Synthesis and Physico-Chemical Properties of Zinc Layered Hydroxide-4-Chloro-2-Methylphenoxy Acetic Acid (ZMCPA) Nanocomposite

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Abstract: Hybrid nanocomposite zinc layered hydroxide-4-chloro-2-methylphenoxyacetic acid (ZMCPA) was successfully synthesized via direct reaction of 4-chloro-2-methylphenoxy acetic acid (MCPA) with zinc oxide (ZnO) under an aqueous environment. The pure phase and well-ordered ZMCPA was obtained when ZMCPA was synthesized at 0.3 M MCPA. The resulting nanocomposite, ZMCPA was characterized by powder X-ray diffraction (PXRD), fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), thermogravimetric and differential thermogravimetric analyses (TGA/DTG) and CHNS Analyzer. Basal spacing showed that the gallery height of zinc layered hydroxide (ZLH) expanded from 11.Å to 24.1 Å, indicating that the MCPA anions were successfully intercalated into the interlayer space of ZLH. The FTIR spectrum of the ZMCPA shows it resembles the spectra of ZnO and MCPA that confirms the intercalation of MCPA between the ZLH sheets. FESEM shows the ZnO precursor has granular structure and transformed into a flake–like structure when the nanohybrid is formed. Percentage loading of MCPA interleaved in the nanohybrid is 50.2%.

Excellent intercalation properties of 2D layered material offer a new scope for developing hybrid materials at nanoscale dimensions or the so-called nanocomposite[1]. This brucite-like layered compound can be classified into two types from their structural anisotropy and chemical composition to produce intercalated compounds. Layered double hydroxide (LDH) and layered hydroxide salts (LHS). LDH can be represented by a general formula, \[ M^{2+}_{x}M^{3+}_{3x}(OH)_{2}\] \( (A^{n-})_{x/n}YnH_2O \), where \( M^{2+} \) is a divalent cation (Ca²⁺, Mg²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Mn²⁺), \( M^{3+} \) is a trivalent cation (Al³⁺, Cr³⁺, Fe³⁺, Co³⁺, Ni³⁺, Mn³⁺), \( A^{n-} \) is an interlayer anion such as (Cl⁻, NO₃⁻, ClO₄⁻, CO₃²⁻, SO₄²⁻). The x value is the molar ratio, \( M^{3+}/(M^{2+} + M^{3+}) \). LHS can be represented with the general formula \( M^{2+}(OH)_{2.5}(A^{n-})_{0.5}yH_2O \), where \( M^{2+} \) is the metallic cation (e.g., Mg²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Cd²⁺, Co²⁺, and Cu²⁺) and A is a counterion with \( n^- \) charge[2]. LDH and LHS consists positively charged brucite-like inorganic layers and exchangeable anions and water molecules in the interlayer. Layered metal
hydroxide (LMH) have various potential to be used in various industry such as ion exchanger [3], drug delivery system [4] and control release formulation [5].

**Figure. 1.** Molecular structure of 4-chloro-2-ethylphenoxy acetic acid.

This paper reports our work on the intercalation of phenoxyherbicides namely 4-chloro-2-methylphenoxy acetic acid (MCPA) (Fig. 1) into ZnO via direct reaction of aqueous solution. MCPA is one of the derivatives phenoxyalkane carboxylic acid used as herbicide and a plant growth regulator. It is commonly used to control the broadleaf weeds, including thistle and dock, in cereal crops and pasture. It is selective for plants with broad leaves, and this includes most deciduous trees.

2. Experimental.

All solution was prepared using deionized water. MCPA (97%) was purchased from Aldrich, pure zinc oxide:ZnO(99%) and sodium hydroxide, NaOH (99 %) was purchased from R&M Chemical used without any further purification. MCPA was dissolved in 50ml of 90% ethanol into a beaker with a different concentration. Then, 0.2 g of ZnO was added into MCPA solution. The solution was titrated with NaOH and stirred for 24h using a magnetic stirrer. The white precipitate was aged in oil bath shaker at 70 °C for 18h. After cooling, the resulting material was centrifuged, washed with deionized water and dried in an oven at 70 °C for 48h until fully dried. The resulting material was kept in the sample vial for further characterizations.

3. Characterization.

Power X-ray diffraction (PXRD) patterns were recorded with a XRD-6000(Shimazdu, Kyoto Japan) using Cu-Kα radiation (λ= 1.5418 Å) at 30kV and 30mA. The data was collected from 2 – 60° at a dwell time of 2°min⁻¹. Fourier Transform infrared (FTIR) spectra were recorded by a Perkin Elmer 1725x spectrophotometer in the range of 4000-450 cm⁻¹. The CHNS Analyzer 3400 Perkin Elmer Series II was used to determine the carbon and hydrogen percentage in the intercalation compound. The thermal decomposition behavior of the samples was carried out by using a thermogravimetric and differential thermogravimetric analyses (TGA/DTG) using a MettlerToledo instrument model TGA/SDTA851 thermogravimetric analyzer by heating rate at 10 °Cin the range of 35-1,000 °C under N₂ gas with a flow rate of 50 ml min⁻¹. Surface morphology of the samples was observed by a field emission scanning electron microscopy (FESEM) using a Zeiss Supra 40VP.

4. Results and Discussion

4.1 Power X-ray diffraction.

Fig. 2(a) shows the PXRD patterns for ZnO, MCPA and ZMCPA nanohybrids synthesized at different concentration of MCPA. The PXRD patterns of ZnO indicate high crystallinity shows by a distinctive pattern of metal oxide with five sharp reflection peaks in the range of 2θ at 30-40°. However, comparing both 0.2 and 0.3 M ZMCPA together, the nanolayered structure material obtained using 0.3 M ZMCPA, shows a symmetric peak with reflection up to 4 harmonics, respectively. This indicate the formation of the well-ordered 2D layered structure of the nanocomposite. Hence, the nanolayered structure material obtained from 0.3 M ZMCPA was selected for further characterizations and labeled as ZMCPA. The shifted diffraction peaks to the lower 20 indicating an expansion of the inorganic layer host of zinc oxide layer. This confirmed the ZMCPA formation from simple reaction of ZnO with MCPA under aqueous environment was transformed into a layered hydroxides, and at the same time the intercalation of MCPA anion and the interlayer of the zinc-layered hydroxide took place.
4.2 FTIR Spectroscopy.
Fig. 2(b) shows the FTIR absorption spectra of ZMCPA nanohybrids, MCPA anions and ZnO. For MCPA, a broad band at 2907 cm\(^{-1}\) is due to the O-H stretching vibration of the COOH. A strong and distinct band at 1746 cm\(^{-1}\) is ascribed to C=O stretching. 1629 cm\(^{-1}\) and 1429 cm\(^{-1}\) is due to C=C vibration of the aromatic ring, and 1495 cm\(^{-1}\) and 1429 cm\(^{-1}\) was due to O-H in-plane bending. The symmetric and asymmetric stretching mode of C-O-C vibration can be observed at 1247 and 1257 cm\(^{-1}\) and a band at 802 cm\(^{-1}\) is due to the C-Cl stretching vibration. ZnO displays a broad peak below 600 cm\(^{-1}\) which is the characteristic of Zn absorption bands [6]. The FTIR spectrum of ZMCPA nanohybrids shows a broad absorption band at 3421 cm\(^{-1}\) which corresponds to the O-H stretching vibration due to the absorbed and interlayer water molecules [7]. A strong band at 1606 cm\(^{-1}\) is due to the C=C vibration of the aromatic ring. The band at 1497 and 1424 cm\(^{-1}\) are due to the COO- stretching and C-O-C vibration of intercalated MCPA. At the lower wavenumber, the disappearance of the ZnO absorption band for the ZMCPA nanohybrid confirmed that all the ZnO was completely reacted with the MCPA in the aqueous solution, resulting in the formation of ZMCPA nanohybrid. This is evident by the FTIR spectra which shows combination spectra of both the inorganic host, ZnO and the guest anion, MCPA. This suggests that the MCPA anion was intercalated into the interlayer of the ZFH. Due to the intercalation process, some of the absorption bands shown were slightly shifted in position, due to the existence of interaction between the MCPA guest anion and the ZnO host as a result of the formation of new bonds.

4.3 Elemental Analysis.
From the results, MCPA content 53.6 % of carbon (w/w) compared to 27.0 % of carbon (w/w) for the nanohybrid, ZMCPA. The high content of carbon in ZMCPA showed that MCPA anion was
successfully intercalated between the interlayer of the layered material. The percentage loading of MCPA in ZMCPA nanohybrid estimated from the percentage of carbon is 50.2%.

4.4 Thermal Analysis.
The TGA/DTG thermogram of MCPA, ZnO, and ZMCPA are shown in Fig. 3. The TGA/DTG curve for MCPA shows a temperature maxima at 243.9°C with weight loss of 89.9%. This corresponds to complete decomposition of the organic compound MCPA. The TGA/DTG curve for ZMCPA shows a temperature maxima of 309.5°C with weight loss of 52.6%. This indicates that MCPA encapsulated into the inorganic interlamellae is thermally more stable than their counterpart in the pure form. ZMCPA shows four intense of weight losses of 2.1 %, 52.6 %, 4.1 % and 33.9 % at temperature maxima of 101.1°C, 309.5°C, 141.8°C, and 946.4°C, respectively. The first mass loss due to the removal of surface physisorbed and intercalated water molecules. The second mass loss is attributed to the decomposition of the intercalated MCPA. The third mass loss is attributed to the decomposition of the organic moiety in ZMCPA nanohybrid.

4.5 Surface Morphology.
The surface morphologies of ZnO and ZMCPA are shown in Fig. 4. ZnO shows granular structure with irregular particles of different sizes and various shapes at the nanometer scale. This structure was transformed into agglomerates of plate-like structure when the ZMCPA nanohybrid was formed by a direct reaction of ZnO with MCPA under an aqueous environment. This showed that the intercalation of MCPA into the interlayer of zinc-layered hydroxide resulted in a changed of surface morphology from well-defined hexagonal and square like structure to a plate-like structure with a thickness in a nanometer range.

Figure. 3 TGA/DTG thermograms of the inorganic host ZnO (a), the guest anion, MCPA (b), and its nanohybrid, ZMCPA (c).

Fig. 4 FESEM of ZnO (a), 0.2 M ZMCPA nanohybrid (b) and 0.3 M ZMCPA nanohybrid (c) at 100,000 x magnification.

5. Conclusion
An inorganic-organic nanohybrid of Zinc Layered Hydroxide 4-chloro-2-methylphenoxy acetic acid was successfully synthesized using a simple direct reaction of MCPA anion with ZnO under an aqueous environment with loading of MCPA interleaved in the nanohybrid of 50.2 %(w/w).

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