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Original

Synthesis of nanostructured metal–, semiconductor–, and metal/semiconductor–mordenite composites from geothermal waste

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Abstract

Successful synthesis of metal–, semiconductor–, and metal/semiconductor–mordenite nanocomposites, using geothermal solid waste as precursor is reported. Powders of nanostructured composites, consisting of metal and/or semiconductor nanoparticles grown on a mordenite-type zeolitic matrix surface, were synthesized by a one-step solvent-free and organic template-free process. The developed methodology is capable of controlling and tuning the final properties of composites from their synthesis and is also reproducible and repeatable. For comparison and demonstration of the application of the final products, dye photocatalysis degradation tests were done using commercial TiO_2 as reference (degradation reached ~75% in 215 min, $k = 0.004\ min^{-1}$), [M]–S–MOR samples revealed better performance (≥95% in 100 min, $k = 0.009\ min^{-1}$).

Keywords: Organic pollution remediation; Multifunctional nanocomposites; Aqueous synthesis; Photocatalysis; Geothermal waste remediation

1. Introduction

Contemporary chemical industries are searching for new techniques that reduce manufacturing costs and mitigate environmental impact. Processes without emissions and free of risky chemicals have therefore become a challenge for researchers, technologists and engineers (Ambec, Cohen, Elgie, & Lanoie, 2013). The lagoon of mineralized waters at the Cerro Prieto geothermal plant, in Mexicali, Mexico (Fig. 1a), is an excellent source of silicon; in an area of approximately 12.5 km^2, it is located between 115°12′ and 115°18′ west longitude and between 32°22′ and 32°26′ north latitude, 36 km away from Mexicali city. Beside the process of geothermal energy conversion, the saturated silica water is conducted to the precipitation lagoon to separate the silica residues from the reinjection water. The silica salts precipitate as amorphous silica, which is used in this work.

On the other hand, porous materials have potential applications in the chemical industry; likewise, the inclusion of transition metals and/or semiconductors into matrices to modify their properties has gained importance for the development of convenience materials (Bibby & Dale, 1985; Cooper et al., 2004). In the field of porous nanostructured materials, zeolites have been applied in areas such as catalysis, water treatment, H_2 production, among others (Zaarour, Dong, Naydenova, Retoux, & Mintova, 2014).

In this work, nanostructured composites based on metal, semiconductor or metal/semiconductor nanoparticles were grown on a mordenite-type zeolite matrix from geothermal

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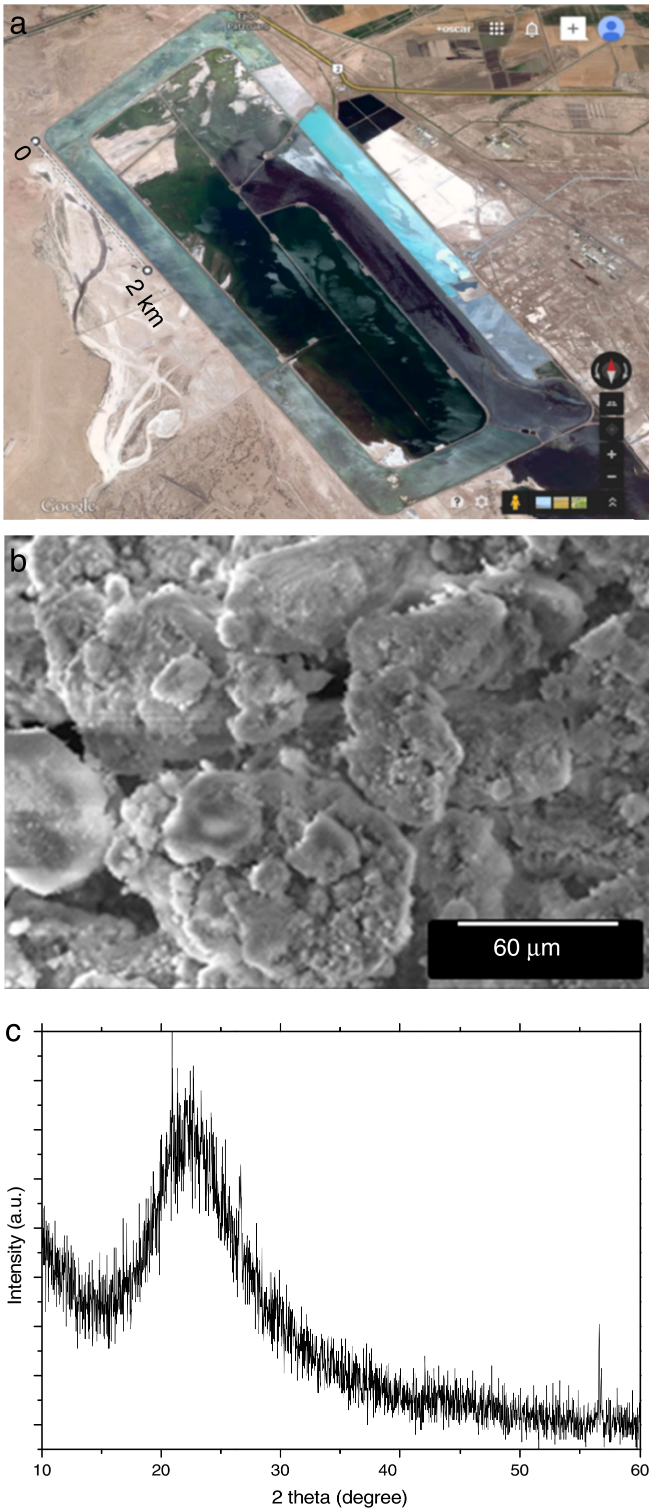

Fig. 1. (a) Aerial view of lagoon of mineralized waters at Cerro Prieto, Mexicali (INEGI-GOOGLE, 2015), (b) SEM image, and (c) DRX pattern of solid waste powders.

energy conversion solid waste materials by a solvent- and organic template-free process, with the inclusion of desired ion or ion combinations in a one step process leading to a series of materials with several potential applications. To demonstrate some of the potential applications, the use of [M]–S–MOR as photocatalyst is reported.

2. Materials and methods

Precursor SiO_2 powders (Fig. 1(b)) were obtained from geothermal energy conversion solid waste materials at Cerro Prieto plant.

Solid materials obtained from Cerro Prieto were cleaned by two mechanical wash processes, briefly, consist of mixing by stirring the solid residue obtained from the geothermal plant with deionized water, these washings are necessary to remove the clay that may have been mixed with the residue. X-ray diffraction (XRD) pattern analysis (Fig. 1(c)) revealed only an amorphous phase with the morphology shown in Fig. 1(b).

Elemental analysis by energy dispersive spectroscopy (EDS) confirmed the absence of any other element that could come from clays (Table 1).

Using this amorphous SiO_2 source, metal/mordenite ([M]–MOR) composites were synthesized with M = lithium, sodium, magnesium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, strontium, molybdenum, silver, cadmium, barium, lanthanum, gold, bismuth, and/or their mixtures, following the one-step route described in the MX/a/2012/013218 patent (Raymond, 2012). This process is solvent-, seed-, and organic template-free (avoiding the calcination processes to remove templates commonly used in the synthesis of zeolites), which involves 110 mL of a mixture of 0.1 M aqueous solutions of sodium silicate and aluminum sulfate (with SiO_2/Al_2O_3 molar relation of 15) that was stirred for 30 min; then, 30 mL of 0.1–0.3 M aqueous solution of desired ion salt was mixed with the first solution (this step is responsible to form nanoparticles in different concentrations). The final solution, with pH value of 9 ± 1, was autoclaved at 155 °C for 48 h. It eliminates the typical ion exchange process (to clarify, ion exchange is the most followed route to embed nanoparticles in silicon matrices, briefly, matrices were exposed to an concentrated solutions of the desired ion salt for at least 48 h then be washed) as it enables the inclusion of the desired ion (type and concentration) before the reaction. The possibility to select the ions before synthesis allows tuning the electro-optical properties and drastically reduces the obtaining time for this kind of materials because it does not require a calcination or evaporation process (Ren et al., 2012). The semiconductor/mordenite composites ([M]–S–MOR) are synthesized by exposure of the activated composites to an H_2S atmosphere for 24 h at room temperature.

Material composition, morphology and structure were studied by XRD with a Philips X'Pert diffractometer (CuKα radiation), by SEM using a JEOL JSM-5300 microscope with EDS attachment; by TEM with a JEOL JEM-2010 (with accelerating voltage of 200 kV), and by N_2 adsorption isotherms using a Tristar II 3020 Surface Area Analyzer. Optical properties were studied by UV–Vis spectroscopy using an AvaSpec-ULS2048-UA-50 spectrophotometer.