Evolutions of self-assembled Bi_2O_3/LDHs nanostructures to mixtures of mixed oxides and their photocatalytic effiecency under UV and solar light

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ABSTRACT

In this work we report self-assemblies of nanoparticles of Bi_2O_3 and layered double hydroxides (LDHs) obtained by exploiting the manifestation of the "structural memory effect" of ZnAlLDH and ZnCrLDH anionic clay matrices in $Bi(NO_3)_3$ aqueous solutions. Controlled thermal treatment of Bi_2O_3/ZnAlLDH and Bi_2O_3/ZnCrLDH self-assemblies gives rise to photoresponsive mixtures of mixed oxides, types Bi_2O_3/ZnO-$ZnAl_2O_4$ and Bi_2O_3/ZnO-$ZnCr_2O_4$, respectively. Powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (TEM) and UV-Visible spectroscopy (UV-Vis) showed that the LDHs reconstruction in $Bi(NO_3)_3$ solutions gives rise to specific nanoarchitectonics characteristics in which small NPs of Bi_2O_3 (~5 nm) are highly dispersed on the larger NPs (~150 nm) of ZnAlLDH and ZnCrLDH. UV-Vis analysis indicates the cooperative absorbance capabilities of the novel catalytic systems that were evaluated in the degradation process of phenol from aqueous solutions under solar and UV light.

Keywords: Bi_2O_3, LDHs self-assembled nanocomposites, solar irradiation, photocatalyst

1 INTRODUCTION

In recent years increasing attention is given on designing complex nanocomposites systems engineered to act as efficient photocatalysts; the unique nano size-dependent transport properties related to photons are able to establish specific photoresponsive functions that cannot be achieved by their bulk counterparts [1]. In this regard, manipulation of the photocatalytic properties by selective control of the catalyst nanoarchitectonics and by utilizing the collective properties of nanoassembly systems is a continuous challenge [2]. Design of photocatalysts nanoarchitectonics refers not only to their simple construction as nanomaterials but also to ensemble different nanoscaled structural building units in designed and defined ways for creating complex formulations owning collective and synergic properties [3]. Layered double hydroxides (LDHs) are a class of anionic clays. An important property of LDHs is their structural "memory effect"; it refers to the structural reconstruction of the layered clay matrix when the metal mixed oxides, evolved after the calcination around 550°C, are exposed to the aqueous solutions containing anions [4]. Using the manifestation of the LDHs structural "memory effect" in the aqueous solutions of metal salts, we have recently reported a simple fabrication procedure of nanoparticles of metal oxides-LDHs (MexOy/LDHs) as self assemblies [5]. According to this procedure LDH matrix is able to rebuild its structure by using the anions of the solution as interlayer anions and also to adsorb the metal cations of the aqueous solution and organizing them as nanoparticles (NPs) of metal oxides on its surface [6, 7]. MexOy/LDHs self-ensembled composites with a large compositional diversity can be designed by modifying either the nature of the metal cations of the LDHs layers and/or the nature of the NPs of MexOy. NPs of Bi_2O_3 has attracted a great deal of attention in the last years [8]. Hence the joined functionalities of NPs of Bi_2O_3 and LDHs might give rise to unique photoresponsive characteristics.

Herein, we report for the first time the self - assemblies of NPs of Bi_2O_3 with the specific compositions of ZnAlLDH and ZnCrLDH and their evolution, after the thermal treatment at 800°C to nanstructured mixtures of mixed oxides, types Bi_2O_3/ZnO-$ZnAl_2O_4$ and Bi_2O_3/ZnO-$ZnCr_2O_4$. The fabrication procedure of Bi_2O_3/LDHs is simple and cost-effective. It is based on the reconstruction of the LDH clays, due to the "structural memory" in the aqueous solution of $Bi(NO_3)_3$, at room temperature [6]. Results show that nanoarchitectonics of Bi_2O_3/LDHs and

the derived mixed oxides systems are active photocatalysts in the process of phenol photodegradation from aqueous solutions.

2 RESULTS AND DISCUSSIONS

2.1. XRD, TEM and XPS analyses

The crystalline structure of Bi_2O_3/ZnAlLDH and Bi_2O_3/ZnCrLDH - as reconstructed in Bi_2O_3 solution and after calcination at 800°C - was first characterized by XRD. Fig. 1A illustrates the characteristics of the obtained powder X-ray diffraction patterns of Bi_2O_3/ZnAlLDH and Bi_2O_3/ZnCrLDH. It reveals that Bi_2O_3/ZnAlLDHs consists of crystalline phases with reflections clearly assigned to the regular layered structure of hydrotalcite-like clay (ICDD file No. 22-700), in which a series of sharp and symmetric basal reflections of the (00ℓ, ℓ = 3, 6, 9) planes and broad, less intense, reflections for the nonbasal (01ℓ, ℓ = 2, 5, 8) planes are easily recognized [5].

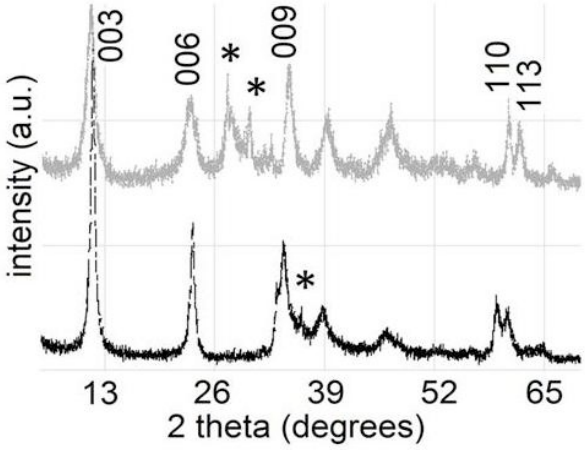

Fig. 1A. The XRD patterns of (-) Bi_2O_3/ZnAlLDH and (-) Bi_2O_3/ZnCrLDH.

On the other hand, besides the reflections assigned to the regular layered structure of LDH some weaker reflections, (marked by (*) in Fig. 1A), with positions which roughly coincide with those of mixed oxides that define the structure of the calcined LDHs can be also identified indicating that the structural reconstruction of the LDHs was not complete. Further, the structural characteristics of the mixtures of mixed oxides obtained after the calcination at 800°C of the as-synthesized and the reconstructed LDHs are shown in Fig. 1B for ZnAlLDH and Fig. 1C for ZnCrLDH, respectively. In Fig 1B some sets of diffraction peaks that can be indexed to hexagonal wurtzite ZnO (JCPDS file no 36-1451), $ZnAl_2O_4$ spinel (JCPDS file No. 5-0669) can be clearly identified while the new peaks observed at *2θ* values 27.9, 33.7, 46.6, and 47.1° might correspond to (121), (122), (041) and (104) diffraction planes of α-Bi_2O_3 (JCPDS no. 71−2274). Hence, in this case, a mixture of α-Bi_2O_3/ZnO-$ZnAl_2O_4$ was obtained. In comparison the XRD pattern of Bi_2O_3/ZnCrLDH calcined at 800°C indicates the formation of a mixture of mixed oxides, type α-Bi_2O_3/$ZnCr_2O_4$-ZnO.

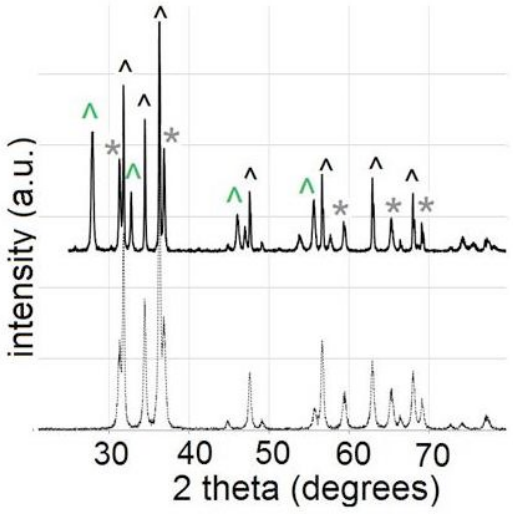

Fig. 1B. The XRD patterns of the mixed oxides derived from - Bi_2O_3/ZnAlLDH and - ZnAlLDH after calcination at 800°C; (^) Bi_2O_3, (^) ZnO, (*) $ZnAl_2O_4$.

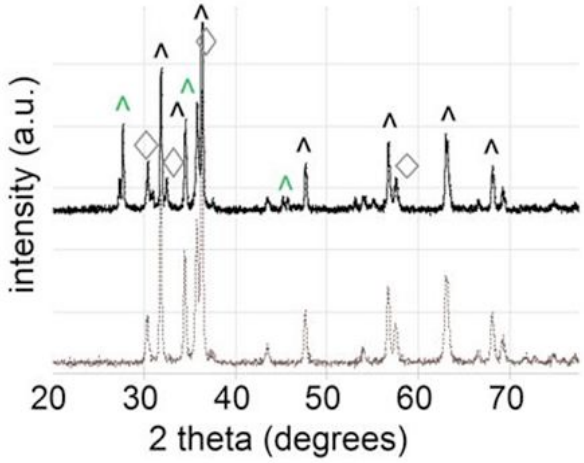

Fig. 1C. The XRD patterns of the mixed oxides derived from (-) Bi_2O_3/ZnCrLDH and (-) ZnCrLDH after calcination at 800°C; (^) Bi_2O_3, (^) ZnO, (◊) $ZnCr_2O_4$.

The detailed crystal structure and morphology was observed by TEM. Fig. 2A-D shows TEM as well as HRTEM images of Bi_2O_3/ZnAlLDH and Bi_2O_3/ZnCrLDH. Fig. 2A illustrates that the reconstructed LDHs shows the conventional LDHs morphology consisting of aggregates of platelet-like particles with average sizes of ~150 nm. In the typical transmission electron microscopy (TEM) image (see Fig. 2B and 2D) very small NPs can be clearly observed as dark spots highly dispersed on the larger particle of the clay; the average size of the loaded NPs is 4.7 nm for

Bi_2O_3/ZnAlLDH and 5.4 nm for Bi_2O_3/ZnCrLDH. The HRTEM image, (see Fig. 2C) indicates that the small NPs are highly crystalline with a well defined spacing of ca. 0.31 nm between adjacent lattice fringes, close to the d-spacing value of the (111) plane of α-Bi_2O_3 [9].

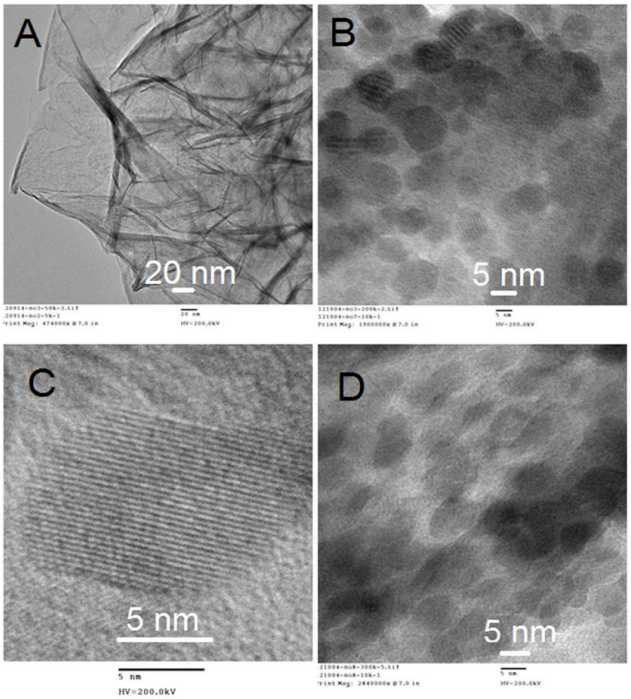

Fig. 2. The TEM and HRTEM images of Bi_2O_3/LDHs.

After calcination at 800°C the evolved mixed oxides presents different nano-sized features. Fig. 3 shows the TEM images of the mixed oxides Bi_2O_3/ZnO-$ZnAl_2O_4$ and α-Bi_2O_3/$ZnCr_2O_4$-ZnO. It reveals that the nanoarchitectonic of the mixed oxides systems might be described by two types of nanoparticles with diameters equal of 9 and 12 nm, respectively. It is interesting to note that in the mixed oxides nanoprticles are interconnected each others revealing a heterojuction between the mixed oxides.

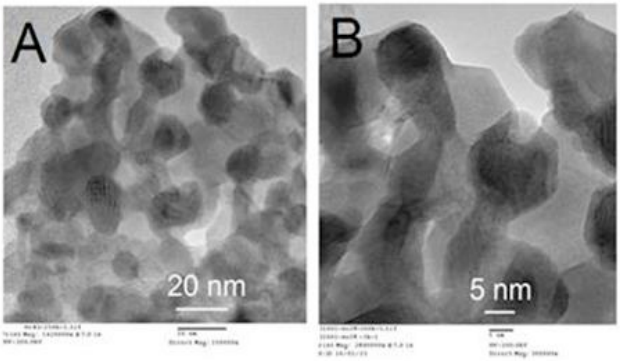

Fig. 3. The TEM images of (A) Bi_2O_3/ZnO-$ZnAl_2O_4$ and (B) Bi_2O_3/$ZnCr_2O_4$-ZnO.

XPS results further confirm the formation of Bi_2O_3/LDHs self-assemblies and indicate that their similar Bi content (equal to ~3%,). For Bi_2O_3/ZnAlLDH the survey EDX-XPS spectra is presented in Fig. 4 while the XPS spectra of Bi_2O_3/ZnCrLDH is given in Fig. 5. The analysis detected peaks from Bi, Zn, Al and O for Bi_2O_3/ZnAlLDH while Bi, Zn, Cr, and O were identified in the surface elemental composition of Bi_2O_3/ZnCrLDH. These results indicate the joined surface composition of AuNPs and specific LDH clay matrix.

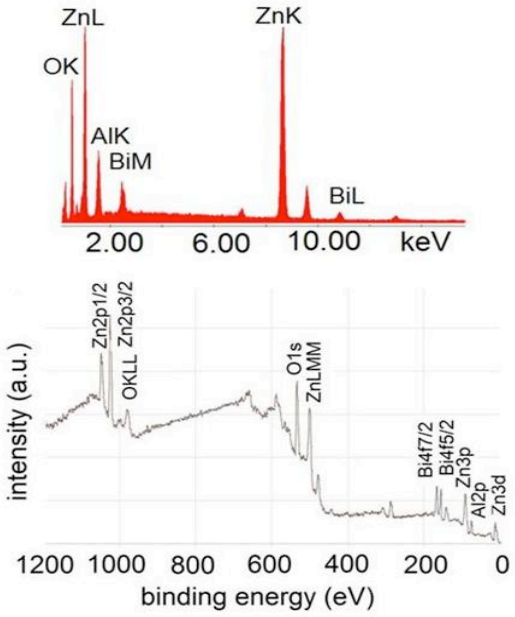

Fig. 4. High resolution XPS and EDX spectra of Bi_2O_3/ZnAlLDH.

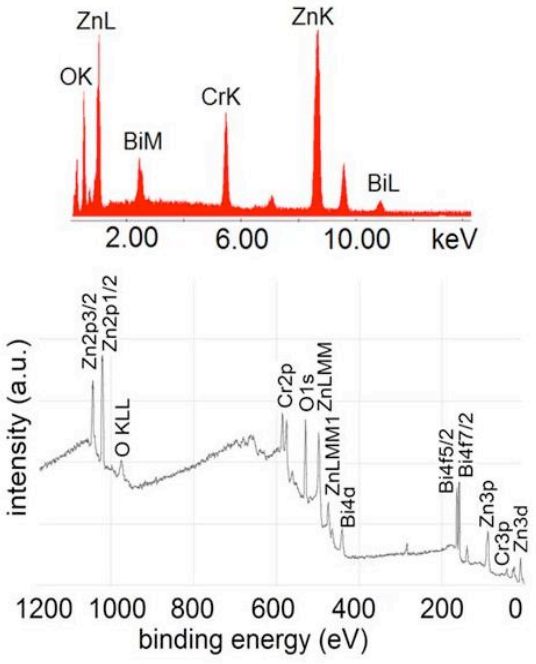

Fig. 5. High resolution XPS and EDX spectra of Bi_2O_3/ZnCrLDH.

2.2. Optical characteristics and photocatalytic properties

Fig. 6 displays the comparison of the room temperature UV-Vis absorption spectra of the studied catalysts. For all the samples the absorption in the UV region is defined by high intensities peaks that can be assigned to the optical responses of the LDHs and their derived mixed oxides.

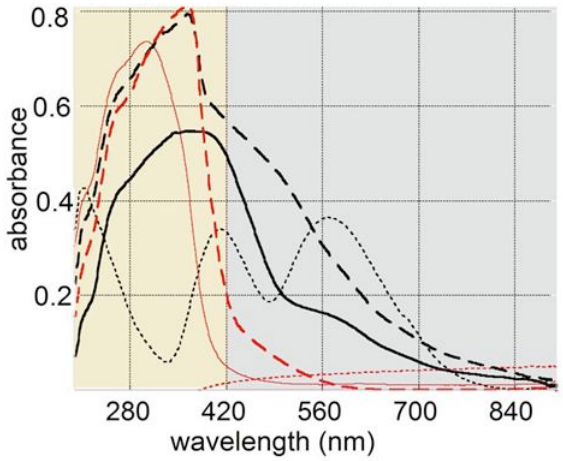

Fig. 6. The UV-Vis absorption spectra of: (-) Bi_2O_3/ZnAlLDH, (-) Bi_2O_3/ZnCrLDH, (---) Bi_2O_3/ZnO-$ZnAl_2O_4$ and (---) Bi_2O_3/$ZnCr_2O_4$-ZnO.

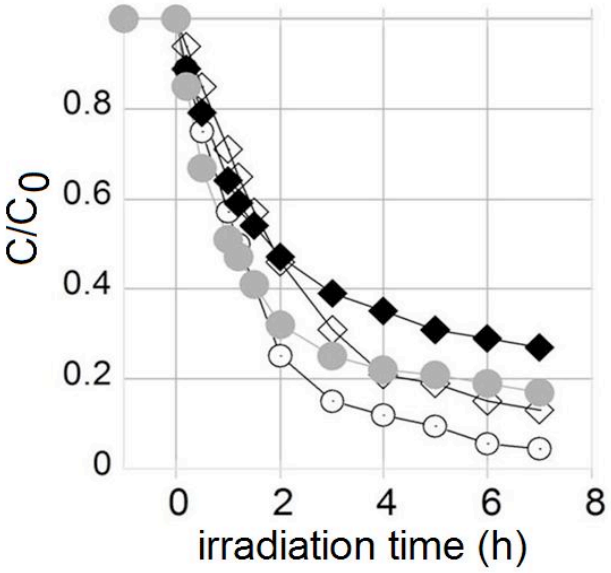

Fig. 7. Comparison of the photocatalytic efficiency of the catalysts during the photodegradation process of phenol over the entire range of wavelength: (●) Bi_2O_3/ZnCrLDH, (♦) Bi_2O_3/ZnAlLDH, (Θ) Bi_2O_3/ZnO-$ZnAl_2O_4$ (◊) Bi_2O_3/$ZnCr_2O_4$-ZnO.

One essential property relevant to the photocatalytic activity of a semiconductor is its energy band configuration. Tuning the energy band gap is a fundamental aspect of the design and fabrication of photocatalysts. The energy band gap configuration will define the absorption of incident photons, the carriers and the redox capabilities of excited-state electrons and holes [11]. Thus, a classical Tauc approach is used to estimate the optical direct band gap (Eg) values of the samples. The obtained Eg values are 3.11 for Bi_2O_3/ZnO-$ZnAl_2O_4$ and 2.27 for Bi_2O_3/$ZnCr_2O_4$-ZnO. For the entire range of wavelength the photocatalytic efficiency of Bi_2O_3/LDHs and the derived mixed oxides are compared in Figure 8. Controlled experiments indicate that that phenol pollutant does not degrade in the absence of photocatalyst. Bi_2O_3/ZnO-$ZnAl_2O_4$ shows the highest catalytic activity with almost complete degradation of the phenol after 6 h under irradiation while in the same conditions Bi_2O_3/ZnAlLDH degrades only 82% of phenol.

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