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C-doped ZnO nanorods for photocatalytic degradation of p-aminobenzoic acid under sunlight

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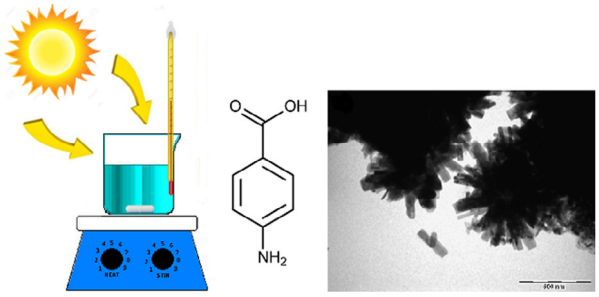
GRAPHICAL ABSTRACT



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ABSTRACT

The photocatalytic degradation of p-aminobenzoic acid was studied using C-doped ZnO nanorods as the catalyst synthesized through a low cost and simple precipitation method. The as-synthesized nanorods were fully characterized by SEM, TEM, XRD, BET and XPS. The photocatalytic degradation of p-aminobenzoic acid was carried out under sunlight irradiation. Optimal experimental conditions were determined for C-doped ZnO nanorods with a catalyst dosage of 0.5 g/L in a p-aminobenzoic acid solution, and 97% degradation was obtained. The results showed that the C-doped ZnO nanorods can be reusable and retain good photodegradation efficiency. A pseudo first order reaction was found to provide the best correlations, with a constant rate of 0.028 min^{-1}.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are a wide range of organic compounds including drugs, musk fragrances and even hormones now widely seen as environmental contaminants [1,2]. Water pollution has emerged as a primary concern in environmental issues due to the production and consumption of PPCPs. Sunscreens with UV filters are often used due to concerns of dangerous diseases caused by sun exposure, such as skin cancer [3]. UV-filters can be inorganic (with two permitted compounds: titanium dioxide (TiO_2) and zinc oxide (ZnO)), or organic (classified into different families: i.e. benzophenone derivatives, salicylates, cinnamates, camphor derivatives, p-aminobenzoic acid (PABA) and its derivatives, etc.) [4]. PABA was one of the first chemical ingredients contained in sunscreen products [5]. A recent research identified PABA metabolites in the urine and blood from children and adults, also in indoor dust [6,7]. UV filters residues are present in many places such as swimming pools; and they are be absorbed through the skin and into the bloodstream where prevail for some time and they can cause allergies [8]. The removal of this contaminant and so many others was studied. Hazardous dyes, or some heavy metal ions, for example, can be removed using waste materials by adsorption [9–15] or by photocatalysis. Photocatalysis

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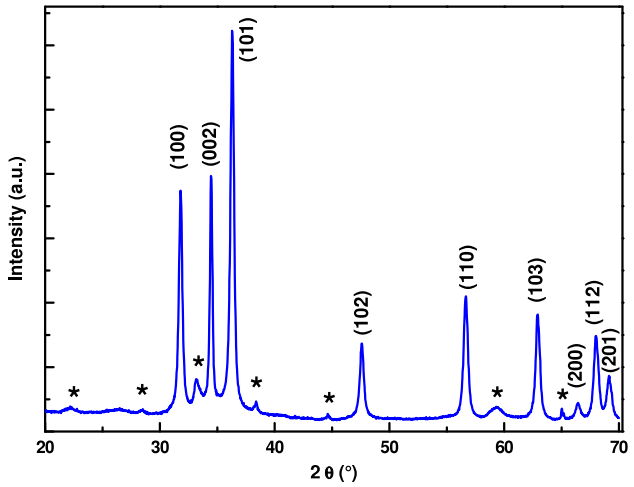

Fig. 1. XRD pattern of the C-doped ZnO nanorods.

has been emerged as a valid alternative to solve this problem. Various photocatalysts, especially metal oxide such as TiO_2, SnO_2 and ZnO have attracted extensive attention for the degradation of non-biodegradable pollutants under UV irradiation [16–20]. The photocatalytic degradation of PABA using TiO_2 has been reported recently [21,22].

ZnO is an interesting chemically and thermally stable n-type semiconductor with a large exciton binding energy of 60 meV, large band gap energy of 3.37 eV at room temperature, and a high photocatalytic activity [23]. The photocatalytic process is a chemical reaction where a semiconductor acts as a catalyst when is activated with an incident radiation. It is demonstrated that photocatalytic reactions can degrade even persistent organic pollutants with high molecular weight such as dyes. Doping the crystal lattice of ZnO with transition metals and non-metals allows a shift of the bandgap from the UV to the visible light. C-doped ZnO is an incipient visible-light-responsive photocatalyst recently used in cleaning up waste water, water splitting and photoelectrochemical cells [24–26]. In this paper we synthesized C-doped ZnO nanorods, by a simple and low cost precipitation method [27], and we have successfully discomposed PABA in a photodegradation reaction, with the obtained nanostructures as photocatalytic agents.

2. Experimental details

2.1. Synthesis of C-doped ZnO nanorods

For catalysts synthesis, all the reagents were analytical grade, and were used without further purification. In a typical synthesis, 2.195 g $Zn(CH_3COO)_2 \cdot 2H_2O$ zinc acetate dihydrate were dissolved in 100 mL deionized water resulting the solution A. With a similar procedure 0.8 g NaOH were dissolved in 50 mL of deionized water, forming the solution B. The molar ratio of NaOH: Zn acetate was 4:1. The solution A was added dropwise into the solution B at 60–65 °C with intensively mechanical stirring at 300 rpm during 1 h. The obtained precipitate was continuously aged for 3 h with vigorous stirring at the indicated temperature [28]. After that, the formed precipitate was cooled at room temperature and then filtered and washed several times with deionized water; finally it was vacuum dried in an oven at 80 °C for 8 h.

2.2. Photocatalytic activity measurements

The experiments were carried out as follows: 0.5 g/L of catalyst were added to a PABA solution (50 μM) in a quartz baker. The sample was kept in darkness for 30 min to achieve the equilibrium of adsorption and desorption and then irradiated. The suspension was continuously stirred (300 rpm) with the aid of a magnetic stirrer. The period of the experiment was between 10:30 and 14:00 during the month of April 2016. The irradiation fluence of the sunlight was estimated to be 0.1 W/cm^2. An aliquot was withdrawn from the system at specific time intervals and centrifuged to remove the photocatalyst. Two mL of deionized water was added to the aliquot each time for every sample to make centrifuge easy. The sample was conserved in the dark before analysis. A control run without ZnO catalyst was used as reference. Each photocatalytic measurement was performed by triplicate.

The degradation process was monitored by measuring the absorption of PABA at 265 nm using a UV–Vis spectrophotometer.

2.3. Characterization

The morphology of as-synthesized C-doped ZnO nanorods was characterized by scanning electron microscopy (SEM) on a Zeiss Supra40 Gemini, 3 kV microscope Transmission electron microscopy (TEM) observation was carried out on a Philips CM200 microscope operating at an accelerating voltage of 160 kV. ImageJ software was used to determine the diameter and length of the nanostructures.

The X-ray diffraction (XRD) patterns were recorded with Cu Kα radiation of 0.15418 nm in a diffractometer (PANalytical model Empyrean) having θ–θ configuration and a graphite secondary-beam monochromator, using a generator voltage of 40 kV and current of 40 mA. The data were collected for scattering angles (2θ) ranging from 20° to 70° with a step of 0.026° for 2 s per point.

The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on the adsorption data. The BET specific surface area and pore distribution of the samples which were degassed at 150 °C for 8 h were determined by N_2 adsorption/desorption method, which were carried out on a Micromeritics Accelerated Surface Area and Porosimetry System ASAP 2020 v 3.01 instrument. The surface chemical composition of samples was analyzed by high resolution X-ray photoelectron spectroscopy (HR-XPS) in a hemispherical electrostatic energy analyzer (r = 10 cm) with Al Kα radiation source (1486.6 eV). Binding energies in all XPS spectra were calibrated using C 1s peak (284.8 eV).

The UV–Vis measurements were recorded using a Shimadzu 1800 UV–Vis spectrophotometer.

3. Results and discussion

3.1. Morphological and structural characterization

The corresponding X-ray diffraction pattern of ZnO powder is shown in Fig. 1. The diffraction peaks at 2θ = 31.7°, 34.3°, 36.2°, 47.5°, 56.5°, 62.7°, 66.2° and 67.8° are identified to be the (100), (002), (101), (102), (110), (103), (200), (112) and (201). All of the indexed peaks in the obtained spectrum are well matched with the planes of ZnO hexagonal wurtzite structure (01-079-0207). The lattice constants calculated from the XRD data for (101) and (002) planes are $a = b$ = 3.259 Å, c = 5.218 Å [29]. The sharp diffraction peaks indicate the good crystallinity of the prepared samples. The secondary peaks (*) are probably associated to the intermediates (e.g. $C_{26}H_{27}O_2$) of the chemical synthesis.

Fig. 2 shows a SEM image of the samples. The images clearly reveal the hexagonal nanorods structure. The average diameter and length of the nanorods are 50 nm and 200 nm respectively. Different sizes of nanorods were observed and its surface was very smooth.

The TEM image obviously shows the tubular morphology of the nanorods. As seen in Fig. 3, a flower like nanostructure is observed and the measurement of the isolated nanorod is 70 nm wide and 250 nm length.