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Exploitation of piezoelectricity for enhancing photocatalytic activity of ZnO nanowires

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ABSTRACT

We report on an investigation of the photocatalytic activity of substrate-supported ZnO nanowires (NWs) with Ag modification and induced bending. By degrading a 50 μM rhodamine B solution, it is found that the zeroth-order kinetic constant of Ag modified bent NWs is 1.4 and 2.2 times as high as that of Ag modified unbent NWs and unmodified as-grown NWs, respectively. The improvement due to bending is related to the piezoelectric property of ZnO that facilitates charge separation. The present work demonstrates the usefulness of piezoelectricity for photocatalysis.

1. Introduction

Photocatalytic activities of ZnO nanomaterials have been widely studied in recent years [1,11]. To improve the photocatalysis efficiency, several strategies have been reported in the literature. A straightforward approach is to modify the morphology of ZnO to increase the surface area [2,6]. Another one is to optimize the defects of ZnO to increase charge separation and/or reduce recombination of the photogenerated charge carriers [1,11]. Deposition of noble metal nanoparticles (NPs) on the ZnO surface is also effective because the metal act as an electron sink [7,9]. Alternatively, the energy band of ZnO can be modified by metal doping and optical absorption can be extended to the visible range [3,8,10].

The piezoelectric nature of ZnO is a well-known physical property. Utilization of the piezoelectric property for ZnO nanowire (NW) based energy generators and piezotronic devices has been studied recently [12,13]. The NW piezoelectricity can facilitate charge separation and improve photocatalysis. Such an endeavor, however, has not been realized so far. In this work, we report the enhanced photocatalytic activity of substrate-supported ZnO NWs with Ag modification and induced bending. By degrading a 50 μM rhodamine B (RhB) solution, it is found that the zeroth-order kinetic constant of Ag modified bent NWs is 40% higher than that of Ag modified unbent NWs and 120% higher than that of as-grown ones.

2. Experimental

The ZnO NWs were grown on Si substrates by thermal evaporation without catalysts [14–16]. The NWs were examined by a scanning electron microscope (SEM) and a high resolution transmission electron microscope (HRTEM). Photoluminescence (PL) spectra were measured by a fluorescence spectrometer with a spectral resolution of 1 nm. Two procedures were used for Ag modification. The first will be called the dry procedure. A NW sample was immersed in a 1 mM $AgNO_3$ solution for an hour, dried in air, and subject to 254 nm ultraviolet (UV) light irradiation for one min. The other will be called the wet procedure. A NW sample was immersed in the same solution, subject to UV irradiation for one min, and then dried in air. The NW photocatalytic activity was evaluated by degrading a 50 μM RhB solution with the use of three 4 W 254 nmHg lamps. A 20 μL drop was taken at a regular time interval. Absorption spectra were measured under an optical microscope that had a fiber-connected spectrometer with a spectral resolution of 1 nm. Six spectra of each drop were measured and averaged.

3. Result and discussion

For comparison, two different batches and two (identical) samples in each batch were prepared. As-grown NW samples with a larger diameter are called Samples A1 and A2, and the others with a smaller diameter are Samples B1 and B2. After Ag modification in the dry procedure, the samples are called A1-Ag and B1-Ag. After Ag modification in the wet procedure, the

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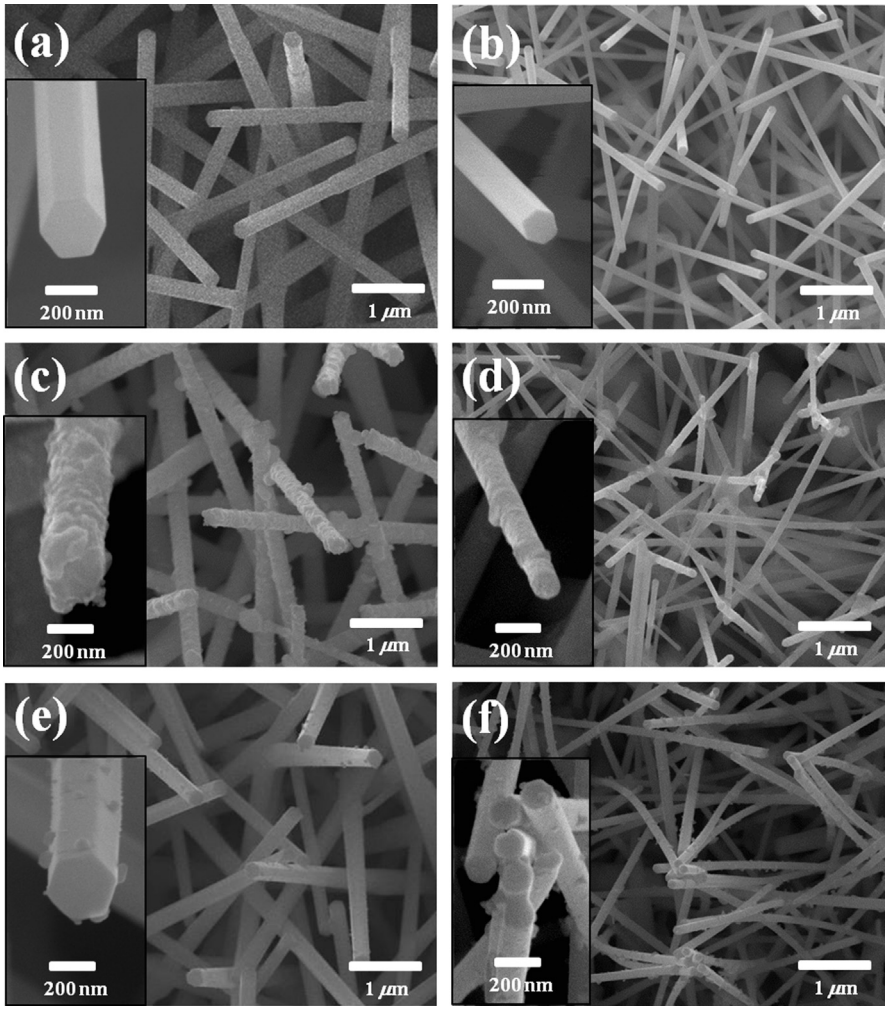

Fig. 1. SEM images of (a) and (b) as-grown ZnO NWs in Samples A1 and B1, respectively, (c) and (d) Ag modified NWs in Samples A1-Ag and B1-Ag, respectively, and (e) and (f) Ag modified NWs in Samples A2-Ag and B2-Ag, respectively. The insets are enlarged NW images.

samples are A2-Ag and B2-Ag. The SEM images of A1 and B1 are shown in Fig. 1(a) and (b), respectively. The insets reveal that the NWs have diameters of around 200 nm in A1 and 100 nm in B1. Fig. 1(c) and (d) are the SEM images of A1-Ag and B1-Ag, respectively. The NW surfaces in both samples are rough and covered with Ag, but the NWs remain straight.

Fig. 1(e) and (f) are the SEM images of A2-Ag and B2-Ag, respectively. As can be seen in the insets, the NW surfaces are smooth and decorated with Ag NPs (see below). The NWs in Sample A2-Ag are still straight, but the NWs in Sample B2-Ag are bundled at the top ends and become bent. As a result, Ag modified bent ZnO NWs are created. (From our experience, bent NWs can be created if the diameter is smaller than around 100 nm and the length longer than around 8 μm.) It should be mentioned that the bending may be partially due to the photoinduced piezo-optical effect of ZnO NWs in the sense that the piezoelectric coefficient is increased [17]. Fig. 2 is an HRTEM image of an Ag modified NW in B2-Ag and it reveals the Ag appears in the form of a NP. The lattice fringes confirm that the Ag NP is polycrystalline and the NWs is single crystalline. It is also clear in the inset that individual Ag NPs are on the surface of the NW.

Fig. 3 shows the PL spectra of the NW samples before and after Ag modification. The spectra of as-grown Samples A1 and A2 (or B1 and B2) are almost identical and only the result for A1 (or B1) is shown. The PL spectra of A1 and B1 exhibit strong UV emission with a peak at around 386 nm and slight blue–green sideband

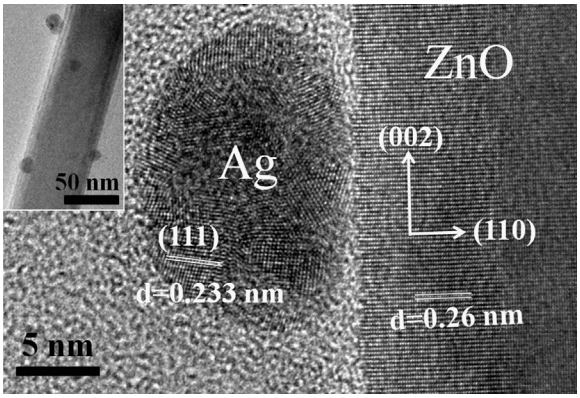

Fig. 2. HRTEM image of an Ag modified NW in Sample B2-Ag. The inset is a larger scale image and reveals that individual Ag NPs are on the NW surface.

emission. Structural defects in ZnO nanocrystals have been suggested to correlate with the green emission in a PL spectrum [11]. The slight sideband emission in the as-grown spectra confirms the good quality of the present NWs. It is also apparent that the thinner NWs in B1 have better crystallinity than the thicker NWs in A1. After Ag modification, the UV emission decreases appreciably. The decrease of UV emission has been attributed to the role of Ag as an electron sink that suppresses charge recombination [18]. In Fig. 3(a), the UV peak intensity of A2-Ag is only slightly lower than that