Ultrasonics Sonochemistry 28 (2016) 327–333

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Fabrication and characterization of silver/titanium dioxide composite nanoparticles in ethylene glycol with alkaline solution through sonochemical process

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ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 12 August 2015
Accepted 18 August 2015
Available online 19 August 2015

Keywords:
Sonochemical process
Surface synthesis
Silver
Titanium dioxide
Composite nanoparticle

ABSTRACT

This paper aims to study fabrication and characterization of silver/titanium oxide composite nanoparticle through sonochemical process in the presence of ethylene glycol with alkaline solution. By using ultrasonic irradiation of a mixture of silver nitrate, the dispersed TiO_2 nanoparticle in ethylene glycol associated with aqueous solution of sodium oxide yields Ag/TiO_2 composite nanoparticle with shell/core-type geometry. The powder X-ray diffraction (XRD) of the Ag/TiO_2 composites showed additional diffraction peaks corresponding to the face-centered cubic (fcc) structure of silver crystallization phase, apart from the signals from the cores of TiO_2. Transmission electron microscopy (TEM) images of Ag/TiO_2 composites, which average particle size is roughly 80 nm, reveal that the titanium oxide coated by Ag nanoparticle with a grain size of about 2–5 nm. Additionally, the formation of silver nanoparticles on TiO_2 was monitored by ultraviolet visible light spectrophotometer (UV–Vis). As measured the optical absorption spectra of as-synthesized Ag nanoparticle varying with time, the mechanism of surface formatting silver shell on the cores of TiO_2 could be explored by autocatalytic reaction; the conversion of Ag particle from silver ion is 98% for the reaction time of 1000 s; and the activity energy of synthesizing Ag nanoparticles on TiO_2 is 40 kJ/mol at temperature ranging from 5 to 25 °C. Hopefully, this preliminary investigation could be used for mass production of composite nanoparticles assisted by ultrasonic chemistry in the future.

1. Introduction

The nanometer scale of materials has become the emerging interdisciplinary areas involving physics, chemistry, and biology. It was known that many fundamental properties of materials, such as optical, electrical, catalytic, and mechanical, could be expressed as a function of their size, composition, and structural order [1]. Accordingly, the design and controlled fabrication of nanomaterials with functional properties were necessary to meet the ever-increasing demands placed on materials science and performance by nanotechnology [2,3].

The term of composite nanomaterial was suggested by Roy and Komarneni [4]. The investigation of applications for Ag/TiO_2 composite particles was widely studied in the literature. On the biological field, Ag/TiO_2 composite nanoparticles could be used on biomedical [5] and antibacterial [6]. Ag/TiO_2 composite nanoparticles were also always used as catalyst to degradation organic pollutants [7] acted as catalyst for photo catalytic activity [8]. In addition, the efficiency of dye-sensitized solar cells (DSSC) could be improved by changing TiO_2 particles into Ag/TiO_2 composite particles to form the layer of dye [9]. The reason was the Ag/TiO_2 composite particles have more specific surface area than pure TiO_2 particles; and Ag particles on the TiO_2 surface increase the electrons mobility. On the other hand, the metal oxide nanoparticle could be used to significantly enhance overall thermal conductivity of fluid [10].

The various methods to prepare shell/core type composite nanoparticles have been presented. Su et al. [11] dispersed TiO_2 in polyethylene glycol (PEG), which TiO_2 could attract PEG by hydrogen bonding by means of Van der Waal's force, and then applying energy, like heat or UV light, inducing the metal ion to be reduced into the metal shell on the surface of TiO_2. Lei and Fan [12] used the copolymers of polyacrylonitrile-block-poly (ethylene glycol)-block-polyacry-lonitrile to fabricate Ag/TiO_2 composite nanoparticles assisted with ultrasonic wave. Lee et al. [13] produced Ag/TiO_2 and Zr/TiO_2 composite particles, respectively, by ultrasonic spray pyrolysis of colloid. They mixed the

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http://dx.doi.org/10.1016/j.ultsonch.2015.08.011
1350-4177/

$AgNO_3$ solution and TiO_2 suspension in a container by the ultrasonic wave, then the use of N_2 as the carry gas takes the TiO_2 and $AgNO_3$ gas mixture into a furnace reactor with temperature of 550 °C for sintering, followed by collecting the product of Ag/TiO_2 composite powders. Jang et al. [14] prepared the Ag/TiO_2 composite particles using poly vinyl pyrrolidone (PVP) as protecting agent. PVP not only prevents the agglomeration of silver particles but also promotes reduction of the Ag^+ ions into Ag particles. In where, PVP in the solution were adsorbed on the surface of TiO_2. The Ag particles were synthesized by PVP when the system was heated. In addition, there was a novel method to make the Ag/TiO_2 composite particles. Mansoob et al. [15] employed an electrochemically active biofilm (EAB) to synthesize the Ag/TiO_2 composite nanoparticles. The biofilm was supported by the carbon paper. The EAB was soaked on a vessel with full acetate. Acetate is an electrolyte that could be decomposed by EAB to generate electrons. These electrons were accumulated on the conduction band of TiO_2. The Ag^+ ion in solution would get an electron from the conduction band of TiO_2 and was then reduced into Ag particles. Additionally, in order to enhance the photocatalytic and antibacterial activity, silver nanoparticles were synthesized sonochemically by the reduction of silver ions with ethylene glycol and simultaneously deposited on the different forms of TiO_2 powders [16]. Based on the experimental results, it was conducted that enhanced antimicrobial activity of the Ag–TiO_2 originated from both the oxidative stress generated by silver nanoparticles and the presence of silver ions on the surface of the silver–titanium composite. Hunag et al. [17] studied kinetics for preparing sliver particle, which reducing agent is isopropanol. They found the reduction of Ag^+ ion is an autocatalytic process, which small metal particles were deposited on the surface of larger oxide particles act as catalyst for autoacceleration with increases in the number of Ag particle. They used the optical absorbance of the Ag colloid, following Beer's law [18], to verify the autocatalytic nature of the spontaneous reduction of silver ions in 2-propanol solution to derive the rate expression for metal formation where reaction constant increased with the concentration of metal ion. This autocatalytic reaction occurred in the system with alcohols, but when the fluid was water, the reaction did not happen. The growing behavior of synthesizing metal nanoparticle could be defined by the optical absorbance varying with reaction time, that is, the stages of nucleation and growth were respectively could be observed from the dynamic optical absorption spectra. The UV–Vis light absorbance of sliver nanoparticle would increase with reaction time, but which is limited by a maximum wavelength of characteristics peak that begins to red shift [19]. The activation energy of synthesis reaction could be derived by Arrhenius equation [20].

The sonochemical process has been developed to fabricate novel nanometer scale of materials [21,22]. In the liquid medium, the ultrasonic waves is produced by transducer for the generation of cavities that grow due to the pressure fluctuations and collapse adiabatically over a very small time scale [23], arising high temperature (>10,000 K) and pressure pulse (>1000 atm) [24] for the formation of radicals by decomposition of water and organic compound, which help in initiating and propagating chemical reactions. [25]. During acoustic cavitation, the extreme conditions of high temperature, pressure and intense micromixing can be achieved for solute transfer and nucleation rate, improving the formation of nanometer sized particles in aqueous suspension [22]. Bhanvase and Sonawane [26] synthesized pure polyaniline (PANI) and PAC using ultrasound assisted emulsion polymerization so as to enhance the reaction rate and micro-mixing of reaction mass. Continuous use of cavitation may facilitate the encapsulation, dispersion and/or segregation of the nanoparticles. Further, continuous ultrasonic irradiation can also be used for generation of efficiently stabilized emulsion by incorporating inorganic core in monomer droplet [27]. The ultrasonic irradiation method was used to fabricate inorganic nanopigments to improve the products' distribution and anti-corrosion function, resulting from the prevention of the agglomeration of the products and the excellent dispersion ability in the coatings [28]. Furthermore, Patel et al. [29] applied ultrasound technique for the synthesis of yellow rare earth cerium zinc molybdate anticorrosion nanopigment. The use of ultrasonic irradiations during synthesis of graphene–Fe_3O_4 nanocomposite resulted in uniform loading of Fe_3O_4 nanoparticles on graphene nanosheets [30]. For the synthesis of core–shell polymer nanocomposites, due to influential efficiency, sonochemistry has been extensively used not only as an aid of dispersion for inorganic nanoparticles and organo-clay, but also acts as an initiator to enhance polymerization rate for synthesis of polymer nanocomposites [31]. Additionally, in the presence of high intensity ultrasound and initiator, the effect of temperature, surfactant concentration and monomer concentration on the extent of conversion has been studied for the semi-batch emulsion copolymerization of methylmethacrylate and styrene [24]. Recently, zinc phosphomolybdate nanoparticle was synthesized by ultrasonic irradiation [32]. It was found that the average particle size is smaller compared to conventional precipitation method, resulting from improving the solute transfer rate and rapid nucleation in the presence of cavitation induced by ultrasonic wave; and Bhanvase et al. [33] employed ultrasound assisted in-situ semi-batch emulsion polymerization to prepare polyaniline (PANI) and PANI/$ZnMoO_4$ nanocomposite with different loading of $ZnMoO_4$ (ZM) nanoparticles. The cavitational effects induced due to ultrasonic irradiations have been shown significant enhancement in the dispersion of functionalized ZM nanoparticles into the PANI during ultrasound assisted in-situ emulsion polymerization process. The remarkable enhancement in the reaction rate is attributed to the intensive bubble collapse conditions, which rapidly generate the oxidative radicals necessary for polymerization.

In this study, we aim to examine surface synthesizing silver nanoparticle on the dispersed titanium oxide particles in ethylene glycol associated with alkaline solution through sonochemical process. In the experiment, the as-synthesized composite nanoparticle were firstly characterized by X-ray diffract meter (XRD), energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) respectively. Finally, applying UV–Vis light absorption technology, the growth rate of Ag nanoparticle on TiO_2 in ethylene glycol associated with alkaline solution was in situ monitored during sonochemical process at the different temperature.

2. Experiment

2.1. Materials

TiO_2 was purchased from Degussa, traded name as P25, which average particle size is 21 nm. The precursor was silver nitrate purchased from Alfa Aesar Co. Ltd, which purity is 99.9995%. Ethylene glycol (EG) was manufacturing by TEDIA. Sodium hydroxide (NaOH) was obtained from SHOWA Chemical Co. Ltd. These materials were used without further purification.

2.2. Preparation of Ag/TiO_2 composite nanoparticle

After baking in oven at 120 °C for 3 h to remove moisture, 0.005 wt% of TiO_2 powders were immediately mixed with 20 mL of solution made from EG and de-ionic water at the ratio of 4 to 1 containing 0.01 wt% of NaOH that amount was limited for surface synthesizing Ag particle on TiO_2, followed by wetting process with magnetic stirrer for 24 h and dispersing with ultrasonic probe (HOYU Ultrasonic 250, Taiwan), which frequency and power are