

SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF NiZnAl-LDH/PVA AND NiZnS₂/NiZnAl-LDH/PVA NANOCOMPOSITES

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Nickel zinc aluminum layered double hydroxides (NiZnAl-LDH) were synthesized by co-precipitation and co-formation methods using urea in polyvinyl alcohol (PVA) solution. On the obtained nanocomposites nickel-zinc sulfide (Ni_xZn_{1-x}S; x=0.25, 0.5, 0.75) nanoparticles were synthesized by successive ionic layer adsorption and reaction (SILAR) method at room temperature (25°C). The photocatalytic degradation of Ponceau 4R (P4R) and Rhodamine 6G (R6G) with obtained LDH and sulphide nonmaterials were studied under visible light source (150W). NiZnAl-LDH and Ni_xZn_{1-x}S/NiZnAl-LDH (x=0.25, 0.5, 0.75) nanocomposites were characterized by Ultraviolet (UV) spectratrometer, X-ray diffractometer (XRD), Energy-dispersive X-ray (EDX), Fourier transform infrared (FTIR) spectratrometer and Scanning electron microscopy (SEM).

Keywords: nanocomposites, layered double hydroxides, NiZnAl-LDH/PVA, NiZnS₂, sorption, photocatalyst.

INTRODUCTION

Layered materials are very important compounds due to the intercalation of various ions and molecules into the layers. These intercalating substances can be gas molecules, cations, anions, organic compounds, and polymers.

Layered double hydroxides are 2D anionic clay nanomaterials, whose main advantage is intercalation with functional compounds and exfoliation in polymer matrix to get wide applications. LDHs are promising materials can be used in catalysis, pharmaceuticals, bioc-hemistry, photonics, electronics, electrochemical biosensors, sorption and catalysts [1-3].

Visible light controllable Co (or Cu) doped ZnAl-LDH photocatalysts were synthesized by co-precipitation method with high efficiency [4]. The atomic ratios of Co/Zn/Al (or Cu/Zn/Al) in the mixed solution were = 0/2/1; 0.1/2/1; 2/2/1 and 4/2/1 (or 0/2/1; 0.1/2/2; 1/2/1 and 2/2/1 for Cu, respectively). It was found that Co (or Cu)-doped ZnAl nanomaterials showed higher light absorption than pure ZnAl-LDH nanomaterials. The authors explain the effective role of cobalt ions by separation of the photo-generated charge resulting in higher photocatalytic degradation of Rhodamine B (RhB) [4, 5].

NiO-ZnO composites were obtained on the base of Ni_xZn_{1-x}OH compound hierarchically synthesized by the surface modification method. Also, spherical nano-sized and holey Ni_xZn_{1-x}S particles were successfully synthesized by hydrothermal method on the base of Ni_xZn_{1-x}OH composite. Electropotential properties of the Ni-Zn system were studied

through electrochemical measurements and it was found that the properties of Ni_xZn_{1-x}S materials were sufficient for supercapacitors [6]. In the synthesis of Ni_xZn_{1-x}OH nanoparticles, Zn(NO₃)₂ and Ni(NO₃)₂ solutions of the same molarity (0.075 M) were prepared, mixed with 50 ml of DMF solution and slowly added to the same volume of 0.4 M Na₂O₂ aqueous solution. The obtained mixture was kept at room temperature for 12 hours, washed and dried in vacuum at 333 K [6]

The preparation and application of nanocomposites obtained by incorporating LDHs into polymers has recently become an important topic. Y. Sugahara and his group synthesized nanocomposites of polyacrylonitrile (PAN) with MgAl-LDH by in-situ polymerization for the first time [7]. Acrylonitrile monomers were mixed with dodecyl sulfate in the experiment, then intercalated to MgAl-LDHs and in-situ polymerization was carried out in the next stage. As a result, nanocomposites with a layered morphology composed of polymer and inorganic layers were obtained. In the last decade, most of the LDH/polymer nanocomposites have been combined with organic ceramics.

EXPERIMENTAL

Mixed solutions of NiSO₄·7H₂O, Zn(NO₃)₂·7H₂O and Al₂(SO₄)₃·18H₂O salts in ratio of (Ni+Zn)/Al = 3/1 were prepared. 6 g of urea and 40 ml of 10% PVA solution were added to the solution and titrated with 5M NaOH solution. Then it was heated at 90°C for 10 hours. Unlike doping by impregnation, here the additive elements entered the crystal lattice during the reaction. The obtained sample was marked as NiZnAl-LDH/PVA nanocomposite.

Three parts of obtained nanocomposite were taken, 5 ml of 0.05 M NiSO₄·7H₂O and 15 ml of 0.05 M ZnSO₄·7H₂O were added to the 1st part, 15 ml of 0.05 M NiSO₄·7H₂O and 5 ml of 0.05 M ZnSO₄·7H₂O were added to the 2nd part, 10 ml of 0.05 M NiSO₄·7H₂O and 10 ml of 0.05 M ZnSO₄·7H₂O were added to the 3rd part. The surface sulphidization by SILAR method were carried out for 10 minutes. The obtained sulfides were marked as Ni_{0.25}Zn_{0.75}S/NiZnAl-LDH/PVA, Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and Ni_{0.75}Zn_{0.25}S/NiZnAl-LDH/PVA.

The structural properties of nanomaterials were characterized using X-ray diffractometer (XRD) (Rigaku-Mini-Flex 600) with Ni filtered CuKα radiation (λ = 1.54Å) and 5°/min scanning speed.

Optical characterizations of nanomaterials were carried out using ultraviolet-visible (UV-vis) spectrophotometer- Specord 210+(Analytical Jena-Germany) and Fourier-transform infrared spectroscopy (FTIR) (Nicolet™ iS™10) at 4000–500 cm⁻¹ wavenumber range.

The average particle size and c parameter of the nanocrystals was determined by Scherrer [8] (1) and Braggs (2) equations using XRD data

$$D = K\lambda / \beta \cos\theta \quad (1)$$

$$n \cdot \lambda = 2d \cdot \sin\theta \quad (2)$$

Where D- is the average diameter of the nanoparticles, K- is the Scherrer constant (0.9), λ- is the wavelength of the X-ray radiation (1.5418 Å), β- is the Full Width at Half Maximum (FWHM), and θ- is the Braggs angle, d- is a distance between layers of atoms, n- is the order of diffraction.

Tauc equation [9] (3) was used to determine the bandgap energy of the synthesized NiZnAl-LDH/PVA and NiZnS@NiZnAl-LDH/PVA nanocomposites at room temperature:

$$\alpha h\nu = [k(h\nu - E_g)]^{n/2} \quad (3)$$

Where ν - is the frequency, h - is the Planck constant, and k - is a constant depending on the value of n . For direct and indirect transitions, n takes the values of 4 and 1, respectively.

RESULTS AND DISCUSSION

Physico-chemical properties of NiZnAl-LDH/PVA nanocomposite.

In the preparation of NiZnAl-based trimetallic layered hydroxides, the amount of nickel and zinc was equal, and the molar ratio of divalent metal to trivalent metal was 3. According to Figure 1 obtained from the X-ray diffractometer, the formation of NiZnAl-LDH into PVA matrix, resulted in high crystallization. As can be seen from the Figure 1, the diffractogram of NiZnAl-LDH/PVA matches that of diffractogram of ZnAl-LDH/PVA, but the characteristic peaks fall at a slightly lower diffraction angle. Although the diffractogram of NiAl-LDH/PVA exhibit many peaks, the peaks corresponding to hydroxalite are the same as NiZnAl-LDH/PVA. From this result, it can be concluded that ZnAl LDH became dominant in ternary metal-containing LDH. External phases corresponding to nickel oxide and hydroxides were not formed at NiZnAl-LDH/PVA diffractogram, and the basal distance increased ($d_{003}=7.72\text{\AA}$) with regard to ZnAl-LDH. This value is higher than NiAl-LDH/PVA ($d(003)=7.68\text{\AA}$) and ZnAl-LDH/PVA ($d(003)=7.36\text{\AA}$).

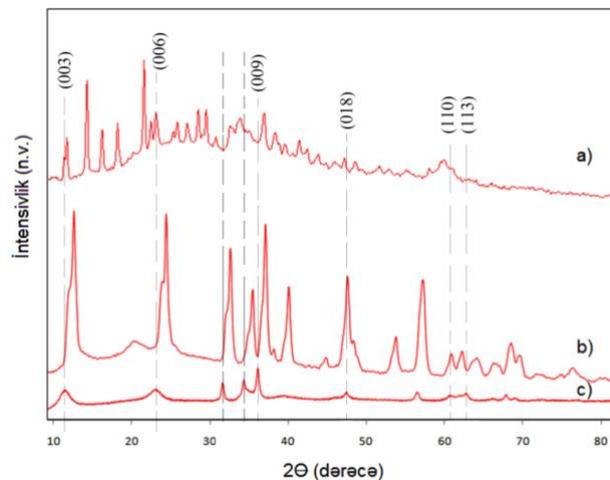


Figure 1. XRD pattern of NiAl-LDH/PVA (a), ZnAl-LDH/PVA (b) and NiZnAl-LDH/PVA (c) nanocomposites.

The band gap energy (E_g) of the obtained nanocomposites was calculated using absorbance spectra. The fact that ternary LDH/PVA nanocomposite has a low band gap is related to a large basal distance, and this fact confirms the XRD results (Table 1). The very low value of E_{g1} in NiAl-LDH/PVA is due to the predominance of monohydroxides in the composition.

Table 1. Bandgap values of obtained nanocomposites.

Samples	E_{g1} (eV)	E_{g2} (eV)	E_{g3} (eV)
NiAl-LDH/PVA	1.5	2.6	4.5
ZnAl-LDH/PVA	3.1	3.2	4.8
NiZnAl-LDH/PVA	2.2	3.0	3.9

Physico-chemical properties of $\text{Ni}_x\text{Zn}_{1-x}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$ nanocomposites obtained on the basis of $\text{NiZnAl-LDH}/\text{PVA}$

The ionic conductivity was supported by the electronic conductivity during the doping of NiZnAl-LDH s with sulfides by SILAR method. Structural analysis of obtained nanocomposite by XRD method showed that as NiS and ZnS have different crystallization nature NiS@ZnS heterostructures were formed instead of NiZnS_2 ternary sulfide (Figure 2). This result could be explained by the fact that because Ni and Zn metals activities are close, none of them could be dominant. As can be seen, the main phase of both compounds corresponds to LDH structure in all cases, the characteristic peaks indicating ZnS and NiS were formed at angles $2\theta=27.85^\circ$ and 28.88 with sulfidation, respectively.

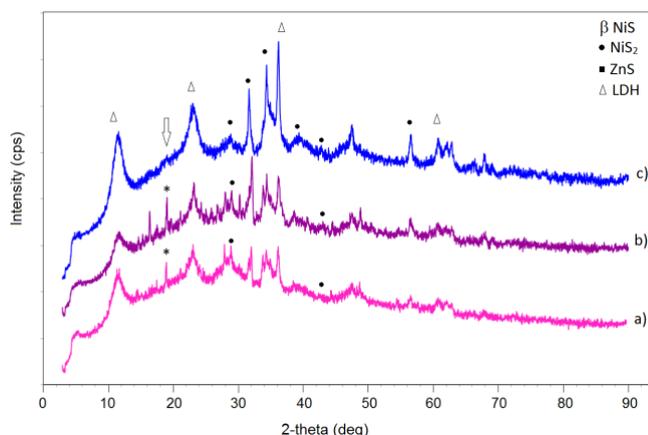


Figure 2. X-ray diffractograms of $\text{Ni}_x\text{Zn}_{1-x}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$ nanocomposites synthesized by 15 SILAR cycles: a) $\text{Ni}_{0.25}\text{Zn}_{0.75}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$, b) $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$ and c) $\text{Ni}_{0.75}\text{Zn}_{0.25}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$

The decrease of bandgap (E_{g2}) by $\sim 0.5\text{eV}$ with the sulfidation of $\text{NiZnAl-LDH}/\text{PVA}$ nanocomposites doped with sulfides is related to the synergistic effect (Table 2) calculated according to the absorption spectra. E_g in bulk NiS and ZnS is 2.1eV [10], [11] and 3.6eV [12], respectively.

Table 2. Bandgap values of obtained nanocomposites calculated according to Tauc's rule.

Samples	E_{g1} (eV)	E_{g2} (eV)	E_{g3} (eV)
$\text{NiZnAl-LDH}/\text{PVA}$	2.2	3.0	3.9
$\text{Ni}_{0.25}\text{Zn}_{0.75}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$	1.65	2.5	3.15
$\text{Ni}_{0.5}\text{Zn}_{0.5}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$	1.69	2.5	2.9
$\text{Ni}_{0.75}\text{Zn}_{0.25}\text{S}/\text{NiZnAl-LDH}/\text{PVA}$	1.5	2.6	2.65

The sorption and photodegradation of cationic and anionic dyes from aqueous solutions was studied in the synthesized and sulfide doped $\text{NiZnAl-LDH}/\text{PVA}$ nanocomposites. The obtained results were related to the physico-chemical properties of nanocomposites. Sorption and photodegradation were carried out at neutral pH and 5 mg/l (R6G) and 20 mg/l (P4R) concentrations of dye molecules. The sorbent amount was taken as 1g/L and the maximum absorbance for P4R and R6G was determined at 517 and 527 nm by UV-Vis spectrometer, respectively (Figure 3; 4).

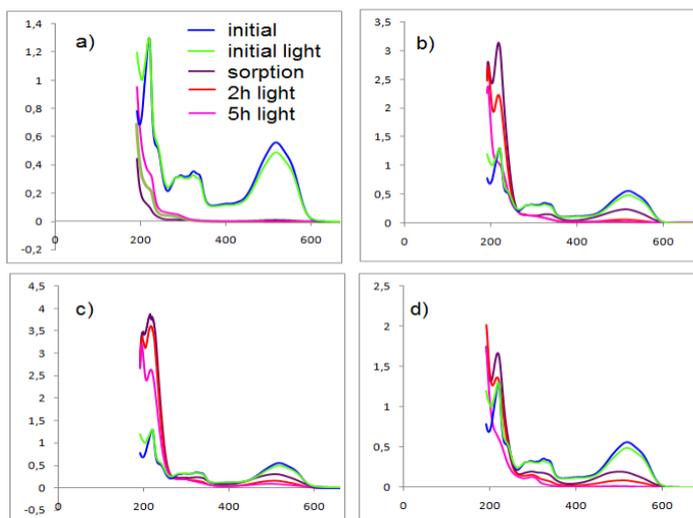


Figure 3. Removal of Ponceau 4R by the obtained nanocomposites. a) NiZnAl-LDH/PVA, b) Ni_{0.25}Zn_{0.75}S/NiZnAl-LDH/PVA, c) Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and d) Ni_{0.75}Zn_{0.25}S/NiZnAl-LDH/PVA

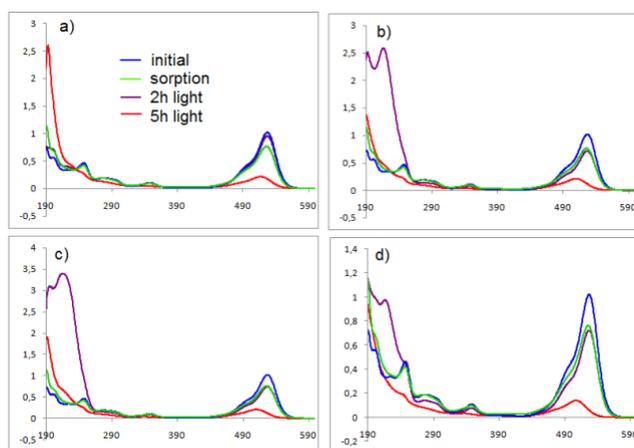


Figure 4. Removal of Rhodamine 6G by the obtained nanocomposites. a) NiZnAl-LDH/PVA, b) Ni_{0.25}Zn_{0.75}S/NiZnAl-LDH/PVA, c) Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and d) Ni_{0.75}Zn_{0.25}S/NiZnAl-LDH/PVA

As can be seen from Figure 3, the sorption rate of R6G with pure nanocomposite is low. It was found that the photodegradation degree of Ponceau 4R and Rhodamine 6G from water was 99.99% and 78.94 % with NiZnAl-LDH/PVA, 95.72% and 79.23% with Ni_{0.2}Zn_{0.8}S/NiZnAl-LDH/PVA, 83.29% and 79.62% with Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and 96.33% and 86.19% with Ni_{0.8}Zn_{0.2}S/NiZnAl-LDH/PVA under visible light for 5 hours under solar light. As can be see, the obtained metal sulfide/LDH/PVS nanocomposites are more effective for the photodegradation of cationic dyes (Figure 4).

CONCLUSION

In the present work, Ni, Zn and Al-based trimetallic layered double hydroxides have been synthesized into polyvinyl alcohol (PVA) matrix. The obtained nanocomposites were characterized by SEM, XRD, FTIR and UV technique. According to the Scherrer formula, the average particle size of LDH nanoparticles is 4.26 nm, 4.3 nm, 5.1 nm and 4.48 nm for NiZnAl-LDH/PVA, Ni_{0.25}Zn_{0.75}S/NiZnAl-LDH/PVA, Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and Ni_{0.75}Zn_{0.25}S/NiZnAl-LDH/PVA nanocomposites, respectively. Photodegradation of obtained

nanocomposites due to dyes was also studied. It was found that the photodegradation degree of Ponceau 4R and Rhodamine 6G from water was 99.99% and 78.94 % with NiZnAl-LDH/PVA, 95.72% and 79.23% with Ni_{0.2}Zn_{0.8}S/NiZnAl-LDH/PVA, 83.29% and 79.62% with Ni_{0.5}Zn_{0.5}S/NiZnAl-LDH/PVA and 96.33% and 86.19% with Ni_{0.8}Zn_{0.2}S/NiZnAl-LDH/PVA under visible light for 5 hours under solar light.

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