Accepted Manuscript

CeO_2 nanoscale particles: Synthesis, characterization and photocatalytic activity under UVA light irradiation

Laouedj Nadjia, Elaziouti Abdelkader, Benhadria Naceur, Bekka Ahmed

PII: S1002-0721(18)30173-X

DOI: 10.1016/j.jre.2018.01.004

Reference: JRE 136

To appear in: *Journal of Rare Earths*

Received Date: 2 August 2017

Revised Date: 30 December 2017

Accepted Date: 2 January 2018

Please cite this article as: Nadjia L, Abdelkader E, Naceur B, Ahmed B, CeO_2 nanoscale particles: Synthesis, characterization and photocatalytic activity under UVA light irradiation, *Journal of Rare Earths* (2018), doi: 10.1016/j.jre.2018.01.004.

CeO_2 nanoscale particles: Synthesis, characterization and photocatalytic activity under UVA light irradiation

Laouedj Nadjia [1], **Elaziouti Abdelkader**[2,*] **Benhadria Naceur** [1], **Bekka Ahmed**[1]

[1] Laboratory of Inorganic Materials and Application L.I.M.A, University of Science and Technology Oran Mohammed Boudiaf (USTO M.B). PB 1505 El M'naouar 31000 Oran, Algeria

[2] Laboratory of Electron Microscopy and Materials Science L.E.M.M.S, University of Science and Technology Oran Mohammed Boudiaf (USTO M.B). PB 1505 El M'naouar 31000 Oran, Algeria

[2,*]*Email :* abdelkader.elaziouti@univ-usto.dz ; elaziouti_a@yahoo.com

Abstract

CeO_2 nanoparticles (NPs) were synthesized in alkaline medium via the homogeneous precipitation method and were subsequently calcined at 80 °C/24h (assigned as CeO_2-80) and 500 °C/2 h (assigned as CeO_2-500). The as-prepared materials and the commercial ceria (assigned as CeO_2-com) were characterized using TGA-MS, XRD, SEM-EDX, UV-vis DRS and IEP techniques. The photocatalytic performances of all obtained photocatalysts were assessed by the degradation of Congo red azo-dye (CR) under UVA-light irradiation at various environmental key factors (e.g., reaction time and calcination temperature). Results reveal that CeO_2 compounds crystalize with cubic phase. CeO_2-500 exhibits smaller crystallite size (9 nm vs 117 nm) than that of bare CeO_2-com. SEM analysis shows that the materials are spherical-like in shape NPs with strong assembly of CeO_2 NPs observed in the CeO_2-500 NPs. EDX analysis confirms the stoichiometry of CeO_2 NPs. UV-vis DRS measurement reveals that, CeO_2-500 NPs exhibits a red-shift of absorption band and a more narrow bandgap (2.6 eV vs 3.20 eV) than that of bare CeO_2-com. On the contrary, Urbach energy of Eu is found to be increased from 0.12 eV (CeO_2-com) to 0.17 eV (CeO_2-500), highlighting an increase of crystalline size and internal microstrain in the CeO_2-500 NPs sample. Zeta potential (IEP) of CeO_2-500 NPs is found to be 7.2. UVA-light-responsive photocatalytic activity is observed with CeO_2-500 NPs at a rate constant of 10×10^{-3} min^{-1}, which is four times higher than that of CeO_2-com (K_{app}=2.4×10^{-3} min^{-1}) for the degradation of CR. Pseudo-first-order kinetic model gives the best fit. On the basis of the energy band diagram positions, the enhanced photocatalytic performance of CeO_2-500 nano-catalyst can be ascribed to $O_2^{\bullet-}$, $^{\bullet}OH$ and $R^{\bullet+}$ as the primary oxidative species involved in the degradation of RC under UVA-light irradiation.

Key word: CeO_2 NPs, Congo red, photocatalytic activity, Bandgap, Urbach energy of Eu, band theory.

Corresponding author: Elaziouti Abdelkader

E-mail : elaziouti_a@yahoo.com

Tel: (213) 0550288630

1. Introduction

The release of recalcitrant organic pollutants into the environment from industrial activities such as the textile, dyeing, leather, pharmaceutical, paper, cosmetic, plastic and synthetic detergent is a primary concern. Among organic pollutant compounds, the organic AZO dye such as Congo red (CR) is one of the most widely used in almost all these industries. It has a highly stable complex structure, carcinogenic, hazardous, mutagenic and toxic to the human's health as well as ecosystem, potential bioaccumulation and persistence in sediments of their degradation/biotransformation by-products. Thus, the treatment and refinement of wastewaters via a judicious route is crucial for environmental pollution control and industrial applications. In recent years, various technologies for treating organic dyes, such as oxide-reduction and the exchanging resins of ions, coagulation/flocculation, sedimentation, filtration, adsorption, membrane separation, have been explored. However, the most conventional methods either can only transfer pollutants to other phases rather than destroy them completely or generate by-product toxic pollutants during the treatment process [1]. Hence, researchers are looking forward for alternative inexpensive and suitable technologies to solve this drawback. Recently, advanced oxidation processes (AOPs) have received significant attention in terms of ecology, sustainable development and environmental protection . Among the various advanced oxidation processes, heterogeneous photocatalysis using UV and visible light is one of the best prominent, efficient, low-cost, potentially advantageous and green environmentally friendly techniques for this purpose. The major semiconductor photocatalysts employed for the effective remedy of organic pollutants are TiO_2, SnO_2, ZrO_2, CeO_2 , Fe_2O_3, Bi_2O_3, Al_2O_3, WO_3 and ZnO metal oxides and CdS, CdSe, CdTe, ZnS, PbS and HgS metal chalcogenides. Their environment applications take benefit of oxide's high selectivity and stability conditions, nontoxicity and sufficient energies of their band gap [2]. Cerium (electron configuration [Xe] $4f^15d^16s^2$) is a lanthanide series rare earth element (Z=58) and exists in both the + 3 (Ce^{3+} = [Xe]$4f^1$) and +4 (Ce^{4+} = [Xe]) oxidation states. Nano-sized CeO_2, as an n-type semiconductor, is a cubic fluorite-type oxide in which each cerium site is surrounded by eight oxygen sites in FCC arrangement and each oxygen site has a tetrahedron cerium site. As an important inorganic rare earth metal oxide, CeO_2 has been attracting great interest in the past decade as potential substitutes of TiO_2 owing to their widespread variety of environment and energy-related applications including solid-state electrolytes for electrochemical devices [3], catalysts for three-way automobile exhaust systems (TWC) [4], polishing agents for chemical–mechanical planarization process [5], and ultraviolet (UV) blocking materials in UV shielding [6], the adsorption and reaction of formaldehyde [7], oxygen storage capacity [8], hybrid solar cells [9], H_2S