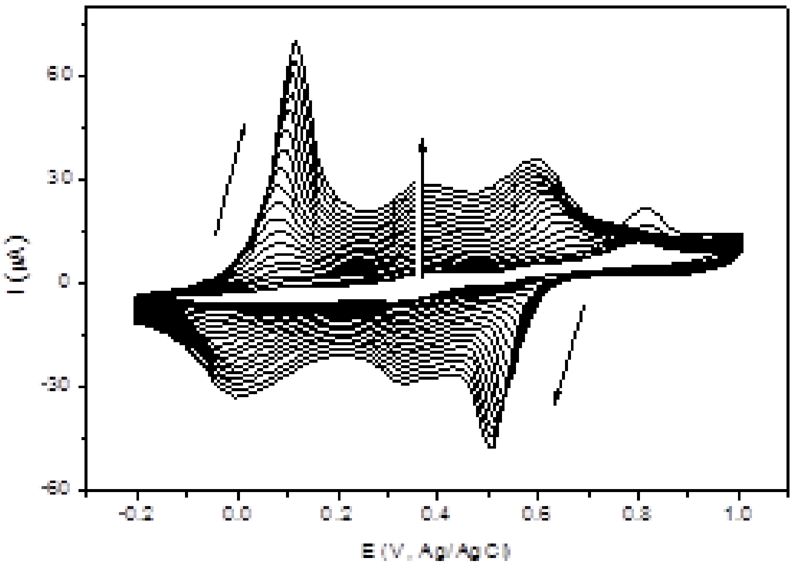
Mô tả quá trình trùng hợp điện hóa PPy trong hệ ba điện cực

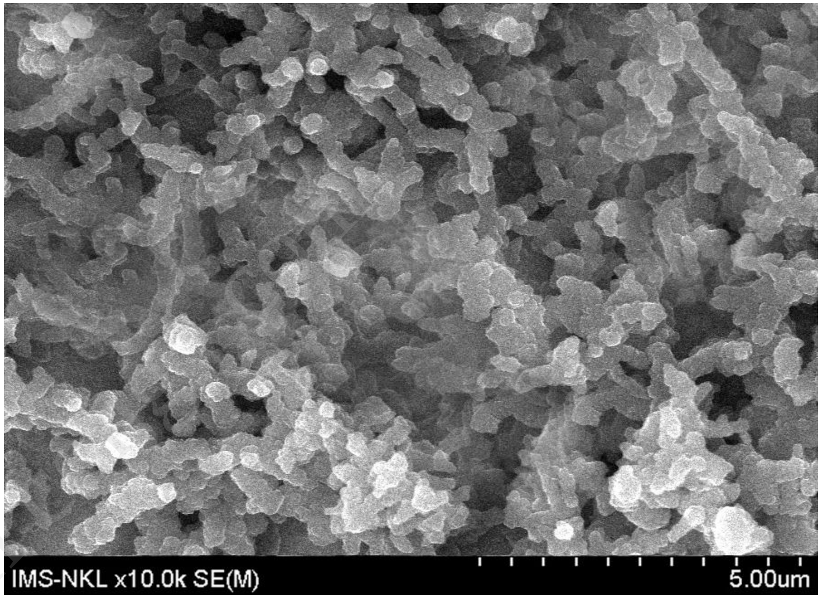


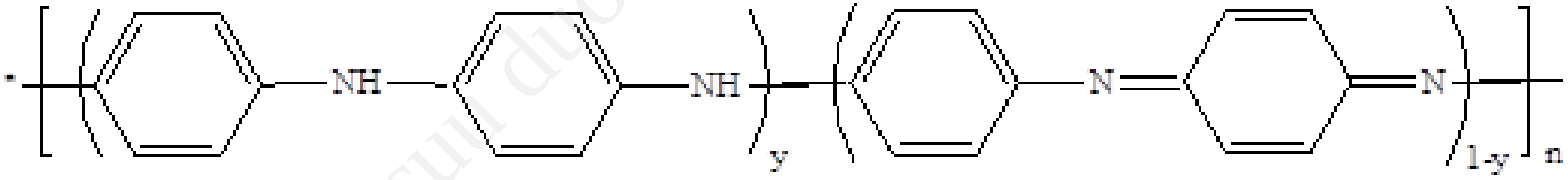
Sơ đồ hệ phun tĩnh điện



Cơ chế hình thành PANi từ Ani bằng phương pháp điện hóa



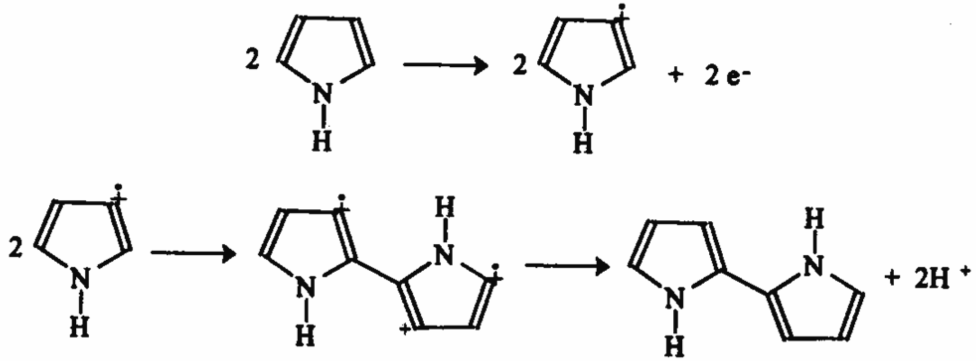




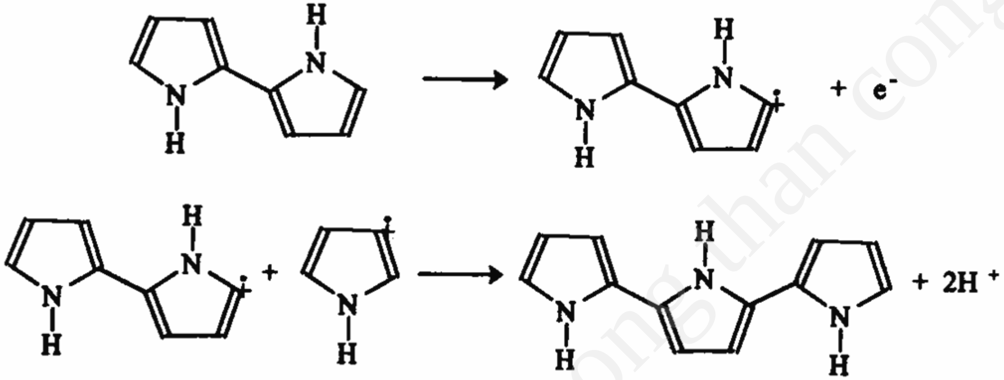
Công thức tổng quát của PANi

(Khi y = 1: Leucoemeraldin; y = 0,5: Emeraldin; y = 0: Pernigranilin)

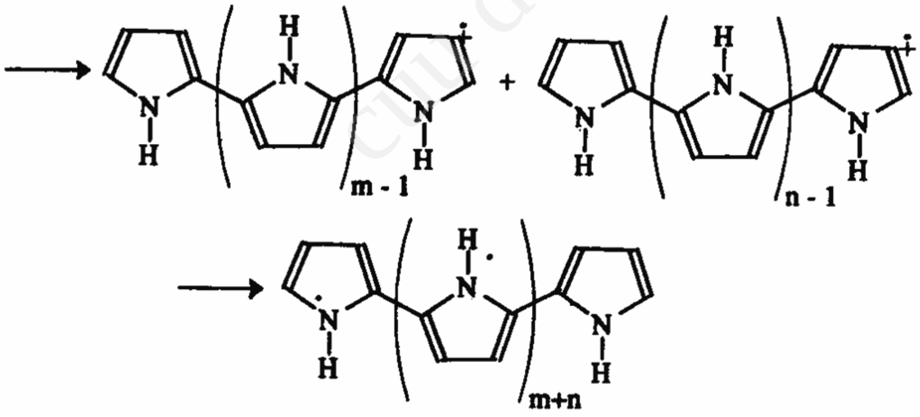
KHƠI MÀO



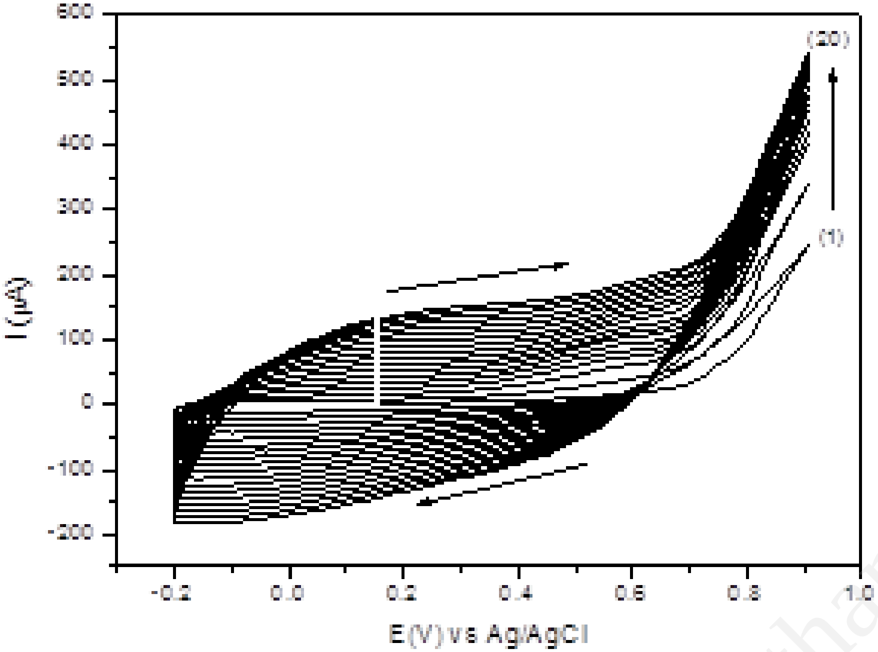
PHÁT TRIỂN MẠCH

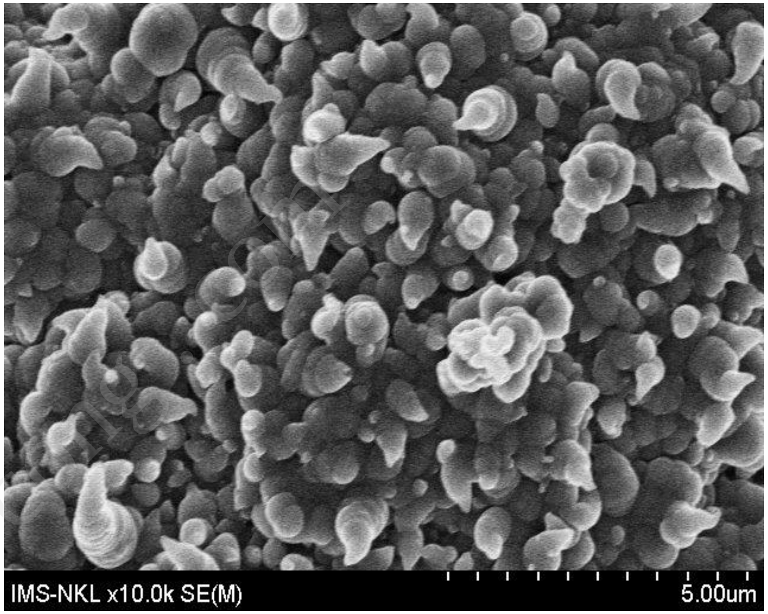


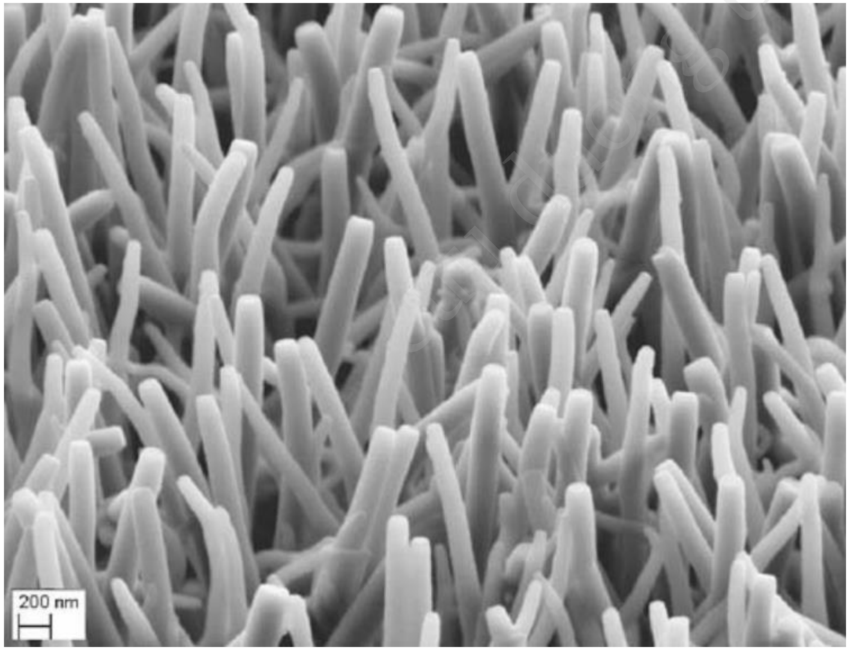
NGẮT MẠCH

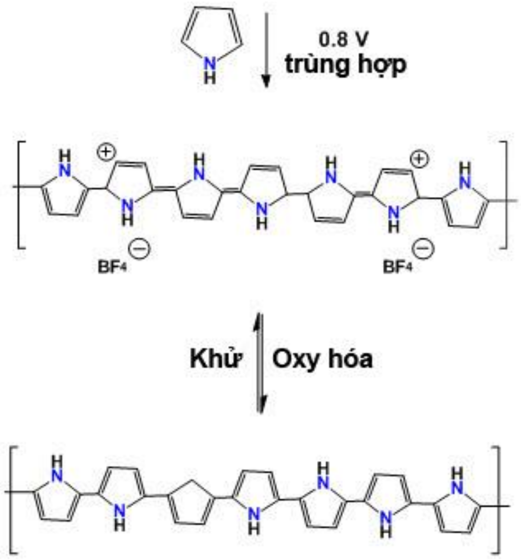


Cơ chế phản ứng trùng hợp PPy







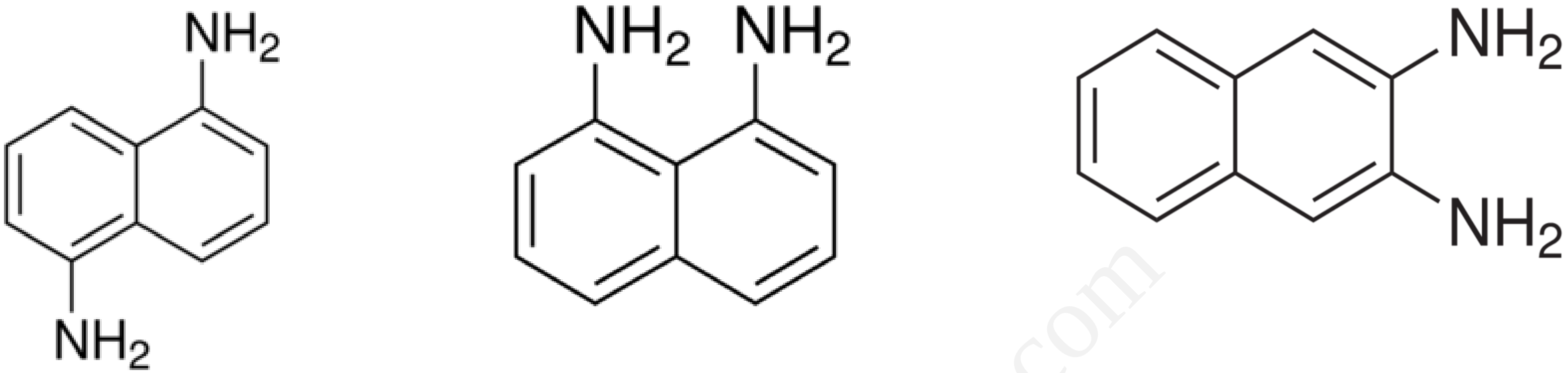


0.8 V
trùng hợp

Polypyrrole
dạng oxy hóa
Bipolaron

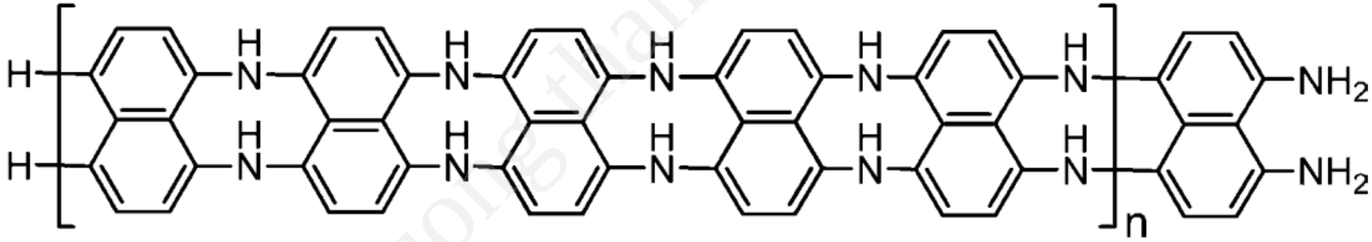
Khử **Oxy hóa**

Polypyrrole
dạng khử

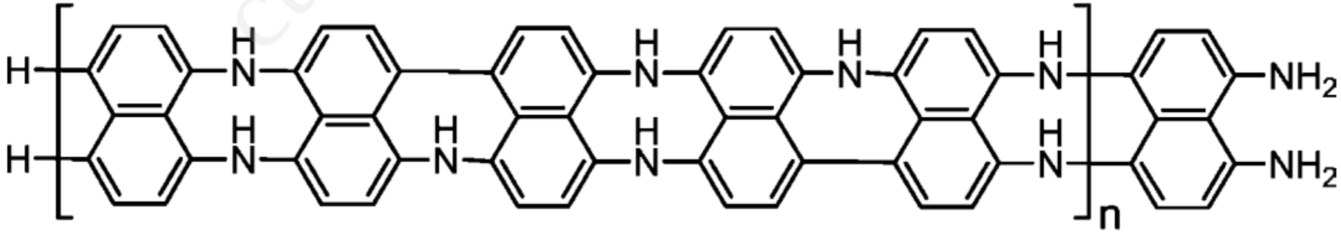


Cấu trúc hóa học của (a) 1,5-; (b) 1,8-; (c) 2,3- diaminonaphthalen (DAN)

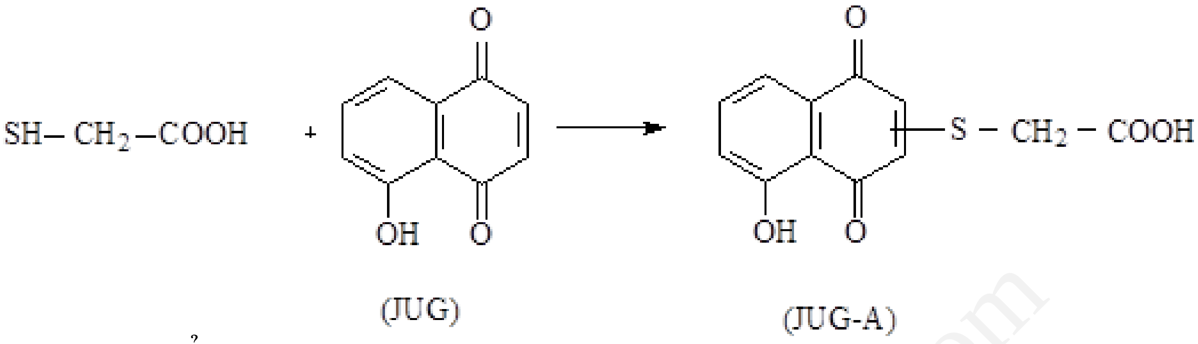
$C_{10}H_6N_2$



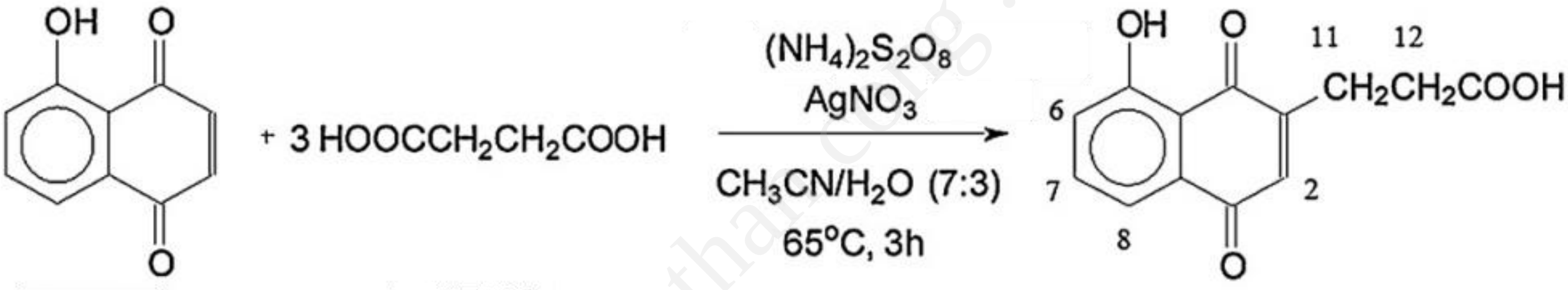
$C_{10.0}H_{5.60}N_{1.60}$



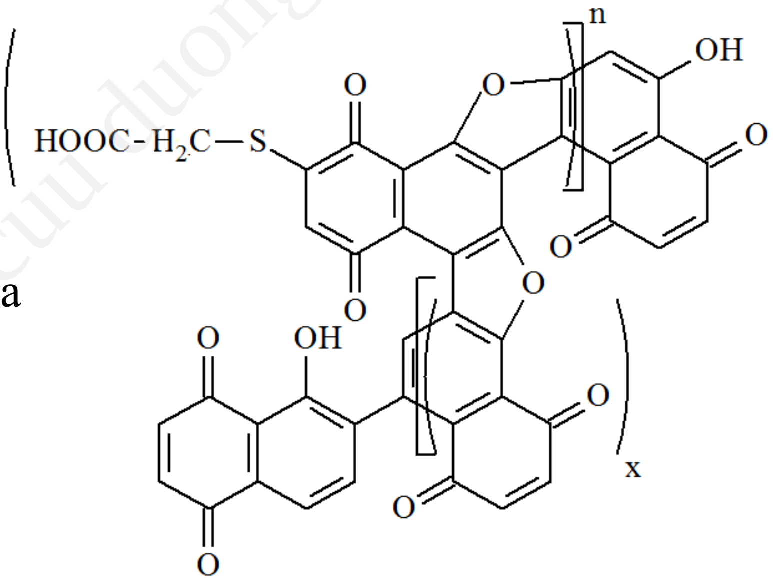
Các dạng cấu trúc của poly 1,8- diaminonaphthalen



Phản ứng tổng hợp monome 5-hydroxy-3-thioacetic acid-1,4-naphthoquinone



Phản ứng tổng hợp 5-hydroxy-2-carboxyethyl-1,4-naphthoquinon



Công thức cấu tạo của poly(JUG-co-JUGA)