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Effective surface disorder engineering of metal oxide nanocrystals for improved photocatalysis



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ABSTRACT

Metal oxide (MO) semiconductors such as titanium dioxide (TiO₂) are often used in many photochemical processes (e.g. waste-water remediation). However, their large band gaps limit their catalytic performances. Various techniques have been developed to improve the photocatalytic activity of TiO₂ nanocrystals (NCs), e.g., via chemical doping, designing hybrid electronic structures, and creating surface disorders. Unfortunately, these techniques suffered from various disadvantages including complex/expensive operations and still poor photoactivity of modified TiO₂ under near-infrared (IR) light (53% of the full solar irradiation). Here, we demonstrate a simple but universal route to introducing continous internal energy levels in MO semiconductors, including TiO2, zinc oxide (ZnO) and indium oxide (In_2O_3) NCs. This new technique just requires simply heating a mixture of an MO NC with potassium (K). Distingctly from conventional MO NCs, NCs prepared using the present technique were all in black color and able to adsorb nearly full solar spectrum. As-prepared black TiO₂ NCs performed >300 times better than their conventional counterparts in the photocatalytic degradation of methylene blue (MB) dye under visible light irradiation. Similar levels of improvements in the photocatalytic performance were also achieved with as-prepared ZnO and In₂O₃ NCs. In addition, we show how NCs could be changed to black ones with tailored electronic structures. Our results suggested that the improvements in the NC's photoactivity were mainly attributed to the surface disorder induced, oxygen (O) vacancies and metallic phases likely formed during the reaction process with K.

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1. Introduction

As cost-effective semiconductors, metal oxides (MOs) such as TiO_2 and ZnO have been extensively investigated for various photocatalytic processes such as waste-water remediation, self-cleaning surfaces, and clean energy production (*e.g.* water splitting), because of their ability to capture and transfer abundant natural solar energy to chemical energy [1–12]. Unfortunately, due to their intrinsic large band-gaps, their light absorption efficiency is poor [13]. For example, TiO₂ has a band gap of ~3.2 eV and can only absorb UV light (only <4% of the full solar spectrum) [14]. The efficiency in utilization of the solar energy is further lowered when a nanosized MO is used (due to quantum confinement effect) though

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http://dx.doi.org/10.1016/j.apcatb.2016.10.054 0926-3373/© 2016 Elsevier B.V. All rights reserved. its high surface areas could be beneficial to a surfacial catalytic process.

The light absorption of MOs, in the case of catalysis, could be improved by designing a composite with a hybrid band structure [15,16] or introducing defects via chemical doping [17,18]. Although these two techniques could narrow down the band gap of MO via formation of new internal energy levels, the introduced defect levels are discontinuous and thus only active to specific narrow light regions. For this reason, the modified MO materials were usually not effective enough in utilizing solar light for photocatalytic reactions. Recently, a more promising approach was suggested for introducing continuous defect levels in TiO₂ to improve its photoactivity, via surface disorder and modification achieved by hydrogenation [12,19], Al/CaH₂ reduction [20,21], and other similarly-derived routes [22-25]. Nevertheless, the implementation of these techniques is still being hindered by several factors including a prolonged reaction time (5 days) [12], high processing temperature (e.g. 500 °C) [20,21], and poor light utilization efficiency in the near-infrared (IR) region (which accounts for nearly 53% of the full solar spectrum) [17]. Although some other improved routes (*e.g.* hydrogen plasma assisted chemical vapor deposition [26], water plasma assisted synthesis [27], magnesiothermic reduction with H₂ at a temperature as high as $650 \degree C$ [28]) were also attempted to disorder the surface of TiO₂, they were very complex and expensive. Moreover, few of these techniques have been demonstrated to be universally applicable to the cases of other MOs (*e.g.* ZnO and In₂O₃).

In this paper, we report a simple but more effective and universal technique based on surface disorder engineering, by which conventional MO nanocrystals (NCs) can be converted into excellent full solar light absorbers for photocatalytic reactions. The key step of this new technique is just simply mixing and heating an MO (TiO₂, ZnO and In₂O₃) NC with K. Although the reaction process is simple, it is very effective in forming MO NCs having various surface disorders, O vacancies, and considerably improved light absorbance in the full visible-near IR region. Differently from conventional MO NCs, all the as-prepared NCs were in black color and showed considerably improved photocatalytic performances.

2. Experimental

2.1. Materials

The main raw materials used included $TiO_2 NCs$ (<25 nm, product No. 637254), $In_2O_3 NCs$ (<100 nm, product No. 632317), MB (product no: M9140), methylene orange (product no: 114510), K (product no. 244864), NaNO₂ (product no: S2252) and KCl (product no. p9333), from Sigma-Alrdich, and ZnO NCs (10–30 nm, product No. US3590) from US Research Nanomaterials, Inc. Absolute ethanol (EtOH) and acetone were purchased from Fisher Scientific, and distilled water was prepared in our own laboratory.

2.2. Preparation of black MO NCs

For the preparation of black TiO₂, initially \sim 0.6 gK was put into a Pyrex tube with side connections to a vacuum pump. 1 g of white anatase TiO₂ NC was placed quickly into the tube and then vacuumed (10^{-3} Torr). Intense reaction between the NC and K was observed upon gently shaking the tube, and most of the original white NC was changed rapidly to black in just a few seconds. The tube was then kept at 140°C in a silicon oil bath (heated by a hot plate) for 1 h to allow the reaction to be completed (*i.e.*, until no original white powder remained). After the tube was cooled to room temperature, 20 mL absolute EtOH was poured into the Pyrex tube to safely react with K phases. The resultant black product was washed with 30 mL EtOH before being transferred to a 200 mL beaker. The black powder was collected via centrifugation, and washed repeatedly with 1:1 (volume ratio) EtOH/H₂O solvent until pH value of the dispersed product was close to 6 (the pH value of distilled water used), and finally dried for later use.

Preparation and purification procedures for black In_2O_3 were the same as those used for black TiO_2 , except 3 g of faint yellow In_2O_3 were reacted with 0.9 g K. As for the black ZnO, 1 g white ZnO was reacted with 0.6 g K at ~170 °C for 2 h. Its purification procedure was slightly different from that for black TiO_2 or In_2O_3 NCs. Upon black ZnO being transferred to a 200 mL beaker, 1:4.5:4.5 acetone/EtOH/H₂O (volume ratio) was used to wash away the residual K. The resultant black ZnO was rinsed with pure acetone, air-dried and then stored for later use.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda \sim 0.154$ nm,

40 kV, 40 mA) at 2° (2 θ)/min. For comparison, identical amounts of as-received NCs and as-prepared black NCs were used for XRD. Raman spectra of samples were recorded using a Renishaw Raman spectrometer with an excitation wavelength of 532 nm (2 mW laser). Since Raman response from as-received NCs was much stronger than that from as-prepared black NCs, for better comparison, 1% and 10% laser powers were used respectively for the cases of the former and the latter. 10% laser power was also used in the measurement of as-received NCs to confirm that the fine Raman response was the same as that in the case of using 1% laser power. The Raman peak of pure Si wafer at 520 cm⁻¹ was used to calibrate all the Raman modes of the NCs. Micro- and crystalline-structures of the NC samples were examined using a JEOL JEM-2100 TEM at an accelerating voltage of 200 kV. A Shimadzu-3600 spectrometer was used to record the UV/Vis absorption spectra (Fig. S6a) of as-received NCs (dispersed in distilled H₂O, in quartz cuvette with 1 cm light path). However, for UV/Vis-near IR diffusive reflectance and transmittance spectra (Figs. 3a, 6a and b, Fig. S3 and Fig. S6b-d) of NCs, a Shimadzu ISR-603 Integrating sphere attachment was used. In this measurement (200-2500 nm), identical amounts of as-received and as-prepared NCs were pressed respectively in the sample holder (with a standard scan speed). To investigate the absorption tail in the near IR region (Fig. S6b-d), a very slow scan rate was used to alleviate the influence from the instrument response and environmental background. The Shimadzu-3600 spectrometer was also used to measure the characteristic absorbance of the MB and methylene orange dye in the photocatalysis studies (no integrating sphere was used; the dye solution was measured in guartz cuvette with 1 cm light path). XPS was performed on a Kratos AXIS Nova X-ray photoelectron spectrometer with an excitation source of Al K α . The binding energy of XPS was calibrated based on C1s (284.6 eV). AC impendence measurements of NCs were carried out using a CHI 650C electrochemical workstation with three electrodes [reference electrode: Ag/AgCl, 1 M KCl, E (potential) = 0.235 V versus RHE; counter electrode: Pt; working electrode: glassy carbon (0.003 m effective diameter)], at an overpotential of 100 mV and a frequency between 10⁵ Hz and 0.01 Hz with an AC voltage peak of 1 mV. Photo-generated current was measured using a 0.5 M KCl electrolyte. Identical amounts (~10 mg) of as-received and as-prepared black NCs were deposited respectively on $1 \times 1 \text{ cm}^2$ ITO and airdried. The measurement was performed with a bias voltage of 0.1 V with and without AM 1.5G solar light illumination (Newport Oriel full spectrum solar simulator, 92250A-1000, 1.5 G, 150 W Xenon lamp) in an otherwise dark environment. The measurement of incident photon conversion efficiency (IPCE) was performed in air with an Oriel QE/IPCE measurement kit. N2 gas adsorption/desorption isotherms were determined using a Quantachrome Autosorb-iQ gas sorptometer via the conventional volumetric technique. The Brunauere-Emmette-Teller (BET) surface area was calculated based on adsorption data in the partial pressure (P/Po) range of 0.02–0.22.

2.4. Evaluation of photocatalytic performance

Solar-driven photocatalysis measurements were conducted by irradiating samples with a Newport Oriel full spectrum solar simulator (92250A-1000, 1.5 G, 150 W Xenon lamp). The average intensity of solar irradiation onto the solution was measured as 5.2 mW cm^{-2} by the ILT 550-RAA spectroradiometer at 9 different spots. 50 mg black NCs and 100 mL 20 ppm MB or methylene orange (50 mL 40 ppm MB or methylene orange was diluted with 50 mL NCs suspension) were placed in a beaker (inner diameter: 5 cm) to evaluate the catalytic performance. Control measurements of MB or methylene orange were carried out under the identical conditions but 50 mg white NCs or no NCs were used. To achieve only visible light irradiation, a 1 M aqueous solution of NaNO₂ was used

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