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The dc thermal plasma synthesis of ZnO nanoparticles for visible-light photocatalyst

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Abstract

It is known that ZnO is an n-typed semiconductor with band-gap energy of ∼3.2 eV and thus only absorbs UV light with the wavelength ≤385 nm. However, as far as photocatalytic efficiency and practical applications are concerned, it is desirable that ZnO absorbs not only UV but also visible light. In the present study, a novel dc thermal plasma reactor was used to synthesize ZnO nano-particles. We found that the kind of plasma affects the nanoparticle morphology and N_2 plasma favors formation of the spherical nanoparticles. Visible light absorption of the ZnO nano-particles was achieved by doping up to a few thousands ppm of nitrogen into the material. The effect of doping concentration and particle morphology on photocatalytic characteristics of the ZnO nanoparticles will be described.

Keywords: Nano particle; dc plasma; Visible-light photocatalyst

1. Introduction

Zinc oxide (ZnO) nanoparticles have recently received much attention due to a variety of applications such as UV absorption, NO_X decomposition, deodorization, and anti-bacterial treatment [1–3]. Various techniques have been used to synthesize ZnO nanoparticles and can be categorized into either chemical or physical methods [4]. The former are, for example, thermal hydrolysis technique [5], hydrothermal processing [6], and sol–gel method [7–9] while the latter are vapor condensation method [10], spray pyrolysis [11–13], and thermochemical/flame decomposition of metal-organic precursors [14,15]. It is known that ZnO is an *n*-type semiconductor with band-gap energy of 3.2 eV and thus can absorb UV light with the wavelength equal or less than 385 nm. However, for higher photocatalytic efficiency and many practical applications, it is desirable that photocatalyst such as ZnO should absorb not only UV but also visible light due to the fact that visible light accounts for 45% of energy in the solar radiation while UV light less than 10%. In order to absorb visible light, band gap of ZnO has to be narrowed or split into several sub-gaps, which can be achieved by implanting transitional metal ions, e.g. V, Cr or Fe [16–19], or by doping N [20–23].

In the present study, we used a novel dc thermal plasma technology to synthesize N-doped ZnO nanoparticles. The effect of nitrogen doping and particle morphology on photocatalytic characteristics of the ZnO nanoparticles will be described.

2. Experimental

2.1. Synthesis of ZnO nanoparticles

In the present study, a novel dc plasma reactor (Fig. 1) operated at 70 kW and atmospheric pressure was used to synthesize ZnO nanoparticles. Commercial zinc powder (Alfa Aesar) with an average particle size of 10 μm and containing impurities of Cr Fe and Pb less than 50 ppm were used as the raw material. The Zn powders were fed into plasma flame through carrier gas and subsequently underwent vaporization, oxidation and quench processes. Dop-

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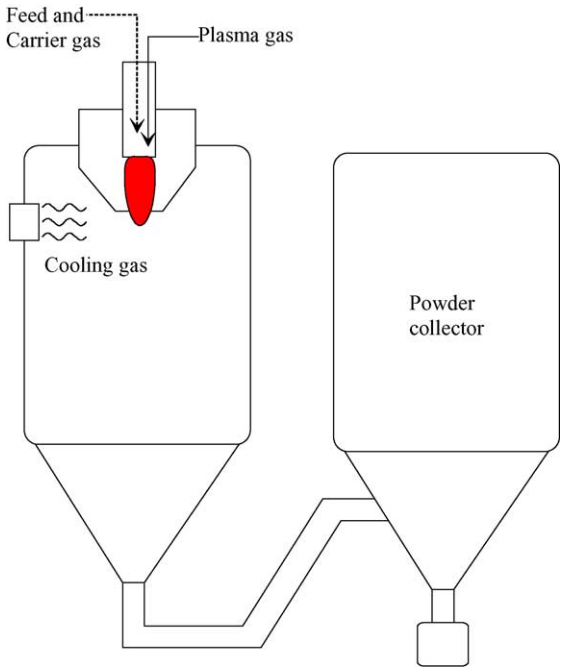

Fig. 1. Schematic of the dc plasma reactor.

Table 1
Processing conditions of the ZnO nano-powder

Specimen name	R-ZnO	T-ZnO	S-ZnO
Plasma-forming gas	50% Ar 50% N_2	50% Ar 50% N_2	100% N_2
Carrier gas	Air	N_2	N_2
Quenching gas	Air	Air + N_2	Air + N_2

ing nitrogen into ZnO nanoparticles was achieved by introducing nitrogen gas into the plasma-forming and carrier gases. Flow rates of the plasma, carrier and quenching gases are respectively in the range of 200, 10 and 3000 slm. The processing conditions are summarized in Table 1. Chemical compositions of the resulting nanoparticles are listed in Table 2.

2.2. Characterization of ZnO nanoparticles

The phase identity and crystallite size of the ZnO nanoparticles were determined using an X-ray diffractometer (XRD, Philip PW1700) operated at 40 keV and 40 mA with Cu Kα radiation. The scanning step size and the collection time for each step were set at 0.02° and 5 s, respectively. Nanocrystal size was analyzed through broadening of the XRD peaks

Table 2
Specific surface area (BET) and chemical analysis of the ZnO nanoparticles

Specimen	BET ($m^2\ g^{-1}$)	Pb (ppm)	Cr (ppm)	Fe (ppm)	N (ppm)
R-ZnO	7.2	10	<1	1.8	1250
T-ZnO	7.5	41.0	<1	1.8	1200
S-ZnO	15.1	30.0	<1	1.8	1770

using the Scherrer's formula as follows:

$$B_s = \frac{0.94\lambda}{d\cos\theta} \quad (1)$$

where B_s is the broadening from the sample, λ the wave length of X-ray, d the crystal size, θ the Bragg's angle. In addition, instrumental broadening (B_I) caused by slit width, sample size, sample penetration, imperfect focusing, and non-monochromaticity of the beam (α_1 and α_2 for example) was carefully calibrated. Assuming Gaussian shape for the peaks, the broadening from the sample (B_s) is calculated through

$$B_s^2 = B_m^2 - B_I^2 \quad (2)$$

where B_m is the measured broadening.

A field emission scanning electron microscope (FE-SEM, LEO 1530) and a transmission electron microscope (TEM, Jeol 2010) were used for morphological observations of the ZnO nanoparticles. The specific surface area of the resultant ZnO powders was determined by a nitrogen gas adsorption instrument (Micrometrics ASAP 2010) based on the BET method. Nitrogen elemental analysis was done with a nitrogen/oxygen determination (LECO Corporation, TC-436). The chemical composition of the nanoparticles was analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS, Spectro-P).

2.3. Photocatalytic testing

Methylene blue (MB) decomposition and anti-microbial testings were carried out to study photocatalytic ability of the ZnO nanoparticles. Based on the Beer–Lambert law [24], the methylene blue aqueous solution with 10^{-5} M is linearly proportional to the intensity of the measured spectrum. In the present study, the MB (10^{-5} M) solutions containing 0.2 wt.% of well-dispersed ZnO nanoparticles were illuminated employing a 6 W Xenon UV-lamp with the wavelength of 365 nm and a 13 W fluorescent lamp. To ensure no UV light radiation, irradiation from the fluorescent lamp was filtered through a 400 nm UV cut filter. The incident intensities of illumination of the UV and the visible light were set to 750 μW cm^{-2}, and 7000 lx, respectively. Photocatalytic decomposition of the MB solutions was characterized by a UV–vis spectrometer (HITACHI U-3010). The wavelengths that are prevailingly absorbed by MB are 665, 292, and 246 nm whereas the maximum peak occurs at 665 nm. The extent of decomposition was calculated from the integrated area of the peak at 665 nm.

Anti-microbial experiments using *Escherichia coli* (BCRC 11634) were performed with the suspension containing 0.2 wt.% ZnO nanoparticles of specimen in distilled water. The same bacteria were also cultured in distilled water as a reference specimen. Both samples were illuminated with the wavelength of 543 nm UV light and the intensity of 1500 lx for 6 h. Afterward, the samples were examined in the number of bacterium using an optical microscope.