Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Photocatalytic, photoelectrochemical, and antibacterial activity of *benign-by-design* mechanochemically synthesized metal oxide nanomaterials

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ARTICLE INFO

Article history:
Received 21 May 2016
Received in revised form 6 July 2016
Accepted 14 July 2016
Available online xxx

Keywords:
Green synthesis
Photocatalysis
Environmental remediation
Mechanochemistry
Nanostructures

ABSTRACT

In the search for highly active and stable photocatalysts, significant efforts are devoted to find both new materials and innovative synthetic methods. In this study, an environmentally friendly and sustainable approach, dry reactive milling, was employed to synthesize two different semiconducting oxide nanomaterials, namely TiO_2 and ZnO using polysaccharides as sacrificial templates. The as synthesized nanomaterials were characterized by powder X-ray diffraction, transmission electron microscopy, scanning electron microscopy, diffuse reflection UV-vis and Raman spectroscopy, and N_2 adsorption tests. Their photocatalytic activity was tested in ethanol degradation, followed by gas chromatographic analysis. Photoelectrochemical measurements were performed to assess the optoelectronic properties and the antimicrobial activity of these photocatalysts was also tested under visible light irradiation. Overall, we found that the performance of the synthesized nanomaterials was comparable to the benchmark P25 EVONIK titania, with ZnO exhibiting a remarkably superior antibacterial activity against *E. coli*.

1. Introduction

Sunlight is undoubtedly the most valuable resource in the quest for a sustainable chemical and energy industry [1]. Photocatalytic (for thermodynamically downhill) and photo-driven (for thermodynamically uphill) processes [2] can both contribute to the efficient and selective transformation of raw materials to either useful fuels or chemicals. In this regard, nanoparticles of oxide semiconductors are attractive candidates to be employed in environmental remediation [3,4] (e.g., water purification), solar energy conversion (i.e., water splitting [5,6] or CO_2 reduction [7,8]), and biomass valorization [9,10] to obtain value-added products from earth abundant resources.

While there is an extensive and exponentially growing literature covering various fundamental and application oriented aspects of semiconductor photocatalysis (ranging from enhanced light absorption, through size effects, to crystallinity related phenomena) [2], much less attention has been devoted to synthetic procedures targeting a benign-by-design approach for nanomaterials preparation. TiO_2 nanomaterials have been extensively synthesized by means of different strategies [11], mostly related to sol–gel or hydrothermal methods. Despite these efforts, there is a continuously growing need for new methods, which result in crystalline samples with high specific surface areas and excelling physicochemical properties.

In addition, time and energy-efficient methods came to the forefront of interest recently, because they offer shorter energy payback time, which is of prime importance in all solar energy application schemes. For example, solution combustion synthesis [12,13] can be an attractive approach where the exothermicity of the reaction together with the release of different gases results in the formation of crystalline nanoparticles. Mechanochemical protocols ensure a rapid, mild, simple, and highly reproducible alternative to

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http://dx.doi.org/10.1016/j.cattod.2016.07.010
0920-5861/

conventional methods [14]. In addition, solvent-free (dry milling) mechanochemistry can offer additional remarkable possibilities in the development of advanced catalytically active materials [14]. For example, a composite of two different metal oxides (ZnO and SnO_2) has been reported to be obtained in a one pot synthesis [15]. Mechanochemically synthesized ZnO could also be directly embedded into synthetic polymers during the synthesis with promising uses as antibacterial coating [16].

One important drawback of these methods is the limited control over particle size and morphology (thus specific surface area) of the resultant material. The application of soft and hard templates is a feasible avenue to circumvent this issue. There are nice examples in the literature for template synthesis [17–19], where the shape and size of the synthesized nanostructures were precisely controlled. Most of these studies, however, employed synthetic polymer or anodized alumina templates, which are prepared in procedures with significant environmental footprint [20]. As an alternative, biopolymers can also be used as sacrificial templates, thus achieving biomass valorization while synthesizing oxide semiconductor nanostructures [21]. Different metal oxides and metal/metal oxide hybrids were obtained in this manner, such as CeO_2 [22] and TiO_2/Au [23].

We have previously reported the benign-by-design preparation of ZnO nanocrystals via an efficient dry reactive milling methodology using $Zn(NO_3)_2$ as metal precursor and various polysaccharides (including a biomass-derived agar extracted from macroalgae) as sacrificial templates [24]. This approach united the benefits of mechanochemistry and template synthesis, while employing a template from environmentally sustainable sources.

In continuation with such studies, the proposed work was aimed to: (i) study the feasibility of the mechanochemical templating approach for a range of photoactive nanomaterials as well as (ii) to investigate the photoelectrochemical, photocatalytic, and antimicrobial properties of mechanochemically synthesized nanostructures. In this regard, two different oxide semiconductors (ZnO, TiO_2) were prepared via dry reactive milling, using polysaccharides such as starch as biotemplate. The most important finding of this study was that the performance of mechanochemically synthesized nanomaterials was similar to those of a commercial benchmark material (EVONIK P25 TiO_2) in terms of photocatalytic and photoelectrochemical activities, while ZnO exhibited an outstanding antimicrobial activity.

2. Experimental section

2.1. Materials

The metal oxide precursors, namely $Zn(NO_3)_2{\cdot}6H_2O$ (>99%), titanium isopropoxide (>97%) were all purchased from Sigma Aldrich. Commercially available P25 TiO_2 (EVONIK) was used for benchmarking purposes. Na_2SO_4 (Alfa Aesar, anhydrous 99%) and Na_2SO_3 (Sigma Aldrich, >98%) were used in all the photoelectrochemical (PEC) experiments along with N_2 (Messer, 99.995%) gas. All chemicals were of the highest purity commercially available, and were studied without further purification. Deionized water (MilliPore, 18 MΩ) was used to prepare all solutions.

2.2. Synthetic procedure

The preparation of bio-templated nanomaterials was carried out employing a ball milling protocol similar to that previously reported by the Luque group [24]. In a typical experiment, the desired quantity of metal precursors, namely $Zn(NO_3)_2{\cdot}6H_2O$ and titanium isopropoxide were milled separately with a certain quantity of starch to reach a 1:4 metal precursor/starch weight ratios (i.e., 2 g zinc nitrate milled with 8 g starch) in a 125 cm^3 stainless steel recipient of a Retsch PM100 planetary ball mill at 350 rpm for 30 min (optimized conditions) [24]. 18 stainless steel balls of 1 cm diameter were employed. Upon milling, the slightly colored solids were directly transferred to a ceramic vessel and subsequently calcined in air at 600 °C for 4 h. Calcination temperature was selected based on previous thermal decomposition studies which indicated that most organics were removed from the material after 500 °C [24].

2.3. Characterization methods

Diffuse reflectance UV-vis spectra were recorded by an Avantes AvaSpec2048 equipped with an Avasphere-50 type integrating sphere. Raman spectra were obtained with a Thermo Scientific™ DXR™ Raman microscope at an excitation wavelength of 532 nm, applying 10 mW laser power, and averaging 20 spectra with an exposition time of 6 s. The X-ray diffractograms of the powdered photocatalyst samples were recorded on a Philips X-ray diffractometer (XRD) (PW 1930 generator, PW 1820 goniometer) with Cu Kα (λ = 0.1542 nm) as the radiation source at ambient temperature, in the 10–70° (2Θ) range applying 0.02° (2Θ) step size. For Rietveld refinement the software GSAS [25] was used with an EXPGUI [26] graphical user interface. Transmission electron microscopic (TEM) investigation was performed using a FEI Tecnai G^2 20 X-Twin type instrument, operating at an acceleration voltage of 200 kV. Scanning Electron Microscopic (SEM) images were captured on a Hitachi S-4700 FE-SEM instrument.

Specific surface area of the powdered photocatalyst samples was determined by a Micromeritics gas sorption analyzer (Gemini Type 2375) at 77 K in liquid nitrogen. The adsorption and desorption branches of the isotherms were determined. Prior to measurements the samples were pre-treated in vacuum (ca. 0.01 Torr) at 393 K for 2 h. The sample holder was loaded with ca. 0.1–0.3 g sample. The adsorption isotherms were analyzed by means of the BET equation.

Photoelectrochemical measurements were performed with an Autolab PGSTAT302 instrument, in a classical one-compartment, three-electrode electrochemical cell. The various metal oxide nanoparticles were spray coated from a 2-propanol solution (1 mg cm^{-3} concentration) on ITO glass electrodes (~0.1 mg cm^{-2}) and were used as working electrodes. A large Pt foil counterelectrode and an Ag/AgCl/3 M KCl reference electrode completed the cell setup. The light source was a 300 W Hg-Xe arc lamp (Hamamatsu L8251). The radiation source was placed 3 cm away from the working electrode surface. Photovoltammetry profiles were recorded in both 0.1 M Na_2SO_3 and 0.1 M Na_2SO_4 electrolyte, using a slow potential sweep (2 mV s^{-1}) in conjunction with interrupted irradiation (0.1 Hz) on the semiconductor coated electrodes. All procedures were performed at ambient temperature (20 ± 2 °C).

The photocatalytic activity of the photocatalyst films was probed by ethanol degradation tests under LED-light illumination (General Electric, Hungary, 7 W, λ = 405 nm) [27]. Photooxidation of ethanol vapor on catalyst films was performed in a circulation reactor (volume ca. 165 cm^3) at 25.0 ± 0.1 °C. The light source was fixed at 50 mm distance from the 25 cm^2 films. The irradiance reaching the sample was 14.8 mW cm^{-2} (determined by actinometry). After injection of ethanol and water vapor, the system was left to stand for 30 min for the establishment of adsorption equilibrium, and C_0 was always determined after the adsorption completed. The composition of vapor phase was analyzed by a gas chromatograph (Shimadzu GC-14B) equipped with a thermal conductivity (TCD) and a flame ionization detector (FID). The flow rate of the gas mixture in the photoreactor system was 375 cm^3 min^{-1}. The initial concentration of ethanol was 0.36 ± 0.018 mmol dm^{-3} at a relative humidity of ~70%.

Please cite this article in press as: G.F. Samu, et al., Photocatalytic, photoelectrochemical, and antibacterial activity of *benign-by-design* mechanochemically synthesized metal oxide nanomaterials, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.07.010