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Short communication

Synthesis and characterization of AgNP:ZrO_2 functional nanomaterials by leaf extract assisted bioreduction process

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Abstract

Silver nanoparticle functionalized nanocrystalline ZrO_2 was fabricated by using *Anacardium occidentale* leaf extract assisted bioreduction process at ambient conditions. Introducing *A. occidentale* leaf extract into an aqueous mixture of silver nitrate and ZrO_2 particles caused the speedy reduction of the silver ions and efficiently lead to their nucleation as highly stable, silver nanoparticles on the ZrO_2 surface. A reaction mechanism for the fabrication of functional interfaces was developed to illustrate this process. SEM–EDS and TEM investigations, together with UV–vis spectroscopy, confirmed the formation of 5–20 nm silver nanoparticles on the surfaces of ZrO_2 particles. Further, the X-ray diffraction analysis confirms the phase pure face-centered cubic (fcc) crystal structure of silver nanoparticles formed on the surface of ZrO_2 particles. Increasing concentration of leaf extract in the reaction mixture caused the rapid reduction of silver ions and inhibits the formation of silver nanoparticles over the surface of ZrO_2 particles significantly.

Keywords: A. Bio process; B. Nanocomposites; C. Optical properties; D. ZrO_2

1. Introduction

Silver nanoparticles (AgNPs) play a vital role in creating several types of functional nanostructures by coupling with metals, metal oxides, carbon materials, polymers, and cellulosic fibres [1–5]. Among them, metal oxides/ceramic materials functionalized with AgNPs receive an extensive attention in materials science due to their unusual physicochemical and biological properties, which originates from the unique metal/metal oxide interface [6–9]. Zhao et al., reported the synthesis of silver-coated ZnO nanowires and demonstrated their catalytic degradation of dye molecules [10]. Zhang and his research group fabricated the silver-coated TiO_2 nanostructures and investigated their photocatalytic and bactericidal activities [11]. Kim et al., studied the transport properties of Ag nanoparticles incorporated SnO_2 films and reported their enhanced electrical properties [12]. In addition to that Yokoyama et al., reported the fabrication of ZrO_2 thin films with silver nanoparticles and their optical absorption properties [13]. Current interest on AgNP functionalized ZrO_2 nanostructures arise from their unique properties and their potential applications in the emerging sensor, energy and biomedical sectors [14–17]. The properties of ZrO_2 nanostructures functionalized with AgNPs vary significantly with their size, population, uniformity and adhesion between them. The synthesis process plays an important role in achieving the

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above requirements. Various processing methods such as chemical, polyol, sol gel, and radiation-induced reduction, have been successfully explored for the fabrication of surface enhanced metal oxides with AgNPs [16–21]. These conventional processes face substantial challenges due to unfavorable experimental protocols that use significant amount of solvents and chemicals. Thus there is an increasing demand for eco-friendly "green" processes in order to reduce or avoid the utilization of various chemicals in the synthesis protocol. The basic concept behind the functionalization of metal oxides with metal nanoparticles involves the reduction of metal ions to zero-valent metal and their subsequent nucleation as nanostructures on the surface of metal oxides.

Bioreduction of metal ions to metal nanoparticles using various biochemicals, microbes and plant extracts can be effectively used for the purpose of metal ion reduction by an alternative, green, method [22–25]. They also provide better control in size and shape than currently available chemical routes [26]. Among them, plant extract mediated bio-reduction is found to be simple as well as versatile, and has been widely explored for the conversion of metal ions to metal nanoparticles [27–30]. It has been also demonstrated to functionalize various materials with silver nanoparticles at ambient conditions. For example, Ravindra et al. [31] fabricated antibacterial cotton fibres impregnated with silver nanoparticles through plant leaf extract mediated biological processes as a green approach. Also, we have reported the effective fabrication of silver nanoparticle functionalized carbon nanotubes (CNT) using soy and *tecoma stans* leaf extracts [3,32]. Our recent accomplishment in this context is the fabrication of AgNP:ZnO functional nanostructures by maple leaf extract based bioreduction process [33]. Introducing plant extract into the aqueous mixture of silver nitrate and the dispersed materials (Cellulose/CNTs/metal oxides) caused the reduction of silver ions to silver nanoparticles and effectively nucleated them on the surfaces of dispersed materials. This process can also be an efficient way to create metal oxide nanostructures functionalized with gold, and palladium nanoparticles. To the best of our knowledge, such plant extract based biological processes have not been reported for the fabrication of AgNP functionalized ZrO_2 nanostructures.

We have investigated the reduction performance of various plant leaf extracts on silver ions. Among them, *Anacardium occidentale* (cashew) leaf extract exhibited rapid reduction behavior on silver ions and the formation of phase pure silver nanoparticles. Recently, Sheny et al., [34,35] reported the effective reduction of *A. occidentale* dried leaf extract for the synthesis of silver, gold and palladium nanoparticles. Leaf extract contains various kinds of amino acids and proteins, which have the potential to reduce silver/gold/palladium/copper/nickel ions into zero valent metal. Researchers were very much successful in getting silver and gold nanostructures with different shapes including, spherical, triangles, platelets and rods by varying different plant extracts and their concentrations [36–40]. They were identifies that the biochemical components exist in the plant extracts act as a capping agents and influence in the nucleation of zero valent metal into metal nanoparticles in some specific crystalline orientation and causes the formation of different shapes. Recently, we have investigated the effect of leaf extract concentration on the reduction mechanism of silver ions into silver nanoparticles [29]. It was found that the increasing leaf extract concentration in silver nitrate solution caused the formation of silver nanoparticles with reduced sizes [29]. This reveals that the addition of more leaf extract caused rapid reduction and introduces excess nucleation sites, which causes the particle size reduction. Hence, the research reported here was aimed at the fabrication of AgNP-functionalized nanocrystalline ZrO_2 particles using an *A. occidentale* leaf extract mediated biological process. Also the effect of leaf extract concentration on the functionalization process was investigated. The functionalized ZrO_2 particles were characterized by XRD, SEM–EDS and TEM analyses in order to confirm the formation of a crystalline phase, and determine the morphology and size, respectively.

2. Experimental

2.1. Fabrication of functional AgNP:ZrO_2 particles

Silver nitrate (SQ grade) and alcohol (AR grade) were, respectively, obtained from Qualiegence and Sd-Fine, India and used as received. Nanocrystalline ZrO_2 particles were prepared by the acrylamide-assisted, polymeric citrate process [41]. *A. occidentale* leaf extract was obtained by employing the protocol as follows. 20 g of *A. occidentale* leaves were first washed with distilled water, cut into small pieces. Further, the chopped leaves were boiled with 100 ml of distilled water in a conical flask for 2 min and allowed it to cool. Once it cooled, the obtained leaf extract was filtered and stored at ambient

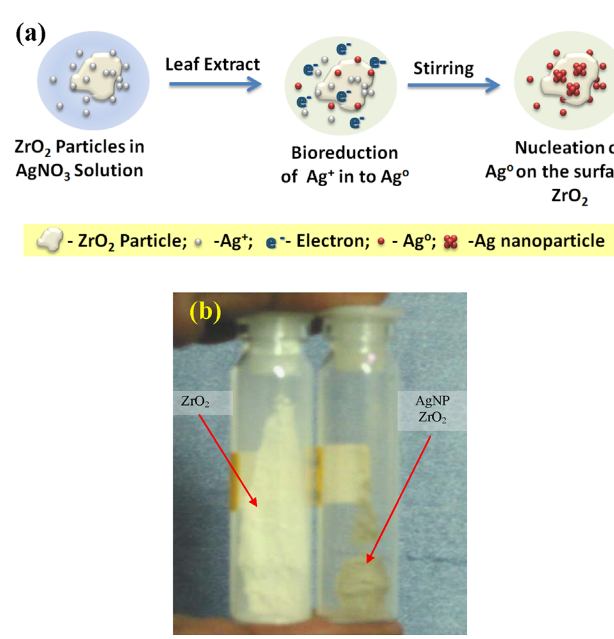

Fig. 1. (a) Schematic representation for the functionalization of ZrO_2 nanoparticles with AgNPs using *Anacardium occidentale* leaf extract, and (b) Photograph of pristine (left) and AgNP-functionalized ZrO_2 (right).