Investigations on encapsulated nanotubes in MCM 41 and dispersion of nanoparticles into carbon nanotubes

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Introduction

Synthesis of nanostructured materials in the so-called mesoscopic size range are currently the topic of intense research as their properties differ considerably from those of the corresponding bulk materials. Specifically, materials with sizes in the range 1-10 nm can exhibit novel electronic, optical, magnetic, and chemical properties due to their extremely smaller size and proportions. These particles have many technological applications, e.g., in magnetic recording media, ferrofluids, and catalysts .A critical obstacle that prevents in making these particles with nanosizes is the high reactivity from the large surface ratio and the spontaneous production of macroscopic-sized agglomerates Hence, conventional approaches are not suitable to make them.In contrast to the conventional synthetic methods, the utility of an inorganic matrix as a host for nanocrystalline particles can be an effective way to tailoring uniform size and controlling the homogeneous dispersion of ultrafine clusters. The higher thermal stability of inorganic host materials offers additional advantages on excellent control of size distribution and morphology. Cross-linked ion-exchange polymer resins, inorganic molecular sieves, and sol-gel derived materials have been utilized as porous hosts for the preparation of nanoclusters [1]. Microporous molecular sieves have been widely used for hosting nanoclusters or nanostrucures

The discovery of mesoporous MCM-41 provides a possibility for synthesizing 3D heterostructures in a previously inaccessible size range [2]. MCM-41 is a porous amorphous silica material with a hexagonal honeycomb structure that can be synthesized with controllable pore diameter in the range 2-10 nm [3]. Inspired by the possibility of alignment of the encapsulated molecules into the host channels, different nanostructured organic-inorganic composites based on mesoporous hosts and carbon, polymer, metal, semiconductors have been investigated.[4]. While using porous templates for making tubular or fibrous conducting polymer, each pore in the template acts as tiny reaction vessel having precise diameter and length. Such a type of conducting polymer

nanotube/nanofibre can exhibit field emission properties for flat panel displays. Recently, efforts have been made on the synthesis of polyaniline (PANI) or polypyrrole nanofibers or nanotubes by chemical or electrochemical oxidative polymerization of the respective monomer. The encapsulation of nanosized conducting polymer filaments into the channels of MCM-41 hosts opened up the possibility of using mesoporous materials for making nanometer-scale electronic devices [5].

We have prepared a conducting polymer, poly(diphenyl amine), PDPA inside the channels of MCM-41 through polymerization of the self assembly of monomer and organic dopant in the channels. The self assembly of the dopant and monomer moleculaes, anchoring into the pores of MCM-41, resulted tubular PDPA. X-ray diffraction (XRD) and N_2-adsorption measurement were used to confirm the polymer formation inside the pores. FTIR spectroscopy and scanning electron microscopy (SEM) were used to characterize PDPA. The polymer formed inside the channels was remived and analyzed for structure and properties. While we have noticed interesting thermal and electronic properties for the polymer, it was difficult to obtain the microstructure using conventional transmission microscopy. We have used high resolution transmission microscopy (HRTEM) for obtaining the microstructure of the polymer.

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [6] and the realization of their unique physical properties that include mechanical, thermal, and electrical aspects, studies have been extended to generate functional materials using them. Especially in the area of catalysis, the potential use of CNTs as a support for metal catalysts has been recently explored. The use of CNTs or graphitic nanofilaments to anchor metal particles as catalysts becomes increasingly interesting as these catalysts can show catalytic activities higher than those of simple metallic catlysts. Further, the combined presence of metal particles can increase the catalytical activities. While application and synthesis are viable and handy, structrual studies on these alloys in the presence of CNTs would help in optimizing the catalytical strength of these alloys. On successful anchoring of alloy nanoparticles in CNTs. it is hoped that it can act as catalysts for hydrogen generation from ammonia and open new avenue for the production hydrogen from non polluting source.

We have used carbon nanotube as supporting matrix to host metal nanoparticles. The carbon nanotube was suitably functionalized to specifically anchor the metal particles and also we could provide conditions for avoiding the agglomeration of nanoparticles. Now, it becomes important to use high volt electron microscope (HVEM) to understand the distribution and crystal structure of

anchored nanoparticles.

Experimetnal Procedure

Hosting polymer nanotubes inside MCM-41 and characterization

MCM 41 was synthesized using ETAB (eicosanetrimethyl ammonium bromide) as surfactant by hydrothermal procedure [7]. PDPA was formed inside the channels of MCM 41 by initial self - assembly of monomer and dopant inside the pores and subequent oxidative polymerization. MCM 41(PDPA) was characterized using FT IR spectroscopy (Perkin Elmer Lamda 9N 1062 spectrometer), N2 sorption (BET) measurements (quantachrome Autosorb 1 with nitrogen as adsorbate at 77K), X ray diffractometer(D8 Advanced Bruker AXS diffractometer using CuKα1 radiationa) Thermogravimetric analyzer(TA instrument 951; ca .10 mg of the sample was placed in a quartz bucket and heated at a rate of 10°C/min in an N2 atmosphere), Proton (1H) NMR measurements (400 MHz Bruker, Advance Digital 400 NMR spectrometer). The microstructure of PDPA extracted from MCM 41(PDPA) was investigated by means of a field emission transmission electron microscope (FETEM) (JEOL, JEM 2000EX) with a field emission electron gun operated at 200 kV). The distribution of nanopartilces into the CNTs were confirmed by HVTEM (Jeol ARM 1300s) operated with 1250 kV. HVEM HRTEM facilities were extended to us by Korea Basic Science Institute (Daejon).

Dispersing the metal nanoparticles in CNTs

CNTs were purified and functionalized . Carboxylation, sulfoxylation and thioamination were used to functioanlize CNTs. Also, the CNTs were coated with conducting polymer having functional groups that could hold the metal nanoparticles without agglomeration. Gold, iron and palladium nanoparticles were dispersed into the functionalized CNTs using the respective metal salts as source for metal and employing γ-radiation (cobalt-60 source in air at room temperature at a total dose of 30 KGy)for reduction. microstructure nanoparticles distributed in the CNTs was investigated by means of a field emission transmission electron microscope (FETEM) (JEOL, JEM-2000EX) with a field emission electron gun operated at 200 kV) using the facilities extend by Korea Basic Science centre (Daejon).

Results and Discussion

PDPA was formed inside the channels of MCM-41 by performing polymerization of adsorbed monomer. We could observe distinct differences in morphology, amount of polymer formed, electronic and thermal properties between MCM-41(PDPA-NSA) and MCM-41(PDPA-SA) through conventional characterization (details are not provided). We have got evidences for the presence of conducting polymer inside the channel of micropores through several conventional techniques. However, the nanostructure of polymer formed inside could not be clearly understood by the conventional techniques. Also, conventional transmission microscopy (TEM) failed to observe the nanostructure, probably due to the low electron scattering cross-section of the main constituents (silicon, carbon and hydrogen) of the host. We have used high resolution TEM like energy loss spectroscopy (EELS) and energy filterd TEM (EFTEM) to obtain clear understanding about the chemical structure, growth direction for the formed nanostuctured polymer, side surfaces, polar direction, surface reconstruction, defect structures and other possible structural features developed in the host, during the inclusion of nano structured polymers

To authenticate the tubular formation of PDPA, the polymer was extracted from MCM-41(PDPA-NSA) and the microstructure of the PDPA was examined by FETEM. Figure 1 shows a typical crosssectional high resolution (HR) TEM photograph of the PDPA extracted from MCM (PDPA-SA). The TEM photograph clearly provides evidence for the nanotubular morphology for PDPA (Fig 1). PDPA nanotubes with a diameter of 20-30 nm and a length of 130-180 nm could be seen (Fig 1).

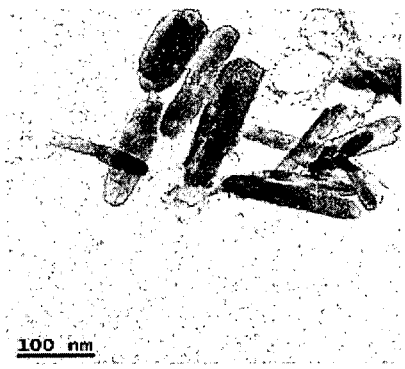
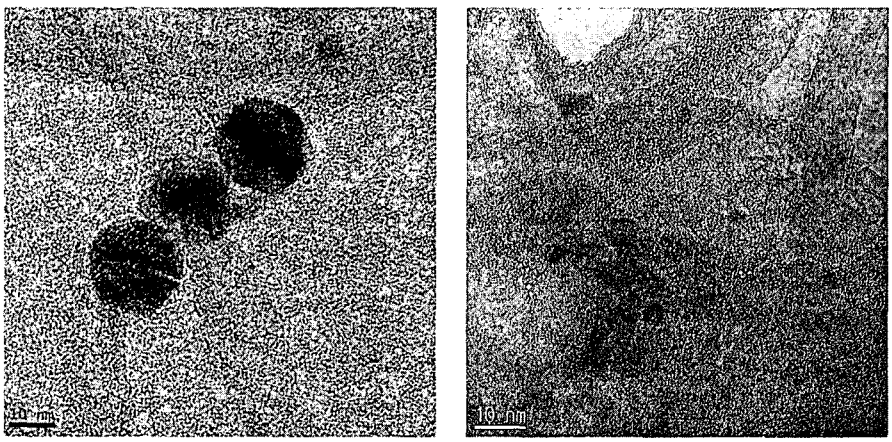


Fig. 1. FETEM photograph of PDPA extracted from the pores of MCM-41

Pd, Au and Pt nanoparticles were formed by gamma ray induced reduction of the metal particles. Generally, CNTS are not ideally suited for holding the metal particles due to their hydrophobic characteristics. We have functionalized CNTs with suitable modifications to hold the metal particles and also to avoid agglomeration of particles. The distributed functional groups effectively avoid agglomeration and such functioanlized CNTs could hold metal nanoparticles. HVEM pictures (Fig 2 -4) clearly reveal that metal particles of nanometer scale are formed and the distributions depend on the extend and nature of functionalization of CNTs.



(a) (b)

Fig. 2. HVEM photographs of Pd particles (a,b) distributed in the conducting polymer coated CNTs

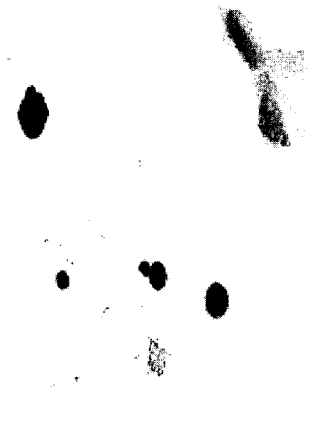
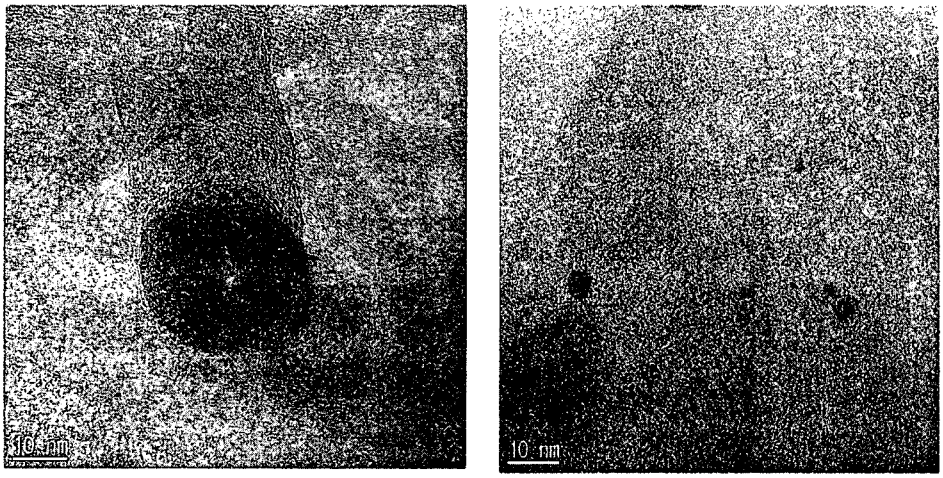


Fig. 3. HVEM photograph of gold nanoparticles anchored in the thioaminated CNTS



(a) (b)

Fig. 4. HVEM photographs of iron (a) and iron palladium alloy nanoparticles distributed in the conducting polymer coated CNTs

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