

Preparation and characterization of gold nanoparticles and nanowires loaded into rod-shaped silica by a one-step procedure



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ABSTRACT

Rod-shaped mesoporous silica nanoparticles (RMSN) with built-in gold nanoparticles or thin gold nanowires in the pore channels were *in situ* synthesized via a one-step procedure. The insertion of a hydrophobic gold precursor into the mesopores of RMSN was reached through a micellar solubilization mechanism and gold nanoparticles were achieved through a thermal reduction. The resulting RMSN and Au-RMSN samples were characterized by using X-ray diffraction, transmission and scanning microscopies (TEM and SEM), X-ray photoelectron spectroscopy (XPS), nitrogen physisorption and solid-state Nuclear Magnetic Resonance (NMR). The interaction of Au precursor (a carbene complex) with the thiol group at the silica surface was identified and found to play a crucial role in the dispersion of the uniform metal nanoparticles at the internal surface of RMSN. Moreover, TEM micrographs revealed the absence of large gold particles outside the mesopore network. The shape of Au nanoparticles and their loading amount in the mesoporous silica could be easily tuned by altering the concentration of gold precursor.

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1. Introduction

The design of materials through the simultaneous control of the morphology, porosity, particle size, and composition at the nanometer scale was crucial for the development of advanced technologies [1–4]. In particular, mesoporous silica nanoparticles (MSN) were used as innovative hosts to support oxide or metallic nanoparticles, thus yielding metallic functionalities readily accessible and highly dispersed. Accordingly, advanced functional materials were achieved and several breakthroughs were made in many fields like heterogeneous catalysis, energy, remediation, bio-imaging, cancer diagnosis, theranostics or photothermal therapy [5–12]. Consequently, the elaboration and processing of metallic nanoparticles has been of growing interest in materials chemistry on account of the possibility to induce remarkable physical or chemical properties related to a particle size in the nanometer range [13–15]. In particular, gold nanoparticles and clusters possessing a particle size ranging from sub-nanometer to few

nanometers, are fascinating owing to their unique optical, magnetic, and electronic properties [16–20]. Nevertheless, metallic nanoparticles generally tend to aggregate which significantly affects their physical properties. In order to limit this drawback, metallic nanoparticles should be stabilized in a manner which makes them accessible and stable. Among the different strategies developed in the past, the preparation of metallic nanoparticles supported on porous substrates appeared to be efficient [21–24]. Since the morphology of mesoporous silica was quite easy to control, the metal insertion into host materials was in general achieved in a post-synthesis step by impregnation, co-precipitation or sonication [25,26]. Despite the easiness of post-synthesis strategies, the backfilling phenomena could result in the clogging of the pore network, thereby reducing the accessibility to the functionalities. Intensive research studies have been thus dedicated to the optimization of one-pot synthesis procedures for the preparation of metal-functionalized silica materials leading to an enhanced metal accessibility at the internal mesoporous surface.

However, this type of synthesis pathway may be complex, especially in terms of managing the interactions between all involved species, which does not always affect the desired properties of the final product. Moreover, the base-mediated conditions

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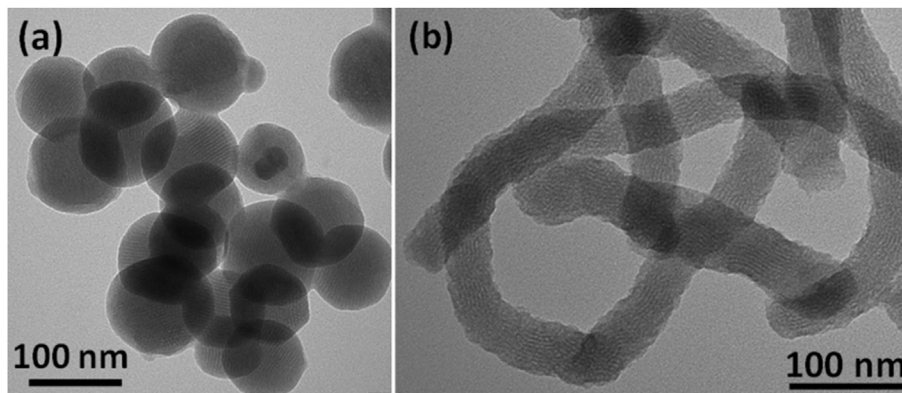


Fig. 1. TEM micrographs of nanosized silica particles: (a) MSN type, (b) RMSN type.

required to tune the morphology and size of silica particles are not compatible with metallic salts often producing the precipitation of hydroxide species. Our group previously reported an alternative approach for the preparation of metal-functionalized mesoporous silica materials which involved an *in-situ* functionalization based on the micellar solubilization of an organometallic compound or a hydrophobic metallic complex [7,27–29]. The main challenge was to prepare a nano-composite with metallic species dispersed throughout the entire porosity of the silica nanoparticles. The present paper reports the incorporation of gold nanoparticles or ultra thin nanowires into the pore channels of rod-shaped mesoporous silica (RMSN) based on this micellar solubilization approach adjusted to the specificity of the system studied. In particular, the addition of mercaptopropyltriethoxysilane allowed the control of silica particle morphology as a result of the mercaptopropyl group solubilization into the micelle core [30]. Moreover, the thiol-functional groups localized into the micelle core resulted in a controlled anchorage of gold carbene complexes within the pore channels, thereby precluding the formation of gold nanoparticles outside the host's porosity.

2. Material and methods

2.1. Chemicals

The following chemicals, tetraethyl orthosilicate (TEOS, 99%), (3-mercaptopropyl)trimethoxysilane (MPTS, 95%), hexadecyltrimethylammonium bromide ($C_{16}TAB$, 95%), sodium hydroxide (NaOH, 98%), and chloro [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]gold(I) ($C_{21}H_{24}AuClN_2$, 95%) were purchased from Sigma–Aldrich and used without further purification.

2.2. Materials characterizations

Scanning electron micrographs associated with energy dispersive X-ray Analysis (SEM/EDS) and transmission electron micrographs (TEM) were obtained with a Hitachi S-2600N (using a secondary electron scintillator as detector) and a JEOL 1200 EX microscope, respectively. For the purpose of TEM analysis, the particles sample were dispersed in ethanol and then dropped onto copper grids with porous carbon films. The specific surface area and pore structure parameters of the materials studied in the present work were determined from the measurements of nitrogen adsorption-desorption at 77 K with the use of a Micromeritics Autochem ASAP 2020 V3.00H unit. Prior to the sorption experiment, the sample (about 40 mg) was evacuated under vacuum at 393 K for 12 h so as to prevent the thermal decomposition of the

hybrid particles. Small-angle powder X-ray diffraction (XRD) measurements were performed with the aid of a PANalytical X'Pert MPD (Philips 1710) diffractometer controlled by a computer. The wide-angle XRD patterns were collected using a Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation; the 2θ diffraction angles in the range from 1° to 7° were recorded at a rate of 0.5 deg min^{-1} . For a sample corresponding to the highest amount of gold precursor, the XRD experiment was continued in the 2θ range up to 80° with an acquisition time of 14 h in order to record well-resolved diffraction lines. X-Ray photoelectron spectroscopy (XPS) analysis was done with a Thermo Electron-ESCALAB 250 apparatus. The spectra were obtained using the monochromatic Al- $K\alpha$ X-ray source (1486.6 eV). The photoelectron spectra were calibrated by referencing all binding energies to the Si $2p_{3/2}$ binding energy of silicon in Si–O bond (103.2 eV) arising from SiO_2 . The cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR spectra of the solid samples were collected by means of an ASX-300 Bruker spectrometer operating at 75.47 MHz with a contact time of 4 ms, a 10 kHz spinning rate and 13 000 accumulations with an interval of 5 s. All the CP/MAS ^{13}C NMR measurements were performed at $300 (\pm 0.1)$ K. Ultraviolet–visible (UV–Vis) absorption spectra were recorded using an UV visible Jasco V-670 spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a FT-IR spectrometer (Avatar 360 FT-IR) using pellets in the frequency of 4000 – 500 cm^{-1} .

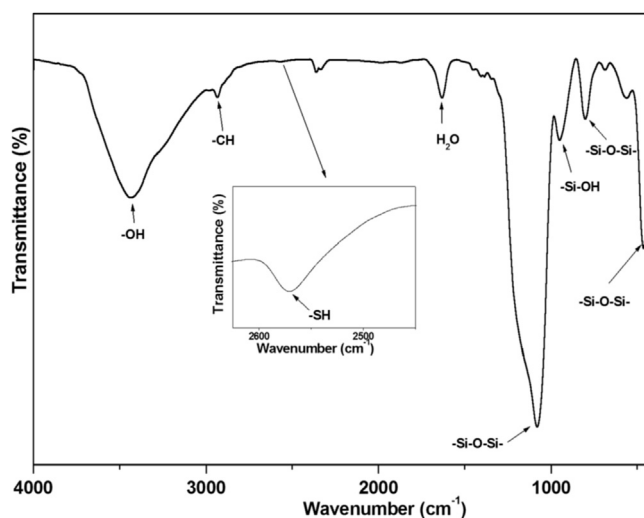


Fig. 2. FT-IR spectra of RMSN after the surfactant extraction.

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