GAMMA RADIATION INDUCED PREPARATION OF FUNCTIONAL CONDUCTING POLYMER HOLLOW SPHERES

K.-P. Lee, A.I. Gopalan, M.F. Philips, K.M. Jeong; KOREA, REP. OF

1. INTRODUCTION

New materials are sought for applications in many of the emerging fields that include catalysis, sensors, biomedical, optics and electronic application. With the advent of nanotechnology, innovative materials with novel properties are being synthesized towards target applications. Changing the sizes of particles, chemical, optical, and mechanical properties of the materials can often be tailored according to the specific needs of the application [1]. Nanocrystalline, nanoparticles, nanocapsules, nanoporous materials, nanofibers, nanowires, fullerenes, nanotubes, nanosprings, nanobelts, dendrimers and nanospheres, ets, are few of the nanostructured materials. The examples of nanostructured materials include semiconducting nanowire quantum dots for gas sensing [2] and self-assembled flower-like architectures [3]. Self-assembly of nanoparticles can result in specific structures with unique and useful electronic, optical, and magnetic properties [4]. Self or induced assemby of simple nanoparticles and rods could result into complex geometries, such as nanoflowers, binary superlattices, optical grating [5,6].

Over the past decade, hollow spherical nanomaterials have received considerable attention due to their interesting properties such as low density, high surface area and good permeation. Various methods like solvothermal, self-assembly, sonochemical, solvent evaporation, chemical vapor deposition, microwave-assisted aqueous hydrothermal and electrochemical are being pursued for the production of hollow spherical materials. Polymer capsules and hollow spheres have increasingly received interest because of their large surface area and potential applications in catalysis, controlled delivery, artificial cells, light fillers and photonics [7].

Recently, conducting polymer (CP) nanostructures such as nanotubes, nanodiscs and hollow spherical nanoshells have received interest because of their physico-chemical properties and potential applications [8]. A variety of synthetic approaches which include interfacial polymerization [9], etc., have been developed for the preparation of CP nanostructures. In recent years, there has been increasing interest in the fabrication of composite hollow spheres consisting of CP as the support matrix and MNPs) or other catalyst particles as the other component [10].

Liao et al [11] reported the preparation of water-dispersible polypyrrole (PPy) nanospheres with diameters of less than 100 nm. A hollow spherical-nanostructured conductive polymer/metal oxide composite has been synthesized [12]. Mallick et al [13] reported the preparation of paramagnetic polyaniline (PANI)) nanospheres (PANI–cerium(III) supramolecular composite) by an in situ synthesis. PANI/Fe3O4 composite hollow spheres have been successfully synthesized using sulfonated polystyrene spheres as the template [7]. A novel method has been established for the preparation of CP nano-spheres with controllable sizes [14]. A simple and one-step method has been reported for the fabrication of poly(aniline-copyrrole) copolymer hollow nanospheres via the oxidative polymerization of a mixture of aniline and pyrrole in the presence of Triton X-100 [15]. Oxidative polymerization of aniline with ferric chloride resulted urchin-like PANI composite hollow spheres [16]. Hollow PANI spheres have been synthesized with latex sphere template [17].

Recently, Wan has developed an "emulsion template" approach to prepare hollow PANI spheres [18]. Li et al [19] reported the preparation of core-shell nanostructured conductive PPy composite. New studies for establishing methods for nanoscale engineering materials, especially towards biomedical applications are warranted.

We report the preparation of hollow spherical nanocapsules (HSNC) and subsequent modification onto hollow spherical composite nanocapsules (HSCNC) by loading MNPs into the HSNC(PPy) through γ-radiation. The HSCNC is designated as HSCNC(PPy/MNP) in terms of the shell (PPy) and loaded metal nanoparticles (MNPs). The preparation of HSCNC(PPy/MNP) involves steps as detailed in Scheme 1. In this case, γ-irradiation was used for loading MNPs onto HSNC(PPy). Also, we have utilized the above methodology for the preparation of HSNC based on PANI using γ-irradiation. We have prepared PANI based HSNC(PANI) and HSCNC(PANI/MNP). HSCNC(PPy/MNP) and HSCNC(PANI/MNP) were independently prepared by different approaches to bring out the effectiveness of γ-irradiation in these preparations. γ-irradiation technique has been previously used to generate nanoscale metals [20] and nanocomposites [21]. Moreover, γ-irradiation technique has several advantages. Importantly, γ-irradiation method can produce pure or clean materials without impurities [22]. It is possible to control the size of particles by proper selection of radiation dose etc.

Trial studies have also been done for the second phase of RCM to develop functional electrospun polymer nanofibers (F-ESPNF) through radiation induced processes. Functional nanostructures are currently the subject of increasing interest. Importantly, it is fairly easy to include functional properties to the ESPNF by incorporating additives during the electrospinning process. Various types of additives could be incorporated into the ESPNF. Large surface area, excellent moisture/gas transport, extremely low air permeability and unique porous structures of ESPNF are effectively used to improve current technology and applications. Our experimental findings give hopes that ESPNF could be suitably modified by radiation to develop F-ESPNF.

2. EXPERIMENTAL

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 98%), pyrrole (98%), aniline, gold (III) chloride, ammonium peroxodisulfate (APS), H2PtCl6·H2O and RuCl3·H2O were purchased from Sigma–Aldrich Co. 25% aqueous solution of ammonia and hydrofluoric acid (HF) was obtained from DC Chemicals Co. Poly(N-vinylpyrrolidone) K-30 (PVP) (Junsei Chemical Co., Japan), FeCl3·6H2O, ethanol (Sam-Chunn Chemical Co., Korea) and sodium carbonate (Duksan Pharmaceutical Co., Korea) were used as received.

2.2. Characterization

Field emission scanning electron microscope (FESEM) (Hitachi, S- 4700, Japan) and high-resolution transmission electron microscope (HRTEM) (JEOL, JEM-2010, USA) have been used to find particle size and morphology. EDAX spectrum was recorded simultaneously with the measurement of FESEM. The specific surface area of HSNCs-PPy/PtRu catalyst was determined using a porosimeter (D.A MOUNTECH, Macsorb HM model-1201, Japan).

2.3. Synthesis of HSCNC(PPy/MNP)

Scheme 1 illustrates the steps involved in the preparation of HSNC(PPy). The steps include the preparation of (a) spherical silica (SiO_2) particles, (b) coating the surface of the SiO_2 particles with a layer of poly(vinylpyrrolidone) (PVP) and adsorption of Fe^{3+} ions over the layer of PVP, (c) polymerization of pyrrole to obtain SiO_2-PPy (core-shell) composite, (d) dissolution of SiO_2 (core) to obtain HSNC(PPy) and (e) loading of MNP onto HSNC(PPy) through γ-radiation to obtain HSCNC(PPy/MNP).

2.3.1. Preparation of SiO2 template

Particles of SiO_2 (in the size range of 500 nm) were synthesized as detailed elsewhere [23]. Briefly, to a solution containing 1.0 L of ethanol and 80 mL of deionized water, 40 mL of aqueous solution of ammonia (25%) was added. 60 mL of TEOS was added into the mixture under vigorous stirring. The reaction mixture was stirred for 12 h at 25°C and spherical SiO_2 particles were obtained.

2.3.2. Preparation of SiO_2-PPy (core-shell) composite

Spherical SiO_2 particles were dispersed into ethanol (30 mL) and sonicated. PVP (2.5 g) was added into the dispersion and stirred overnight to adsorb PVP on the surface of SiO_2 particles. The PVP-protected SiO_2 particles were dispersed into an aqueous solution containing $FeCl_3 \cdot 6H_2O$ (5.0 g). Then, pyrrole (1.1 mL) was added into the solution containing Fe^{3+} ions adsorbed PVP-protected SiO_2 particles and stirred for 12 h . The black colored SiO_2 (core)-PPy (shell) composite was centrifuged, washed several times with distilled water and dried in an oven at 60°C for 8 h.

2.3.3. Preparation of HSNC(PPy)

SiO_2 was etched out from SiO_2 (core)-PPy (shell)/MNP composite by treatment with HF **[24]**.

2.3.4. Preparation of HSCNCs(PPy/MNP) by γ-radiation

A solution containing 188 ml of water and 12 mL of 2-propanol was prepared. 0.5 g of HSNCs-PPY was dispersed into the water : alcohol solution containing 0.21 g of H2PtCl6·H2O and 0.21 g

of RuCl3·H2O. Nitrogen gas was purged into the solution for 30 min and subsequently subjected to γ-radiation (60Co source) at ambient temperature. A total irradiation dose of 30 kGy (dose rate = 6.48×105 h−1) was applied. HSCNs (PPy/MNP) was washed repeatedly with distilled water, centrifuged and dried in an oven at 60°C.

2.4. Synthesis of HSCNC(PANI/MNP)

We have utilized two approaches for the preparation of HSCNC(PANI/MNP) using γ-irradiation.

In the first approach, γ-irradiation was used to load MNPs (Au) on to the PANI shell coated over SiO2 template. PANI coating (shell) on SiO2 (template) surface was performed by oxidative polymerization of aniline in the presence of SiO2 (template). In a typical procedure, PVP coated SiO2 particles were dispersed in a solution of 0.1 M APS for 1 h. The APS adsorbed SiO2 particles were filtered and put into a solution containing 50 mM of aniline in 0.5 M HCl and stirred for 2 h. The PANI coated SiO2 (silica-PANI(shell)) was separated and dried at 60°C. Calculated amount of SiO2-PANI(shell) particles were dispersed in a water and isopropyl alcohol (15:1 v/v) mixture solution containing 2 x 10-3 M HAuCl4. The mixture was irradiated by γ-ray (60Co source at ambient temperature for a total radiation dose of 30 KG. The MNP(Au) loaded silica-PANI(shell) was filtered, washed with water and dried.

In the second approach, γ-irradiation was used for the formation of both PANI (shell) and MNPs (Au). In a typical experiment, a mixture solution containing aniline (50 mM), HAuCl4 (1 x 10-3M) and silica-PVP (0.2g) particles was irradiated with γ-irradiation. The green mass silica-PANI(shell)/MNP(Au) composite was filtered, washed and dried.

3. RESULTS AND DISCUSSION

SEM images in different magnifications (Fig. 1a and b) show that SiO2 particles (hard template) are spherical with nearly uniform diameters in the range of 400-420 nm [25]. FESEM images of SiO2-PANI core-shell composite (Fig. 1c and d) particles show the existence of PANI coating with a thickness of 30-40 nm on the surface of SiO2. Thus, we ensured that PANI layer is present as shell on the surface of SiO2. FESEM images (Fig. 1d and e) of silica(core)-PANI(shell) loaded with AuNPs are presented. AuNPs of sizes in the range 30-50 nm are found on the surface of PANI(shell). EDAX of silica(core)-PANI(shell)-MNP composite confirms the presence of Au (Fig. 2). Silica (core)-PPy (shell)/MNP composite also showed similar features.

We have authenticated the formation of conducting polymer based HSCNCs by removing the core (silica). Typically, HRTEM image of HSCNC(PPy/MNP) (Fig. 3a and b) reveals that PtRu nanoparticles (MNPs) were distributed on both sides of the HSNC-PPy. For comparison, HRTEM image of the HSCNC(PPy/PtRu) prepared by conventional chemical reduction (Fig. 3b) is presented. In this case, PtRu nanoparticles are present only on the outer surface of the HSNC(PPy).

In the literature, chemical and physical methods have been utilized for the preparation of metal or alloy particles in nanometer sizes. The method include photolytic reduction [26], solvent extraction [27] reduction in aqueous/nonaqueous [28, 29]. A close analysis of literature related to the loading of MNPs onto different matrices reveals the following. The chemicals used for the reduction of metal ions generally leave residual impurities, which generally decreases the activity of MNPs.

Also, stringent post-treatment procedures are needed to remove the impurities from the catalyst system to have good electroactivity of MNPs. The loading of "impurity free" MNP onto polymer support is a technical challenge. It is beneficial to avoid chemicals for the reduction process in the preparation of 'clean' MNPs or to prefer a reduction process which will not result products as impurities to the MNPs. Radiolysis has been proved as a convenient technique for the preparation of size-controllable MNPs [30] because hydrated electrons generated from water have very strong reduction capability towards metal ions. Gamma radiation (γ) has been effectively used for the synthesis of MNPs because reduction of metal ions could be achieved at ambient conditions [31].

In the present work, γ-radiation induced reduction of metal ions has been specifically selected. The choice of γ-radiation for reduction is based on effectiveness, in producing 'clean' catalyst particles, on both sides (inner and outer) of the HSNC(PPy). Further, the Pt–Ru nanoparticles were formed by γ-radiation at room temperature. There are two striking advantages on using γ-radiation for the preparation HSCNCs(PPy/PtRu). First, clean PtRu nanoparticles were loaded onto the HSNCs(PPy) as compared to the chemical and other routes. The reduction of metal precursors by conventional reducing agent result in impurities and often need repeated purification for the removal of the adhered impurities from MNPs. However, in the case of γ-radiation route, impurity generating reducing agent is not required for the preparation of MNPs. Further, smaller sizes of MNPs were obtained by γ-radiation induced reduction. Further, γ-radiation can penetrate into the surface of HSNCs(PPy) and can result in distribution of PtRu nanoparticles on both sides of the hollow spheres. We have employed γ-radiation for obtaining uniform distribution of PtRu nanoparticles into HSCNs(PPy) to obtain HSCNC(PPy/MNP) catalyst.

We also wanted to ensure the importance of γ-irradiation for the preparation of CP based HSCNCs. Towards this, we have employed γ-irradiation for the preparation of conducting polymer shell(PANI) as well for simultaneous loading of MNP (Au). Fig. 4 shows the FESEM image of silica(core)-PANI(shell)/Au composite prepared by the simultaneous formation of PANI(shell) and MNPs using gamma radiation. FESEM images reveal that the thickness of PANI layer is around 60-70 nm. Thus, γ-irradiation induced aniline polymerization could result much higher thickness for PANI shell. It is to be noted that chemical polymerization of aniline resulted a layer thickness of around 50 nm. Also, γ-irradiation induced formation of PANI layer (shell) and MNP (AuNPs) resulted larger number of smaller sized AuNPs (Fig.4).

We have also carried out feasibility studies on the preparation of F-ESPNF. The methodlogy adopted for the preparation of F-ESPNF by radiation is briefly mentioned (Scheme 2). Typically, *new poly(vinylidene fluoride) based multi-functional conductive nanoweb membranes were prepared. Gold nanoparticles(AuNPs) were then loaded into the PVdF-Si NFMs by gamma radiation induced reduction method. Thus, new functional conductive nanowebs, PVdF- @AuNP-NWs were prepared.*The interesting features of ESPNFs, such as their flexibility for physical/chemical modification/functionalization, possibility to induct multi-functionalities and unique physical properties, can be effectively utilized for applications in areas that include biotechnology, biosensors, separation science, batteries etc [32-34]. The large surface area to volume ratio and the reusability of electrospun nanofibers/nanowebs provide a basis for generating new multi-functional nanowebs. We anticipate the new F-ESPNF would find application in biosensors and biomedical fields.

REFERENCES

[1] LI, J. R., KUPPLER, R. J., ZHOU, H. C., Chem. Soc. Rev., 38 (2009) 1477-1504.

[2] JOSHI, R. K., HU, Q., ALVI, F., JOSHI, N., KUMAR, A., J. Phys. Chem. C 113 (2009) 16199-16202.

[3] ZHANG, W., CHEN, J., WANG, X., QI, H., PENG, K., Appl. Organomet. Chem., 23 (2009) 200-203.

[4] LIN, Y., SKAFF, H., EMRICK, T., DINSMORE, A. D., RUSSELL, T. P., Science 299 (2003) 226-229.

[5] EURENIUS, L., HAGGLUND, C., OLSSON, E., KASEMO, B., CHAKAROV, D., Nat. Photonics 2 (2008) 360-364.

[6] SINGH, S. C., GOPAL, R., J. Phys. Chem. C 114 (2010) 9277-9289.

[7] KONG, L., LU, X., JIN, E., JIANG, S., BIAN, X., Zhang, W., Wang, C., J. Solid State Chem., 182 (2009) 2081-2087.

[8] STEJSKAL, J., SAPURINA, I., TRCHOVA, M., KONYUSHENKO, E.N., HOLLER, P., Polymer 47 (2006) 8253-8262.

[9] LEE, K.P., GOPALAN, A.I., LEE, S.H., KIM, M.S., Nanotechnology 17 (2006) 375-380.

[10] FENG, X.M., MAO, C.J., YANG, G., HOU, W.H., ZHU, J.J., Langmuir 22 (2006) 4384-4389.

[11] LIAO, Y., LI, X. G., KANER, R. B., ACS Nano 4 (2010) 5193-5202.

[12] GUO, C. X., LI, C. M., Phys. Chem. Chem. Phys., 12 (2010) 12153-12159.

[13] MALLICK, K., WITCOMB, M., SCURRELL, M., STRYDOM, A., Chem. Phys. Lett., 494 (2010) 232-236.

[14] HAN, C. C., BAI, M. Y., YANG, K. F., LEE, Y. S., LIN, C. W., J. Mater. Chem., 18 (2008) 3918-3925.

[15] ZHOU, C., HAN, J., SONG, G., GUO, R., J. Polym. Sci. Part A: Polym. Chem., 46 (2008) 3563-3572.

[16] YANG, M., YAO, X. X., WANG, G., DING, H., Colloid Surfaces A 324 (2008) 113-116.

[17] HUANG, K., MENG, X., WAN, M., J. Appl. Polym. Sci., 100 (2006) 3050-3054.

[18] ZHANG, L., WAN, M., Adv. Funct. Mater., 13 (2003) 815-820.

[19] LI, X., HAO, X., YU, H., NA, H., Mater. Lett., 62 (2008) 1155-1158.

[20] HENGLEIN, A., ERSHOV, B. G., MALOW, M., J. Phys. Chem., 99 (1995) 14129-14136.

[21] YIN, Y., XU, X., XIA, C., GE, X., ZHANG, Z., Chem. Commun., 8 (1998) 941-942.

[22] KARIM, M. R., LIM, K. T., LEE, C. J., BHUIYAN, M. T. I., KIM, H. J., PARK, L. S., LEE, M. S., J. Polym. Sci. Part A 45 (2007) 5741-5747.

[23] STOBER, W., FINK, A., BOHN, E., J. Colloid Interface Sci., 26 (1968) 62-69.

[24] XU, X., ASHER, S. A., J. Am. Chem. Soc., 126 (2004) 7940-7945.

[25] JIANG, J., KUCERNAK, A., Electrochem. Commun., 11 (2009) 623-626.

[26] REMITA, S., MOSTAFAVI, M., DELCOURT, M.O., Radiat. Phys. Chem., 47 (1996) 275-279.

[27] BRUST, M., WALKER, M., BETHELL, D., SCHIFFRIN, D. J., WHYMAN, R., Chem. Commun., 7 (1994) 801-802.

[28] BOUDJAHEM, A.G., MONTEVERDI, S., MERCY, M., BETTAHAR, M. M., J. Catal., 221 (2004) 325-334.

[29] WU, S. H., CHEN, D. H., J. Colloid Interface Sci. 259 (2003) 282-286.

[30] HENGLEIN, A., Langmuir 15 (1999) 6738-6744.

[31] KANG, B., CHANG, S., SUN, H., DAI, Y., CHEN, D., J. Nanosci. Nanotechnol., 8 (2008) 3857-3863.

[32] GOPALAN, A. I., SANTHOSH, P., MANESH, K. M., NHO, J. H., KIM, S. H., HWANG, C. G.,

LEE, K. P., J. Membr. Sci., 325 (2008) 683-690.

[33] MANESH, K. M., KIM, H. T., SANTHOSH, P., GOPALAN, A. I., LEE, K. P., Biosens. Bioelectron., 23 (2008) 771-779.

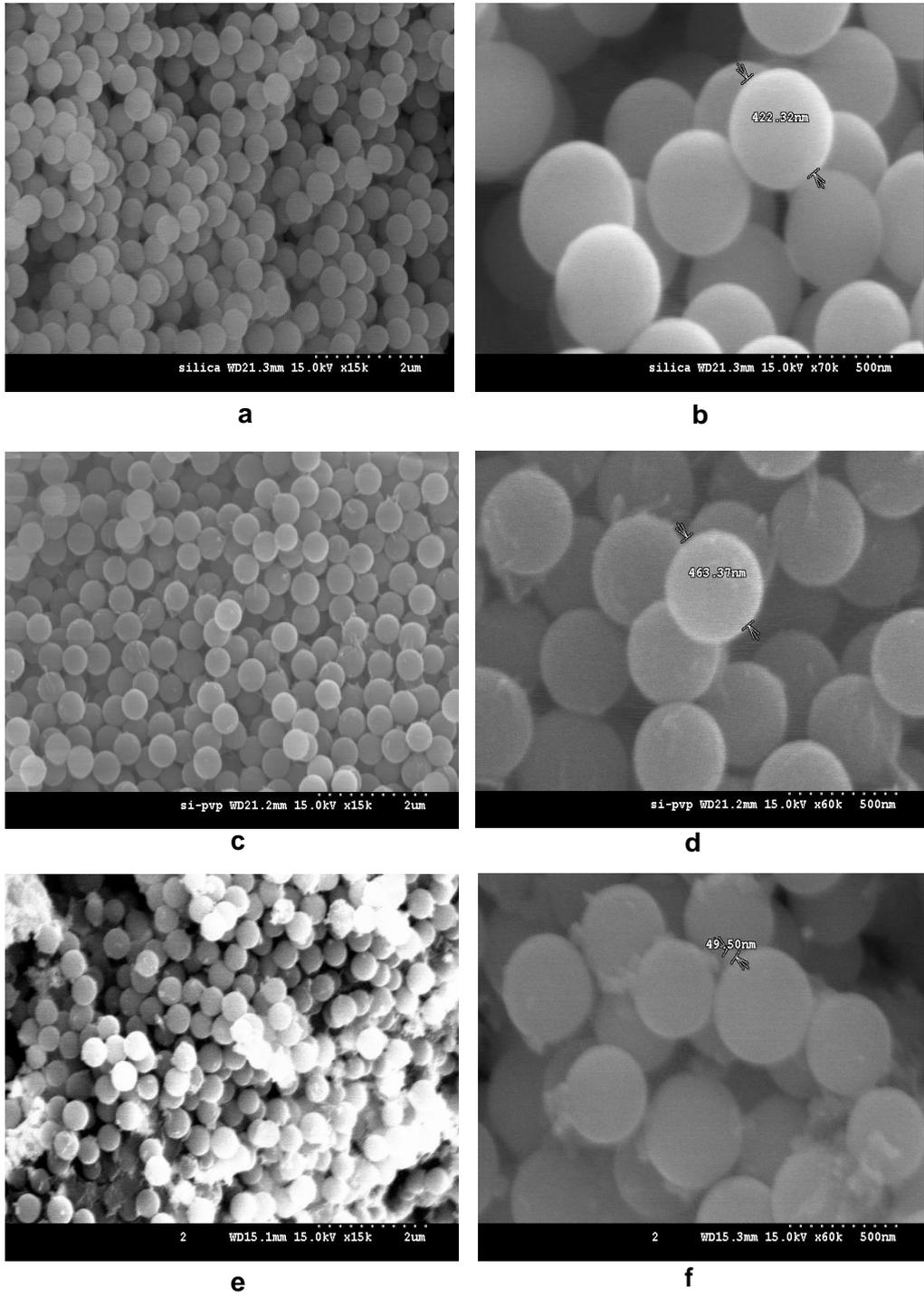[34] GOPALAN, A. I., LEE, K. P., MANESH, K. M., SANTHOSH, P., J. Membr. Sci., 318, 2008, 422-428.

FIG. 1. FESEM images (a and b) SiO$_2$ particles, (c and d) SiO$_2$ (core)-PANI(shell) composites and (e and f) SiO$_2$(core) – PANI(shell)/MNP composite prepared by γ-irradiation.

151
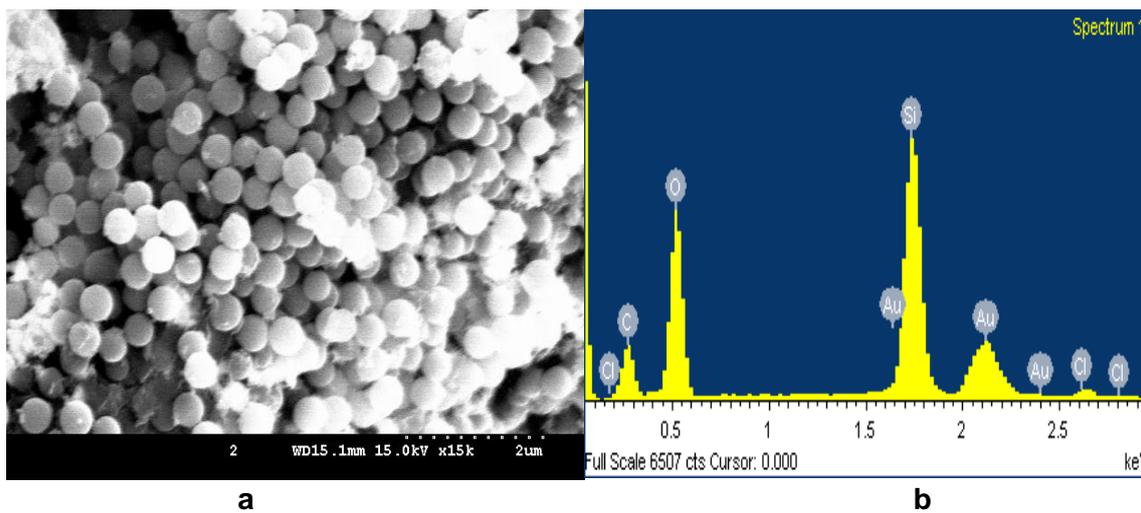
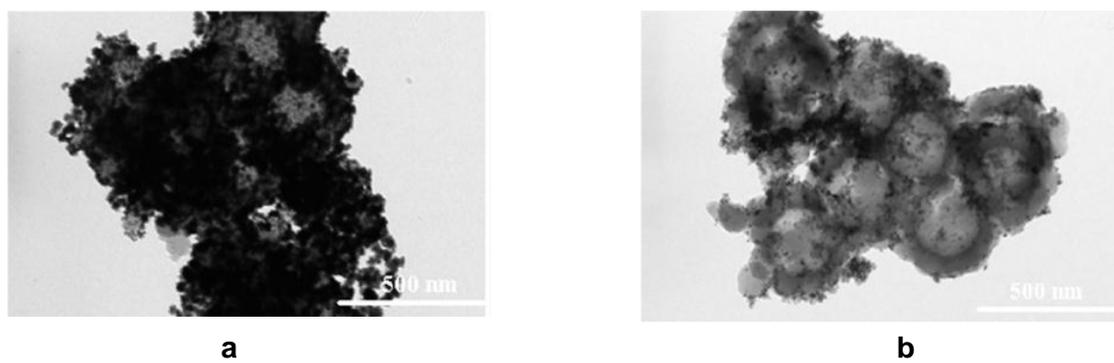*FIG. 2. FESEM image (a) and EDAX spectrum (b) of SiO2(core) – PANI(shell)/MNP composite*

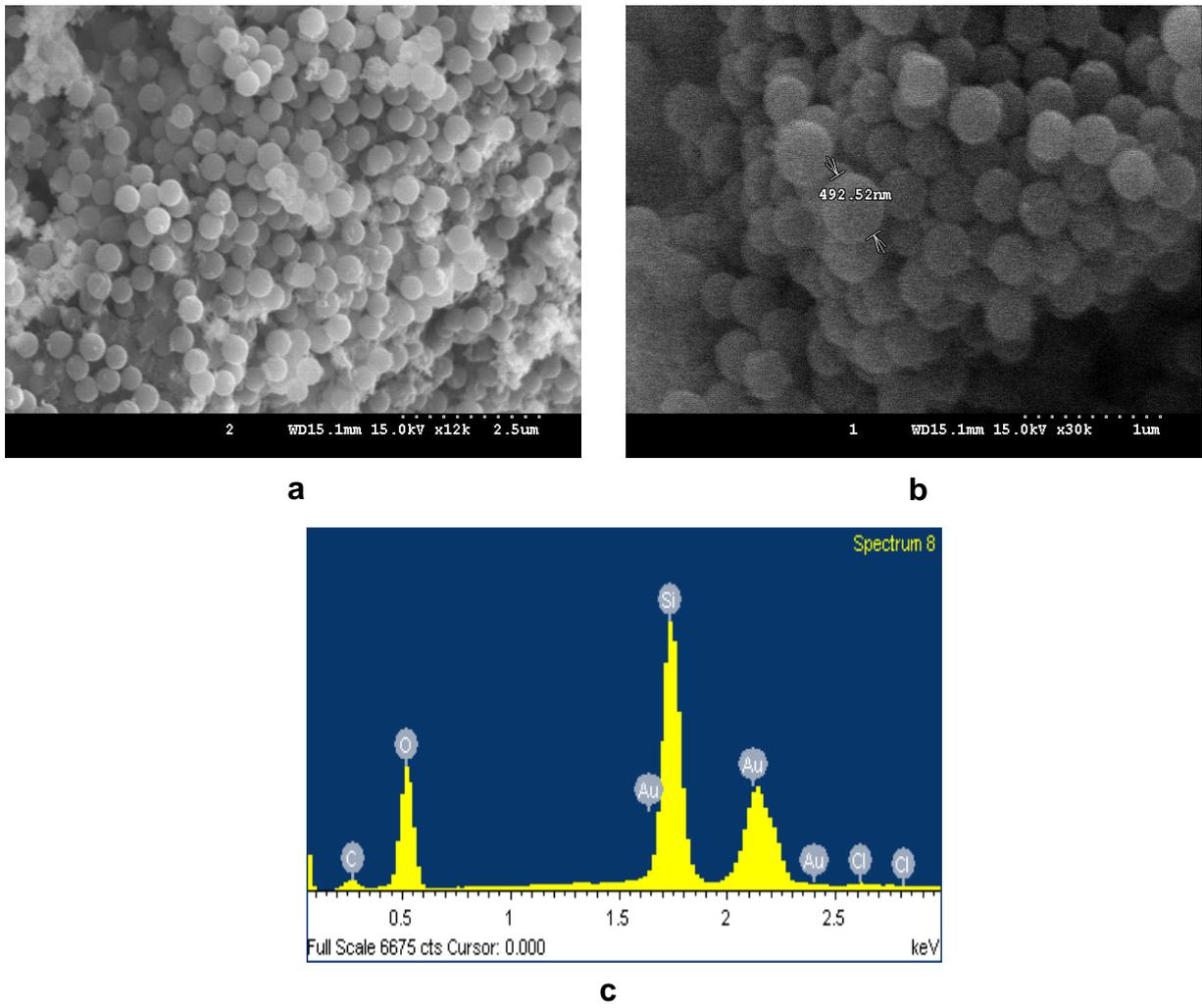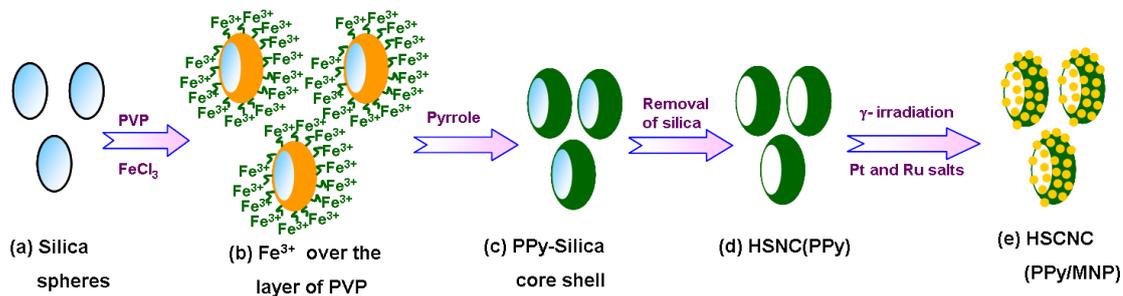*FIG. 3. EF-TEM images of HSCNCs(PPy/MNP) prepared by (a) γ-irradiation (b) chemical reduction*

a

b

c

FIG. 4. FESEM images of SiO2(core) – PANI(shell)/MNP composite prepared by one- step gamma irradiation method.

Scheme 1. Steps involved in the preparation of HSCNCs(PPy/MNP) catalyst.
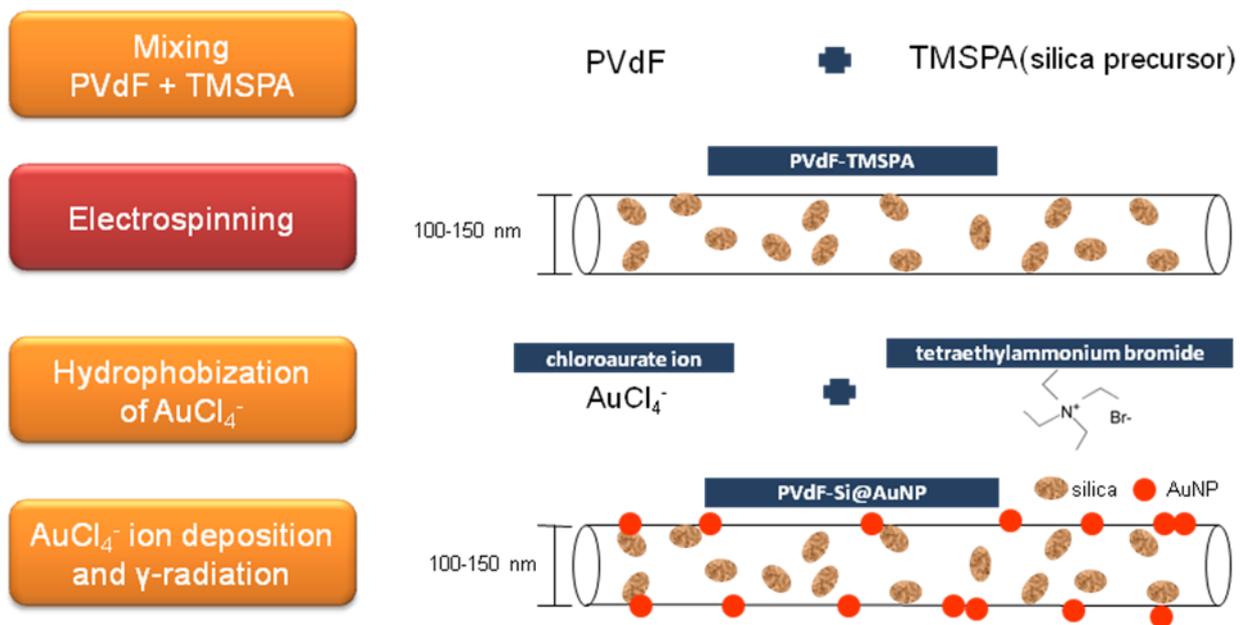
Scheme 2. Steps involved in the preparation of multifunctional electrospun nanowebs

154