UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF NANOCOMPOSITE: I·NAPHTHALENEACETATE·ZINC·ALUMINIUM·LAYERED DOUBLE HYDROXIDE

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Chairman: Associate Professor Dr. Mohd. Zobir bin Hussein, Ph.D.

Faculty: Science and Environmental Studies

Formation of organic-inorganic nanohybrid material of 1-naphthaleneacetate in the lamella of Zn-Al-layered double hydroxide (ZANOL) with and without microwave-assisted aging was done and the properties of the resulting materials were compared. For both methods, the results showed that the intercalation of 1-naphthaleneacetate (NAA) anion into the Zn-Al-layered double hydroxide lamella are readily accomplished, resulting in a Zn-Al-NAA nanocomposite (ZANAN), with the expansion of the interlayer spacing from 9.0 Å in the layered double hydroxide to 20.0 Å in the nanohybrid. This expansion is to accommodate the NAA anion of larger size than nitrate. The resulting materials afforded well ordered organic-inorganic nanolayered structure. Further characterization of the resulting materials including the true density, organic-inorganic content, surface area and morphology, was also carried out.

Both ZANOL and ZANAN exhibited good neutralizing and buffering power toward HNO_3 and NaOH solutions. Deintercalation of the NAA ions from the

interlayer of ZANAN could be done in an excessive volume of HNO_3 or NaOH solutions. NAA ions could be adsorbed on ZANOL if added into an aqueous solution of NAA. At the same time, the NAA ions adsorbed by ZANOL, could also be desorbed into the aqueous solution. The process of adsorption-desorption is a continuous process and no equilibrium was achieved, even up to 14 days.

Both ZANAN and ZANOL used in the tissue culture study of oil palm clones of E7, E8, L272, L273 and L255 did not assist in the initiation of roots. Instead, the results showed that the MS medium with the presence of NAA ions inhibited the growth of roots.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN NANOKOMPOSIT: 1-NAFTALENAASETAT-ZINK-ALUMINIUM-HIDROKSIDA BERLAPIS GANDA

Oleh,

DICKENS WONG VUI FOO

Januari 2002

Pengerusi: Profesor Madya Dr. Mohd. Zobir bin Hussein, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Bahan nanohibrid organik-inorganik yang terdiri daripada 1-naftalenaasetat dalam ruang antara lapisan Zn-Al-hidroksida berlapis ganda (ZANOL) telah disintesis dengan dan tanpa bantuan gelombang mikro dan ciri-ciri hasil sintesis tersebut telah dibandingkan. Untuk kedua-dua kaedah, keputusan eksperimen menunjukkan interkalasi bagi anion naftalenaasetat ke dalam ruang antara lapisan Zn-Al-hidroksida berlapis ganda adalah mudah dicapai, menghasilkan nanokomposit Zn-Al-NAA (ZANAN) yang mengakibatkan pengembangan jarak antara ruang untuk hidroksida berlapis ganda tersebut daripada 9.0 Å kepada 20.0 Å untuk nanohibridnya. Pengembangan tersebut adalah untuk menempatkan anion NAA yang saiznya lebih besar daripada anion nitrat. Bahan terhasil juga mempunyai struktur lapisan nano yang lebih tersusun. Pencirian bagi bahan yang dihasilkan termasuk ketumpatan mutlak, kandungan organik-inorganik, luas dan morfologi permukaan telah juga dilakukan.

Kedua-dua ZANOL dan ZANAN menunjukkan kuasa peneutralan dan penimbalan yang baik terhadap larutan akues HNO_3 dan NaOH. Nyahinterkalasi anion NAA daripada ruang antara lapisan ZANAN juga dapat dicapai sekiranya larutan HNO_3 atau NaOH yang berlebihan digunakan. ZANOL boleh menjerap ion-ion NAA jika ia ditambahkan ke dalam larutan akues yang mengandungi NAA. Pada masa yang sama, ion-ion NAA yang terjerap juga dapat dinyahjerapkan semula ke dalam larutan akues tersebut. Proses jerapan dan nyahjerapan ini berlaku secara berterusan dan keseimbangan didapati tidak tercapai walaupun sehingga 14 hari.

Kedua-dua ZANOL dan ZANAN yang digunakan dalam kajian kultur tisu klon kelapa sawit E7, E8, L272, L273 dan L255 tidak membantu pertumbuhan akar. Sebaliknya, keputusan menunjukkan medium MS dengan kehadiran ion-ion NAA menghalang pertumbuhan akar.

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ASAP	Accelerated Surface Area and Porosimetry
BET	Brenauer, Emmett and Teller
BJH	Barrett, Johner and Halenda
CHNS	Carbon, Hydrogen, Nitrogen and sulfur analysis
ICP-AES	Inductive Couple Plasma – Atomic Emission Spectroscopy
LDH	Layered Double Hydroxide
MS	Murashige and Skoog Medium
NAA	1-Naphthaleneacetic acid
NC	Nanocomposite
PXRD	Powder X-Ray Diffration
R	Ratio of Zn^{2+} to Al^{3+}
R_{form}	Ratio of Zn^{2+} to Al^{3+} formed
SEM	Scanning Electron Microscopy
θ	X-ray diffraction angle
ZANOL	Zn^{2+}-Al^{3+}-NO_3^--Layered Double Hydroxide
ZANAN	Zn^{2+}-Al^{3+}-Naphthaleneacetate Nanocomposite

CHAPTER I

INTRODUCTION

Nanocomposite Materials

In materials science, a "composite" implies that the material is composed of a mixture of two or more constituents that differ in composition (Hawley, 1973). Thus, the term "nanocomposite" implies that the physical arrangement of the different constituents is on a scale of 1 to 100 nanometer (1 nm = 10^{-9} m, *i.e.*, one billionth of a meter) (Roy *et al.*, 1986).

Nanostructured materials are becoming of major significance and the technology of their production is rapidly growing into a powerful industry. These fascinating materials include nanofilms, nanocrystal, alloys, nanocomposites and semiconductors (Nalwa, 2000). The synthesis of materials of nanoscale dimension is important because the small size of these materials endows them with unusual structural and optical properties that might find application in catalysis and electro-optical devices. Such materials may also be valuable precursor to strong ceramic (Sax and Lewis, Sr., 1987). These kind of materials and their base technologies have also opened up exciting new possibilities for future applications in aerospace, automobile, batteries, insulators, printing, color imaging, drug delivery, medicine and cosmetics (Lerf, 2000).

The preparation of nanostructure materials depend on the following four common microstructural features (Gonsalves, 2000):

(1) The grain size and size distribution (< 100 nm).
(2) The chemical composition of the constituent phases.
(3) The presence of interfaces, more specifically, grain boundaries, heterophases interface, or the free surface.
(4) Interactions between the constituent domains.

The presence and interplay of these four features largely determine the unique properties of the nanostructured materials.

A two dimensional layered structure consisting of thin crystalline inorganic layers with a thickness of molecular scale in nanometer range can be used as an ideal host of layered nanocomposite or organic-inorganic hybrid materials. One of the candidates for this type of structure is layered double hydroxide (LDH). A variety of anionic species can be inserted as guests into the interlayer spaces of the LDH, resulting in an expansion of the interlayer distance to a nanometer sized dimension to form a new nanocomposite material (Yamanaka, 1991).

Layered Double Hydroxides (LDHs)

Layered double hydroxides (LDHs) are also known as anionic clays. It was discovered by Feitknecht about 50 years ago, but their structure was only determined in 1970 by Allman for the Mg-Fe LDH (pyroaurite and sjögrenite) and by Brown and O'Hare for the Mg-Al LDH (hydrotalcite and manasseite) (Ehisissen *et al.*, 1993 and Millange *et al.*, 2000). These compounds have a structure of sheet held together by strong covalent bonds in the xy plane to form a two-dimensional polyhydroxyl cation layers. These crystalline layers are stacked by considerable weaker bonds in the z direction, containing anions and water molecules (Hussein *et al.*, 1995).

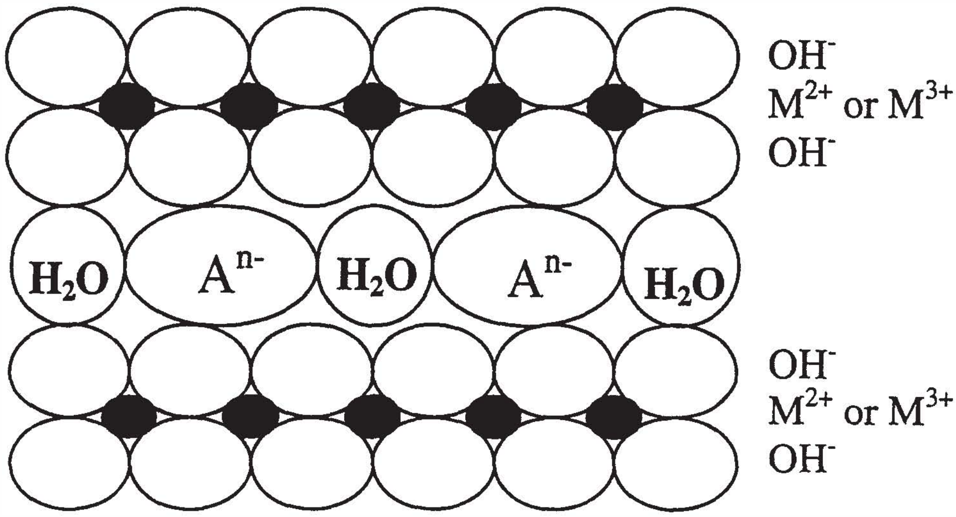

Figure 1.1: Structure of LDH.

The chemical composition of LDHs is generally expressed as

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}H_2O]^{x-}$$

where M^{2+} is a divalent cation such as Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} or Zn^{2+}, M^{3+} is a trivalent metal ion such as Al^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, Ga^{3+} and A^{n-} an anion of charge n such as CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^- or ClO_4^-. The M^{2+}:M^{3+} ratio is usually between 1 and 5 (Zhao and Vance, 1997). The value of x ($x = M^{3+}/(M^{2+} + M^{3+})$ ranges between 0.20 and 0.33 (Cavani *et al.*, 1991).

There are only two types of host lattices carrying positive charges: graphite compounds with a positively charged carbon network and the family of LDH. They differ strongly in their chemical behavior. Graphite is an electronic conductor and a strong oxidizing agent, which sharply restricts the species to be intercalated. The LDH group are electric insulators which are stable in an aqueous environment (if CO_2 is excluded) and are able to take up a large number of anions, ranging from inorganic ones like Cl^- to negatively charged metal complexes and polyoxyanions to anions of organic acids (Lerf, 2000).

Structure of LDHs

LDHs are isostructure with the mineral hydrotalcite, having formula $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ (Puttaswamy and Kamath, 1997). The layers of M^{2+} and M^{3+} cations are coordinated octahedrally by six oxygen anions, as hydroxides. These layers exist with a similar layered structure to that exhibited by brucite,