Diamond-like Carbon Thin Film with Controlled Zeta Potential for Medical Application

[Nitta et. al., Diamond & Related Materials 17 (2008) 1972-1976]

MSE 576 Thin Films & Analysis Presentation
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Outline

- Diamond-like carbon thin films
- Zeta potential
- Discuss paper by Nitta et. al.

Diamond-like carbon

- Amorphous thin films with both graphite and diamond bonds.

- Interesting properties:

  - Low coefficient of friction
  - Wear resistance
  - Wide band gap

- Applications: Dies and automobile parts.

Diamond-like carbon

- DLC thin films are potential medical materials because:
  - biocompatibility
  - antithrombogenicity

- Reason: Medical devices that are in contact with the blood, e.g., artificial hearts and blood pumps.

- Present problem: blood clotting, performance.

Diamond-like carbon

- Present material: Polymers, but they have problems:
  - Blood compatibility is not outstanding.
  - Adhesion is not great to metallic substrate.

Solution: DLC thin film

Diamond-like carbon

- DLC thin film:
  - Chemically stable amorphous hydrocarbon thin film.
  - Smooth with atomic flatness.
  - Superior compatibility with tissue and blood.
- Problem: Not effective in all the situations.
- Account must be taken of the interactions between the cell and the DLC thin film surface.
- Important parameter: Zeta potential !!

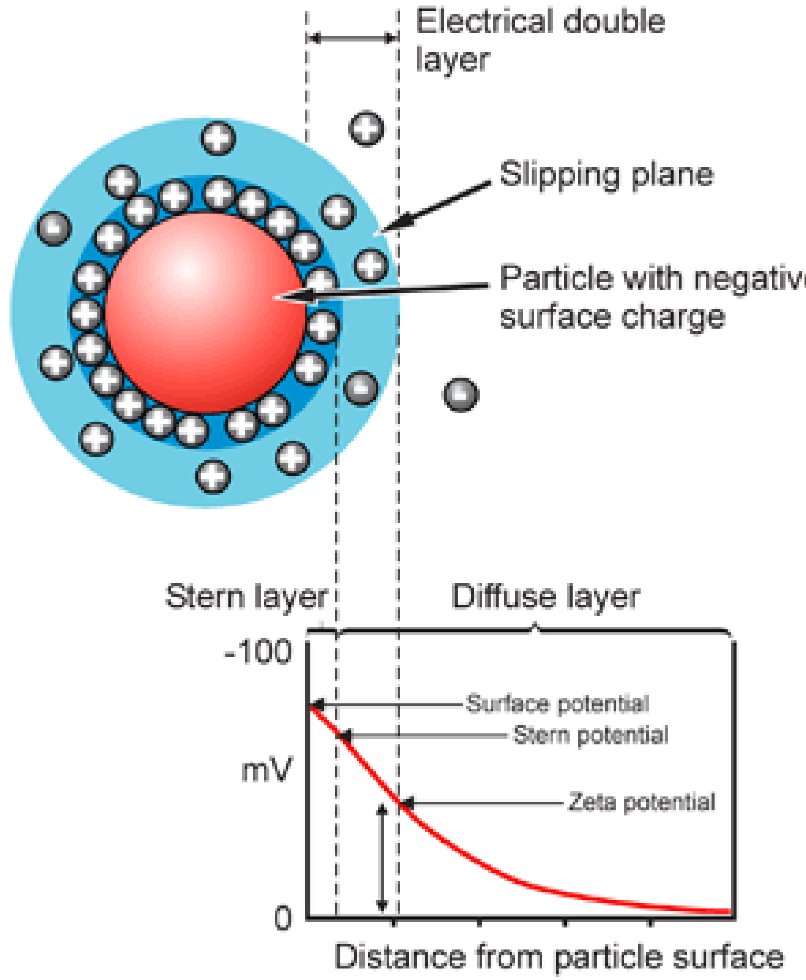
What's zeta potential ?

- It's an abbreviation for electrokinetic potential in colloidal systems (says Wiki).

- Theoretically, it is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface.

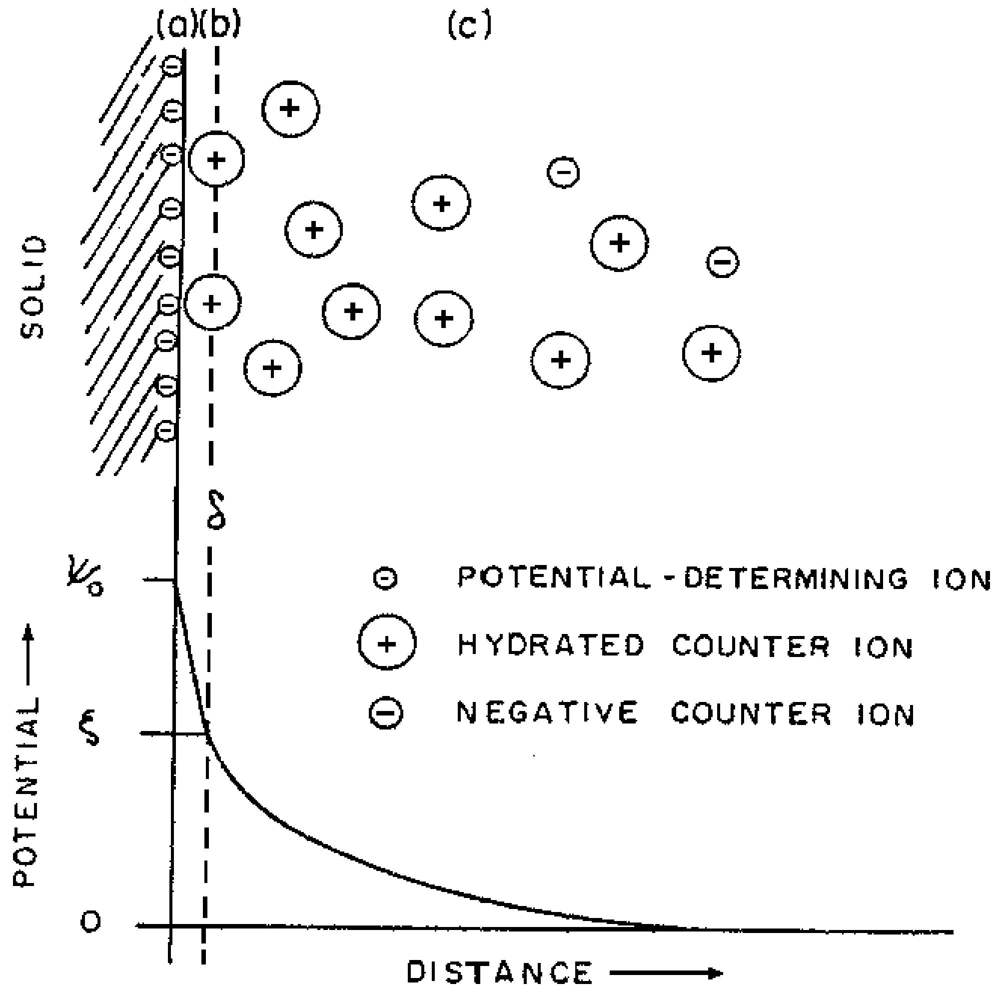
- In simple terms, it is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

What's zeta potential ?



Source: http://www.malvern.co.uk/LabEng/technology/zeta_potential/zeta_potential_LDE.htm

What's zeta potential ?



Source: http://www.geocities.com/CapeCanaveral/Hangar/5555/zeta.htm

The significance of zeta potential

- Its value can be related to the stability of colloidal dispersions.

- It indicates the degree of repulsion between adjacent, similarly charged particles (the vitamins) in a dispersion.

- A high zeta potential: **Stability** ! (+ or -)

- A low zeta potential: **Flocculation** !

  Because attraction exceeds repulsion, and the dispersion breaks.

The significance of zeta potential

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Zeta potential (mV)	Stability behavior of the colloid
0 to ±5	Rapid coagulation/flocculation
±10 to ±30	Incipient instability
±30 to ±40	Moderate stability
±40 to ±60	Good stability
> ±61	Excellent stability

Zeta potential of colloids in water and waste water

Source: ASTM Standard D4187-82, American Society for Testing and Materials, 1985

Zeta potential in biological environ

- Cells: **Negatively charged**, and their surface potential varies depending on the individual cell.

- Stimulation to the cells can be reduced by controlling the zeta potential.

- Method by Nitta et. al.: Introduce functional groups such as amino (-NH_2) and carboxyl groups (-COOH).

- How: Plasma surface treatment.

Zeta potential in biological environ

- Carboxyl groups: high negative charge.
- Amino groups: high positive charge.
- If the quantities of these functional groups can be controlled at the DLC thin film surface, it will be possible to control the zeta potential.

Experimental

- Plasma surface treatment in a chamber (5 Pa)
- Process chamber connected to a RF power supply with an excitation frequency 13.56 MHz at power of 300W.
- RF power of 30 W was injected to generate plasmas.
- Capacitatively Couple Plasmas (CCP) was generated by means of two parallel plate electrodes.
- Gases used: O_2, Ar, NH_3 and C_2H_2 (15 seconds).

Experimental

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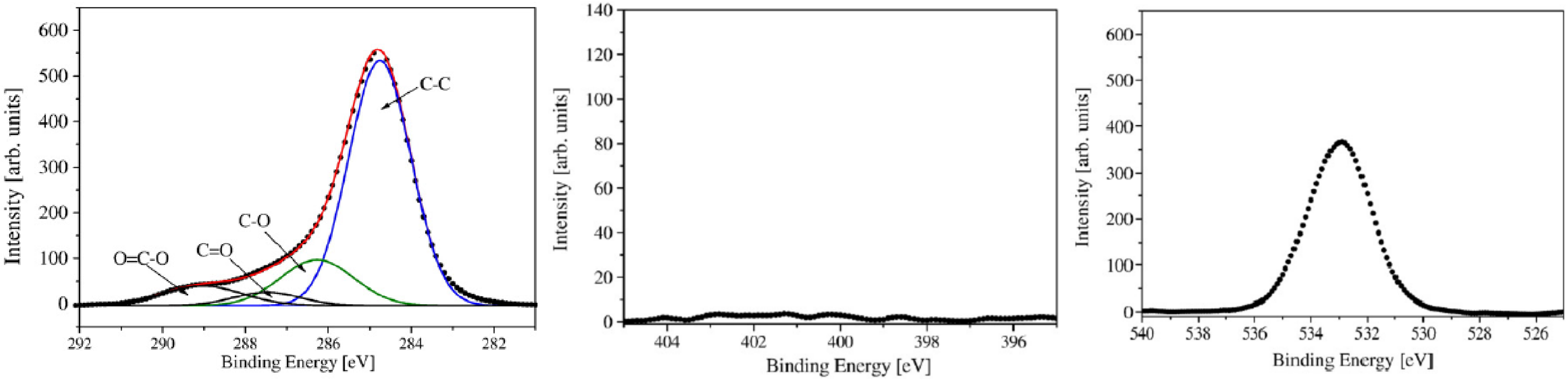
- DLC thin films used were prepared by ionization-assisted deposition using benzene.
- DLC thin film thickness: 40 nm.
- After plasma surface treatment:
  - XPS: Composition ratios of the DLC samples.
  - Contact angle meter: Static contact angle.
  - Zeta potentiometer: Zeta potential of the samples.

Composition ratio: XPS results

	C1s	N1s	O1s
$C_2H_2+O_2$	80.6	0.6	18.8
$C_2H_2+NH_3$	63.05	22.5	14.45

Results: C_2H_2 followed by O_2 treatment



C1s N1s O1s

XPS spectra of C1s waveform. The C1s peak assigned to the binding energy of C-C, C-O, C=O and O=C-O bonded network. The binding amounts were 71.8, 18.6, 2.9, and 6.5 atomic %, respectively.

Results: C_2H_2 followed by O_2 treatment

- Binding amounts in an untreated DLC sample were: **82.7 (C-C), 11.7 (C-O), 3.8 (C=O), and 1.7 (O=C-O)** (atomic %)

Functional Group	Before	After
C – C	82.7	71.8
C – O	11.7	18.6
C=O	3.8	2.9
O=C – O	**1.7**	**6.5**

- Comparing them with the XPS results of the DLC samples show that C-C bonds or C-H bonds were cleaved by **radicals**, **electrons**, and **ions** in the plasma.

- Thereby oxidation reactions such as C-O, C=O and O=C-O were promoted.

Results: C_2H_2 followed by O_2 treatment

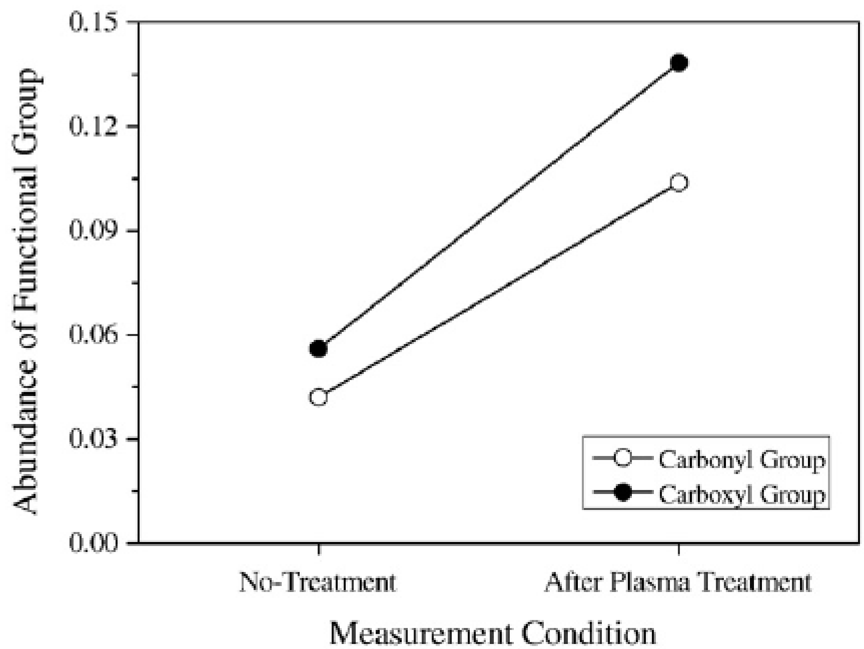
- O_2 or O radicals in plasma mainly drew H from C-H bonds. Amount of C-C bonds or C-H bonds in DLC thin films were dependent on functional groups introduced to DLC surface.

- Thus, it is considered that amount of functional groups introduced to DLC thin films surface can be controlled by controlling amount of C-C bonds or C-H bonds in DLC thin films.

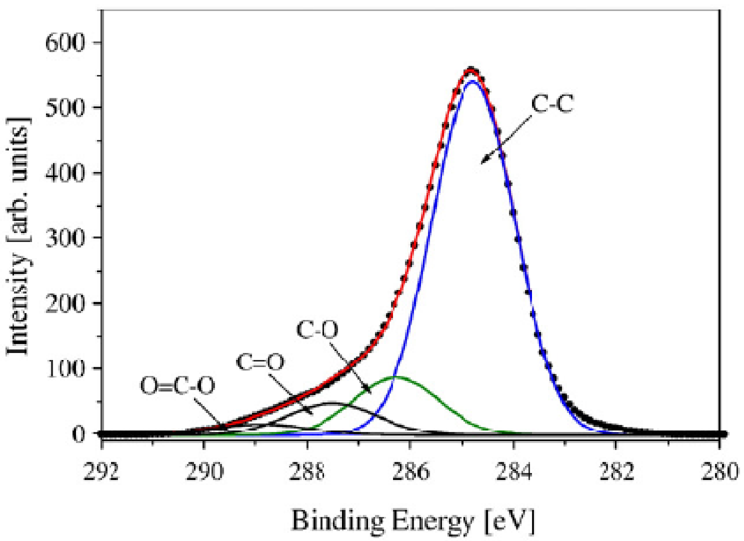
Results: C_2H_2 followed by O_2 treatment

- The O=C-O peaks stem from the carboxyl groups and were three times more numerous than that of untreated DLC sample.

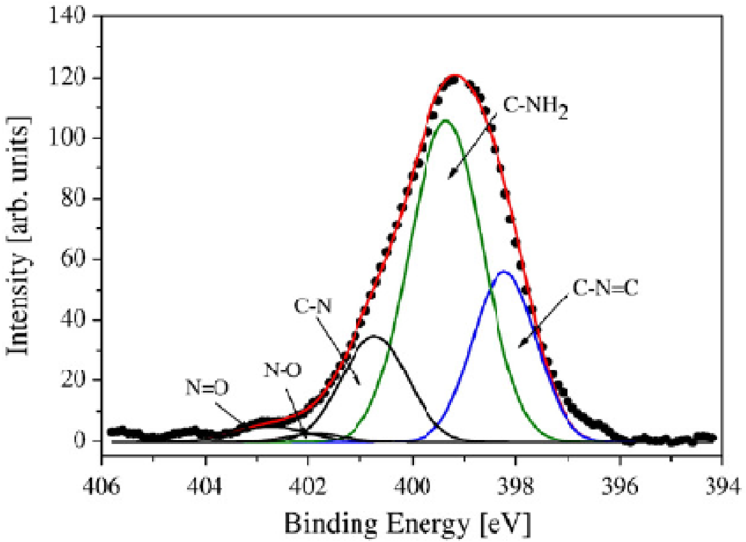
- Carboxyl groups can be introduced efficiently onto the surface of DLC thin films by plasma surface treatment.



Results: C_2H_2 followed by NH_3 treatment

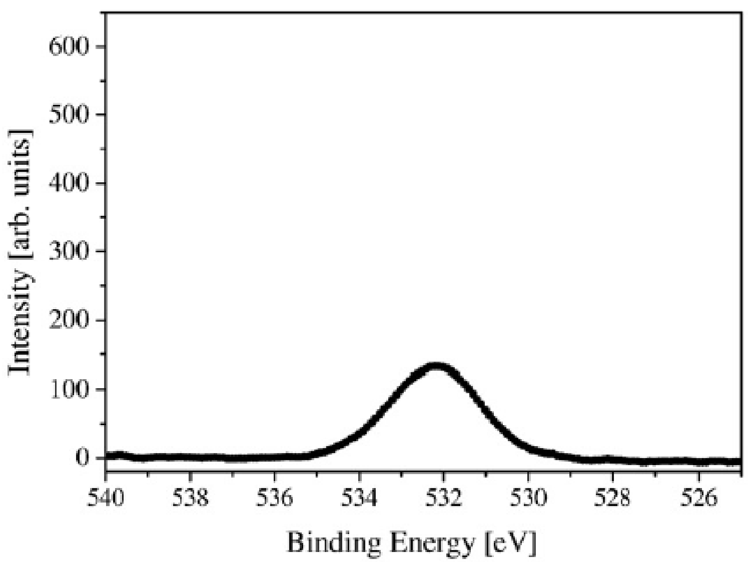


C1s



N1s

Binding amounts
79.1 (C-C)
11.6 (C-O)
7.2 (C=O)
2 (O=C-O)
(atomic %)



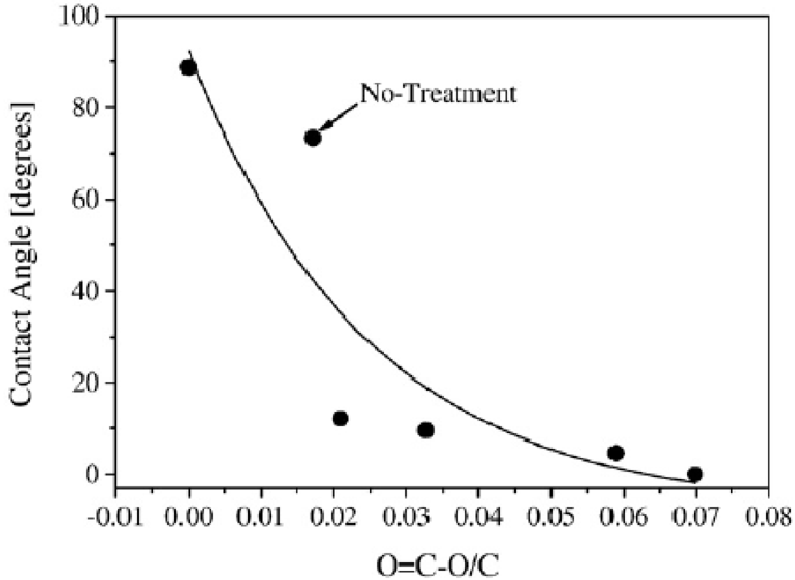
O1s

Binding amounts
20.7 (C-N=C)
58.7 (C-NH2)
16.3 (C-N)
1.7 (N-O)
2.6 (N=O)
(atomic %)

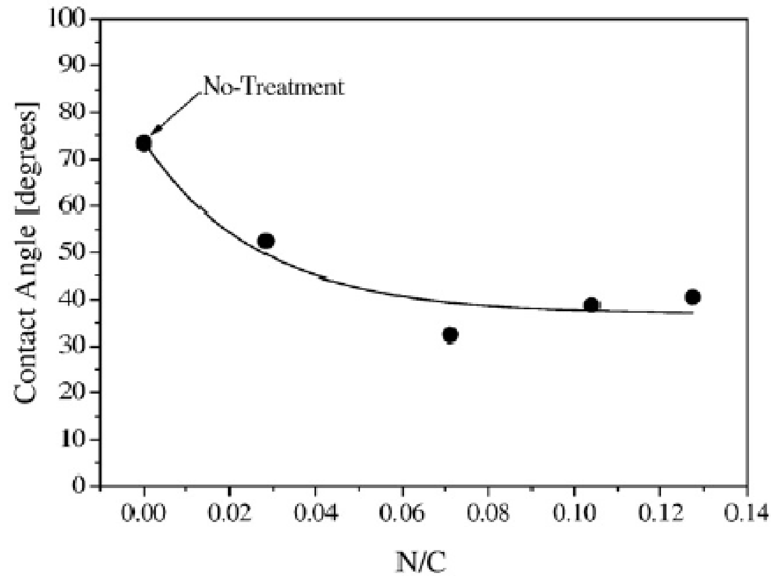
Results: C_2H_2 followed by NH_3 treatment

- C-C bonds were larger than those of $C_2H_2+O_2$ plasma treatment.
- N1s peak was remarkable compared to that of $C_2H_2+O_2$ plasma treatment.
- C-H bonds or C-C bonds were cleaved by radicals, electrons, and ions in the NH_3 plasma, and nitrogen was introduced into the DLC thin films surface.
- C-NH_2 peak dominated
- It is possible to generate amino groups on DLC thin films surface.

Results: Contact angle measurement



$C_2H_2+O_2$ treatment



$C_2H_2+NH_3$ treatment

- Contact angle of conventional DLC film is 70 degrees.
- C-O, C=O, O=C-O are hydrophilic

Results: Zeta potential measurement

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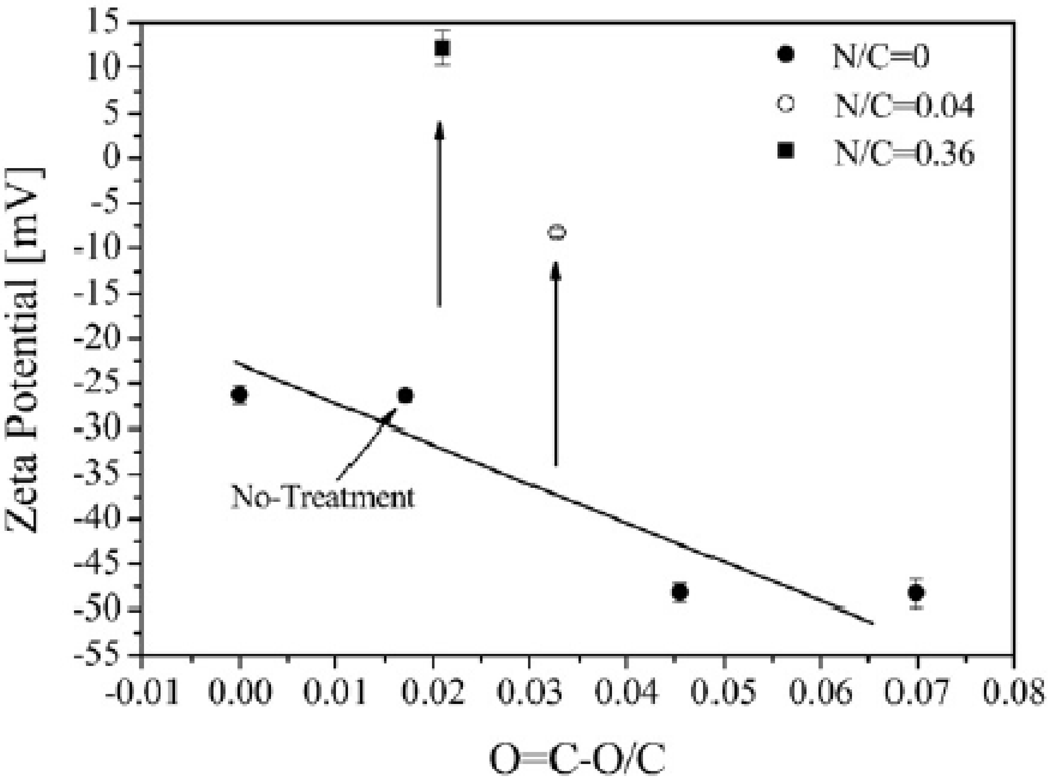

Dependence of zeta potential on O=C-O/C

The zeta potential decreased twice as much as untreated sample with increasing in the O=C-O/C ratio

Summary

- It is possible to control the **zeta potential** of DLC thin films by controlling the amounts of the **carboxyl** groups and **amino** groups.

- A new method discovered to develop a biocompatible material.

Questions ?

Thank You