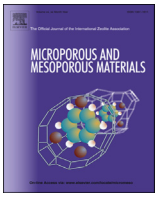
Microporous and Mesoporous Materials 226 (2016) 316–324

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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



Preparation and characterization of monodisperse, mesoporous natural poly(tannic acid)–silica nanoparticle composites with antioxidant properties

Nurettin Sahiner [a], [b], [*], Selin Sagbas [a], Nahit Aktas [c]

[a] Faculty of Science & Arts, Chemistry Department, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey
[b] Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey
[c] Chemical Engineering Department, Yuzuncu Yil University, 65080 Van, Turkey

A R T I C L E I N F O

Article history:
Received 23 September 2015
Received in revised form
5 January 2016
Accepted 2 February 2016
Available online 10 February 2016

Keywords:
Tannic acid/silica
Composite mesoporous nanoparticles
Antioxidant natural polymer composites
Microgel/nanogel composite

A B S T R A C T

Mesoporous poly(Tannic Acid)–Silica nanoparticle composites (p(TA)–Si NPs) were prepared via one pot reaction. At various TA amounts in feed, 50, 100, 250, 500, 1000 mg at different reaction times, 2, 4, 8, 12, 24 h in the presence of TEOS and epoxy crosslinker, trimethylolpropane triglycidyl ether (TMPGDE), NPs composites were readily prepared. The prepared p(TA)–Si NPs by using 1000 mg TA at 12 h reaction time at room temperature as p(TA)1000–Si NPs provided the highest yield (~48%). The particle size, monodispersity, specific surface area, porosity, and the gravimetric yields are greatly depended on initial TA concentration and reaction time. The particles sizes were found as 237–445 nm depending on TA content and reaction time. The highest surface area was measured as 872 m^2/g for p(TA)1000–Si NPs for 2 h reaction time. The thermal stability of p(TA)–Si NPs decreased as TA content is increased. Interestingly, p(TA)1000–Si NPs are found effective antioxidant materials.

1. Introduction

Mesoporous Si NPs and their modified forms have been investigated as promising material for long time for various applications in the field of separation [1], medical devices [2], biosensors, chromatography, drug carrier [3] and delivery [4], catalysis [5], immobilization, and encapsulation [6–10]. Preparation and the design of novel mesoporous Si-organic composite NPs were extensively studied due to their high surface area, high thermal stability, large pore volume, size control ability, monodispersity, and tunable functionality and so on [11,12]. The main objective in many applications of nanocomposite in material engineering is the controlled surface area, particle size, pore structure to obtain the desired physical and chemical properties [13–17].

As a natural hydrolyzable polyphenol, tannic acid (TA) is composed a central glucose molecule that connected with ten gallic acid units [18]. TA has been extensively investigated as remedy for many pharmaceutical and cosmetic application, and coating, and in biomedical applications due to its various attractive properties such as antioxidant, antimicrobial, antiviral, antimutogenic, anticancerogenic, anti-inflammatory, astringent and homeostatic effects [19–22]. In addition to all these, TA can directly interact with various biomacromolecules such as some enzymes, collagen, chitosan by activating or inhibiting their effects in the living organism [19,23]. Gao and Zharov were reported that TA can be used as a surfactant template to create large-scale mesoporous Si NPs [24]. Firstly, different amounts of TA were added to Si NPs synthesized medium. After the synthesis of Si NPs, TA molecules were easily removed by water–ethanol mixture by washing. Thus, manageable porous Si NPs were prepared for encapsulation and immobilization of biomacromolecules with large mesoporous structure of Si NPS. In other words, Gao and Zharov were reported the preparation of mesoporous Si NPS with high surface area using TA as only template materials. On the other hand, in this study, mesoporous composite p(TA)–Si NPs were prepared as intriguing biomaterial with many biomedical potentials to make use of TA's inherently attractive biological functions. Therefore, p(TA)–Si NP composites are generated, and various parameters effecting the control of

---

[*] Corresponding author. Faculty of Science & Arts, Chemistry Department, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey. Tel.: +90 2862180018 2041; fax: +90 2862181948.

E-mail address: sahiner71@gmail.com (N. Sahiner).

http://dx.doi.org/10.1016/j.micromeso.2016.02.012
1387-1811/

composite particle size, monodispersity, surface area, and porosity by changing TA content and reaction time. For this purpose, TA was crosslinked with TMPGDE crosslinker within the Si NP framework during the synthesis to prepare composite mesoporous p(TA)–Si NPs as TA inherently possesses many biological functions e.g., TA can be used in many biomedical and clinical fields, including antioxidant, antibacterial materials as well as therapeutic agent carrier or delivery system, biomedical devices, and even as coating material. Therefore, excess amount of TA was removed from the surface and novel mesoporous composite p(TA)–Si NPs were prepared with high surface area. The size, and size distribution and porosity of NPs are important in biomedical applications. For example, mesoporous NPs are attractive and very efficient to be used as drug carrier material for specific sized molecules [9]. Thus, TA amount of composite particles and the reaction time were also investigated for controlling surface area, monodispersity, and pore structure of the p(TA) based novel composite materials. The surface area, pore volume, and pore size of the prepared mesoporous composite nanoparticles, p(TA)–Si NPs, were determined by scanning electron microscope (SEM) images, dynamic light scattering (DLS), and N_2 adsorption measurements (BET). Moreover, thermal and structural properties of all the prepared particles were investigated with thermogravimetric analysis (TGA), FT-IR spectroscopy and zeta potential measurements. Additionally, antioxidant effects of composite highly porous p(TA)–Si NPs were investigated via total phenol content (FC) and Trolox equivalent antioxidant capacity (TEAC) methods.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, reagent grade, 98%, Aldrich), tannic acid (TA, ACS reagent, Aldrich), trimethylolpropane triglycidyl ether (TMPGDE, technical grade, Aldrich) were used as received. Ammonia solution (NH_4OH, 25%) was obtained from Merck. Ethyl alcohol (99.9%) was purchased from Kimetsan. And, 2,2′-Azino-bis-(3-ethylbenzothioazoline-6-sulfonic acid) (ABTS, ≥98%, Aldrich), Folin-Ciocalteu's phenol reagent (FC, 2N, Sigma–Aldrich), and gallic acid (GA, 98%, Aldrich) were used in antioxidant studies. All aqueous solutions were freshly prepared using ultra-pure distilled water (DI) 18.2 MΩ cm (Millipore-Direct Q UV3).

2.2. Synthesis of silica nanoparticles and mesoporous silica nanoparticles

Nonporous silica and mesoporous silica nanoparticles were synthesized by Stöber method according to previously study with some modification [24]. In short, 25 mL ethanol solution containing 2.67 mL (0.1 mol) TEOS and 1.34 mL (0.2 mol) NH_4OH and 14.4 mL (8 mol) DI water were mixed under vigorous stirring respectively. After 24 h, silica nanoparticles (Si NPs) were precipitated by centrifugation for 10 min at 35,544g. Particles were washed with water–ethanol mixture three times to remove the unreacted chemicals by centrifugation (35,544g for 10 min). TA was used as a surfactant template for synthesized mesoporous Si NPs. Separately, 50, 100, 250, and 500 mg of TA were dissolved in 50 mL ethyl alcohol and 25 mL ammonium hydroxide (25%) was added to this TA solution under vigorous stirring to prepare TA50–Si, TA100–Si, TA250–Si, and TA500–Si NPs, respectively. After complete mixing of each of these solution, 0.3 mL of TEOS was put into these solutions and mixed under vigorous stirring for 2 h. After this time period reactions, the particles were precipitated by centrifugation at 35,544g for 10 min. The mesoporous TA–Si NPs were washed with water–ethanol mixture (50:50% v/v) ten times to remove TA and the unreacted chemicals by centrifugation at 35,544 g for 10 min. The nonporous Si NPs and mesoporous TA–Si NPs were dried with a freeze-drier and kept in a close container for further use.

2.3. Synthesis of mesoporous p(TA)–silica nanoparticles composite

In a separate vial, 50, 100, 250, 500 and 1000 mg TA were dissolved in 50 mL ethyl alcohol and 25 mL ammonium hydroxide (25%) vial were added to these TA solutions under vigorous stirring. Then, 0.3 mL of TEOS was put into these solution and TMPGDE (300 mol% of tannic acid) was subsequently included to these solution under mixing constant vigorous stirring for 2 h for the synthesis of p(TA)50–Si, p(TA)100–Si, p(TA)250–Si, p(TA)500–Si, and p(TA)1000–Si NPs, respectively. Additionally, different reaction times, 2, 4, 8, 12, and 24 h were performed for p(TA)1000–Si NPs. At the end of these reaction periods, the obtained particles were precipitated and washed by the same method as described above to remove unreacted species. The prepared mesoporous p(TA)–Si NPs composite was dried by freeze-dried and kept in a close container for further use.

2.4. Characterization of nonporous Si NPs, mesoporous Si NPs, and mesoporous p(TA)–Si NPs composite

The particles were image by SEM by placing the particles on carbon tape attached aluminum SEM stubs, and after coating with gold to a few nanometers thickness in a vacuum using SEM (Jeol JSM-5600 LV) at an operating of 20 kV. The specific surface areas, pore volume and pore size of silica based particles were determined surface area and pore size analyzer (Micromeritics, Tristar II Surface and Porosity) using the Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods, respectively. Before the analysis, particles were degassed by using a FlowPrep 060 degasser to remove moisture and contaminants at 100 °C for 6 h. The hydrodynamic size of particles was measured by using dynamic light scattering (DLS, Brookhaven Ins. Corp. 90 plus particle size analyzer) with 35 mW solid-state laser detector at an operating wavelength at 658 nm. Zeta potential measurements of silica based particles were also carried out using Zeta Potential Analyzer (Zeta-Pals, BIC) by suspending about 1 mg in 0.001 M KCl solutions in DI water.

The thermal degradation of silica based nanoparticles was determined via thermogravimetric analyzer (SII TG/DTA 6300). About 5 mg of particles were placed in ceramic crucibles and the weight lost over the temperature range of 50–1000 °C was measured at a heating rate of 10 °C min^{-1} under a dry flow of N_2 of 100 mL min^{-1}. The functional groups analysis of particles was done using FT-IR spectroscopy (Nicolet iS10, Thermo) in the spectral range of 4000–650 cm^{-1} with a resolution of 4 cm^{-1} using the ATR technique.

2.5. Antioxidant properties nonporous Si NPs and mesoporous composite p(TA)–Si NPs

2.5.1. Total phenol content of particles

Total phenol content of nonporous Si NPs and mesoporous p(TA) 1000–Si NP composites were measured by Folin-Ciocalteu (FC) method described by Fiol et al. with some modifications [25]. Briefly, 0.1 mL of 170 μg mL^{-1} silica based NPs solution was put into 1.25 mL 0.2 N solution of FC phenol reagent and immediately mixed. After 4 min, 1 mL of 0.7 M Na_2CO_3 solution was added to this solution, and the mixture was kept in a dark place for 2 h. Finally, the absorbance of solution was measured by UV–Vis