Materials Letters 116 (2014) 282–285

Contents lists available at ScienceDirect

Materials Letters

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

Renewable zinc dioxide nanoparticles and coatings

Petr V. Prikhodchenko [a,*], Alexander G. Medvedev [a,b], Alexey A. Mikhaylov [a,b], Tatiana A. Tripol'skaya [a], Luis Cumbal [c], Rimma Shelkov [b], Yitzhak Wolanov [b], Jenny Gun [b,d]

[a] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, Moscow 119991, Russia
[b] The Casali Institute and the Institute of Chemistry, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Jerusalem 91904, Israel
[c] Universidad de las Fuerzas Armadas, Ctr Nanociencia & Nanotecnol, Lab Materiales Avanzados, Quito, Ecuador
[d] The Hadassa Academic College, POB 1114, Jerusalem 91010, Israel

ARTICLE INFO

Article history:
Received 11 September 2013
Accepted 8 November 2013
Available online 17 November 2013

Keywords:
H_2O_2
Zinc dioxide
Clays
AOP
Solid peroxide
Nanoparticles

ABSTRACT

Nanoparticles of zinc peroxide, a well known and convenient solid source of hydrogen peroxide, oxygen or active oxygen species, can be readily regenerated by exposure of zinc oxide to slightly basic hydrogen peroxide solutions after being depleted of their active oxygen peroxide content, and these charge–discharge cycles can be repeated many times. We demonstrate the renewability of zinc peroxide coated mica and neat zinc peroxide powders by permanganometric titration, powder X-ray studies, thermal analysis and Raman spectroscopy, all showing good recovery with a rather small change of properties upon repeated cycling. We believe that renewable zinc peroxide can be useful for rechargeable antibiofouling or antifungal paints, clothing additive, floor coverings and other applications where hydrogen peroxide is slowly depleted and should be reloaded to regain its favorable activity.

1. Introduction

Considering the wide scope of zinc oxide applications [1–6] as pigments, in cosmetics and sunscreens, as photocatalysts, as plastics fillers, and in modern electronics and energy conversion and storage devices, the even wider use of hydrogen peroxide [7] in related fields of biocidal activity, environmentally friendly oxidizers and disinfectants [8], and on top of that the growing recent attention to zinc peroxide synthesis [9–11] and conversion to zinc oxide [12] and its reported antiseptic [13] and biocidal-antifouling activity [14,15], a regenerable zinc dioxide coating that is converted to zinc oxide upon use and then regenerated again and again is a promising generic wide-scope, green-chemistry material. However, to date, as far as we know, such rechargeable anti-biofouling agent has never been described, for any wide-use oxidizer, let alone solid peroxide.

In a recent article, Wolanov et al. [15] demonstrated a new method for production of zinc dioxide nanoparticles from ammoniacal solution of zinc acetate by addition of hydrogen peroxide. They further demonstrated that the zinc dioxide decomposition in water is thermodynamically controlled, and the zinc peroxide maintains its peroxide content in aqueous solutions down to pH 6, over two pH units lower than calcium and magnesium peroxides. As far as we know there is no other reported example of a solid peroxide that can maintain its peroxide content at such low pH. At low pH, Zn^{2+} is the dominant aqueous species, but over a wide basic pH range zinc oxide is stable, and thus at near neutral and slightly basic conditions the zinc dioxide is converted to zinc oxide after its peroxide is used up. This opens the possibility of using the zinc peroxide as a hydrogen peroxide source, be it for photocatalysis, disinfection, antifouling or dioxygen source, and then, after it is depleted of its active oxygen content, use hydrogen peroxide solution to convert the zinc oxide to zinc peroxide. In this communication we describe two materials, zinc dioxide coated mica (Muscovite) platelets and neat zinc dioxide nanoparticles. Coated mica, clays and particulates are of wide use as pigments and plastic additive, but neat peroxides contains higher concentration of peroxide and thus could be better analyzed by conventional material science techniques. Phyllosilicate supported ZnO_2, let alone ZnO_2 nanocoating of mica was never reported before.

A solid form of hydrogen peroxide can be useful in a wide range of applications where the peroxide is slowly depleted but can be renewed by treatment with aqueous solution of hydrogen peroxide. Rechargeable antibiofouling paints, sterile clothings, and floor coverings in sterile areas (e.g. hospital operation rooms) are examples of such applications.

2. Materials and methods

Neat zinc peroxide was produced by Wolanov's procedure [15] and the mica coating by zinc peroxide was produced by a modified

---

[*] Corresponding author. Tel.: +74959554850.
E-mail address: prikhman@gmail.com (P.V. Prikhodchenko).

0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.11.042

procedure, whereby the mica platelets were suspended in the zinc acetate—ammonia solution and the zinc peroxide was precipitated selectively on the mica by addition of 30 wt% hydrogen peroxide. The detailed protocols and details of the instrumental characterization by HR TEM, HR SEM, X-ray powder diffraction, Raman spectroscopy are presented in the Supplementary material. The presence of ammonia was proven pertinent for successful coating, because without the ammonia the zinc peroxide precipitated indiscriminately upon addition of hydrogen peroxide. The ammonia complexes the zinc ions, prevents homogeneous precipitation and directs the zinc dioxide precipitation to the hydrogen peroxide activated surface of the mica. The activation of the mica and other oxygen containing surfaces by hydrogen peroxide was reported for the peroxo-particulates of tin and antimony [16–18]. Indeed, addition of sodium alkaline base instead of ammonia resulted in zinc dioxide precipitation rather than mica coating.

We used conventional instrumental material characterization techniques which are described in the Supplementary material. Wet chemistry permanganometry [7] was used for accurate assessment of the hydrogen peroxide content. The method is based on titration of the hydrogen peroxide by a (purple) solution of potassium permanganate. The accuracy of the method is less than 2%.

3. Results and discussion

SEM and TEM micrographs of the neat zinc peroxide and the coated mica are depicted in Fig. 1a and d. The TEM inset in Fig. 1a shows particles of about 40 nm that are comprised of aggregates of several 4–5 nm nanocrystals. The SEM image of coated mica in frame d shows that the ZnO_2 decorates the entire surface of the larger, 15 μm mica platelets. The procedure can be repeated twice yielding a complete coating of the mica surface (Fig. S1a of Supplementary material). The procedure can be applied also to other substrates. Fig. S1b in the Supplementary material demonstrates a micrograph of a coated glass slide.

Permanganometric titration [7] showed that the zinc dioxide particles contained 13.5 wt% active oxygen (i.e. 27 wt% peroxide), which is 82.2% of the theoretical value expected of pure zinc dioxide. The remaining 17.8% presumably being amorphous zinc hydroxide. The coated mica contained 4.8% active oxygen (i.e. 9.6 wt% peroxide). X-ray studies of the neat zinc dioxide particles and the coated mica confirmed that the material is indeed cubic zinc dioxide (lowest curves in the left and right frames of Fig. 2, respectively). The size of the neat zinc dioxide crystalline grains was calculated to be about 3 nm by the Scherrer equation (not far from the 4–5 nm crystals that are observed in Fig. 1). It was not possible to apply the Scherrer calculation for the mica coating due to the overlapping signals of the Muscovite mica.

Differential Scanning calorimetry (DSC) studies (Fig. 3a, upper curve) show an exothermic peak of peroxide decomposition starting at 180 °C, which does not exist in the thermogram of ZnO (Fig. 3a, bottom curve).

A Raman study of the zinc peroxide (Fig. 3b, curve 2 from bottom) confirmed the formation of the ZnO_2 phase, with a sharp O–O stretching band at 837 cm^{-1} and a small peak at 480 cm^{-1} assigned to the Zn–O vibrations (as demonstrated for the Raman study of ZnO in the bottom curve of the same figure). The small peak around 2900 cm^{-1} is assigned to vibrations of hydroperoxide OOH− ions on the surface of ZnO_2 crystals or to H_2O_2 which can be adsorbed from the solution or obtained due to the reaction with CO_2 or H_2O from the atmosphere [19] and agrees with previously reported data for nano-dimensional zinc peroxide [20].

After full characterization of the zinc peroxide powder and coated phyllosilicate we continue to prove the main claim of this communication, namely, that the zinc peroxide and its mica supported forms can be regenerated after hydrogen peroxide decomposition. We used two methods to decompose the peroxide, 250 °C thermal treatment and Xe irradiation. Detailed procedures are described in the Supplementary material. In both cases the material was regenerated by immersion in 30% hydrogen peroxide after peroxide decomposition.

We conducted ten cycles of decomposition and reloading of the peroxide in the zinc dioxide powder, and the respective instrumental analysis after peroxide reloading is depicted in Figs. 1–3, which present also the response of the as—synthesized material (as described above). The electron images of the zinc dioxide powder (Fig. 1) show only a slight morphological change of the shape of the particles with repeated H_2O_2 charge–discharge cycles. The XRD diffractograms (Fig. 2) show that there is a certain amount of Zincite after repeated cycling, but the calculated Scherrer crystallite size of the ZnO_2 phase remained practically unchanged, around 3 nm upon repeated cycling. The Raman spectra, which are depicted in Fig. 3b, confirm that in all ten cycles zinc dioxide exists after reloading.

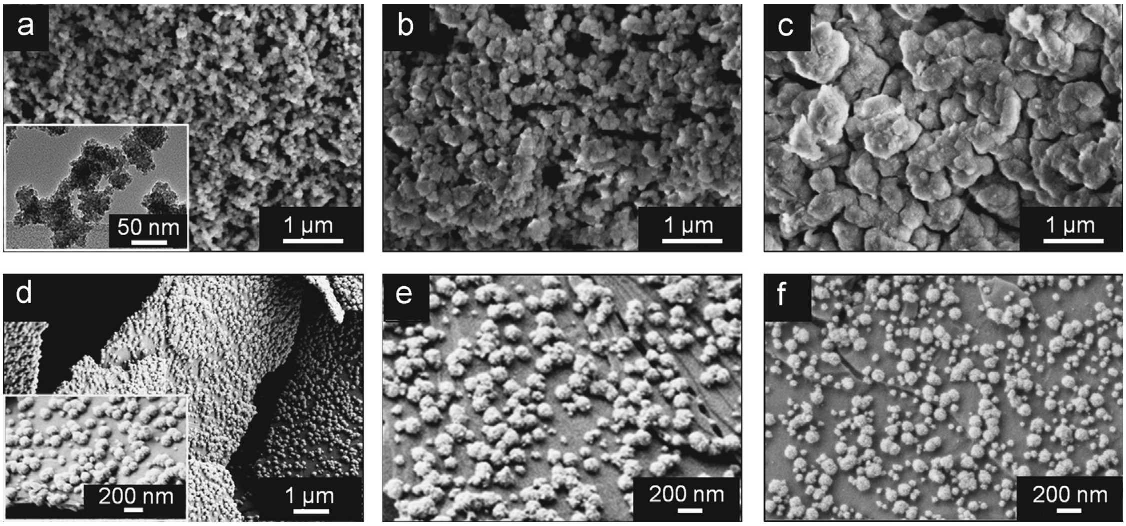

Fig. 1. Upper row: SEM images of neat zinc peroxide nanoparticles as prepared (a) and after the first and sixth reloading cycles ((b) and (c), respectively). Inset (a) shows TEM image of the respective material. Lower row: SEM images of zinc peroxide decorated mica as prepared (d), after heat treatment at 250 °C (e), and after peroxide regeneration (f). The inset in frame (d) presents a higher magnification.