

Carbon onions within silica nanoshells

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Carbon onions have been known since Iijima first observed them in 1980 [1]. In 1992 Ugarte et al. made carbon onions by irradiating carbon soot by an intense electron beam in a transmission electron microscope [2]. There are reports in the literature on the production of carbon structures in water medium by generating an electric arc to create high temperatures [3,4]. It was found that several metals including gold catalyze carbon onion growth from various precursor species. Multi-walled carbon nanotubes have also been coated with silica (SiO₂) [5,6].

It has previously been demonstrated that gold and silver nanoparticles react with halocarbons leading to the complete leaching of the metals along with deposition of carbon in an amorphous form [7]. This method, if used with core-shell nanoparticles such as Au@SiO₂ [8] makes possible the deposition of amorphous carbon species inside ceramic nanoshells. The nano dimension of the cavity may force a reaction between the carbon species in the solution phase itself, with or without catalysis by the metals or their ions. With this conjecture, we investigated the metal oxide nanoshells after leaching the metal core of core-shell nanoparticles. Carbon onion structures within silica shells were detected in these experiments. It may be noted that the main objective of this work is not to introduce a new method for the synthesis of carbon onions, but to introduce a new material where carbon onions have been made inside the silica shell.

Chloroauric acid and trisodium citrate were purchased from CDH fine chemicals, India. (3-amino) propyl trimethoxysilane (APS) and tetra methoxysilane (TMS) were purchased from Aldrich and were used without additional purification. Ethanol and 2-propanol were purchased from E. Merck. CCl₄ was purchased

from Ranbaxy Chemicals, India. Triply distilled water was used for all the experiments.

Gold nanoparticles of size 15 nm were prepared using the Turkevich reduction method [9]. In order to cover this gold particle with silica, a method adopted by Makarova et al. [10] was followed. Further growth of the silica shell was achieved by following the Stober method [11]. To 50 ml of the gold sol, 0.25 ml of millimolar solution of freshly prepared solution of 3-aminopropyl trimethoxysilane (APS) was added with vigorous stirring. This mixture was allowed to stand for around 15 min for complete complexation. A solution of active silica was prepared by adjusting the pH to 10–11 of a 0.54 wt.% of sodium silicate solution by progressive addition of a cation exchange resin, Dualite C 225–Na 14–52 mesh. Two milliliters of active silica thus prepared was added to 50 ml of the surface modified gold sol. The resulting mixture was allowed to stand for one day so that the active silica polymerizes on the surface of the gold particle to form Au@SiO₂. The solution thus obtained was centrifuged for around 1 h and the particles were collected and re-dispersed in about 50 ml of 2-propanol. To this solution, around 5 ml of CCl₄ solution was added.

The reaction between the metal core and CCl₄ happens over a period of several days and was studied by UV/Vis spectroscopy in a time dependent manner. It was found that the reaction between the gold nanoparticle and CCl₄ is quite slow and the reason for this slow rate may be the thickness of the silica shell. It is reported that silica covering of Au@SiO₂ is porous in nature, and gold core is accessible for halocarbons. Earlier studies including ours on Au@SiO₂ shows that after leaching the core with CN⁻ ion a well-defined shell exists showing that shell is permeable for ions [10] and possibly, molecules. Same way clear shells were seen in the case of mineralization of silver core of Ag@ZrO₂ using CCl₄ [12].

The plasmon absorption of the Au@SiO₂ nanoparticles at 524 nm progressively reduces in intensity as the reaction occurs. Once the reaction is complete, a peak corresponding to Au³⁺ appears at around 320 nm in the UV/Vis spectrum of the solution. Chlorine is removed as Cl⁻. At this point, the solution is pale yellow in

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appearance and the nanoshells formed are precipitated by centrifugation. The bubbles thus obtained were centrifuged for around four hrs, and the product collected was washed with 2-propanol and water and re-dispersed in water to yield a clear solution.

The solution thus obtained was dropped onto a copper grid supported carbon film and the solvent was allowed to evaporate leaving the particles dispersed on the carbon film and was examined using a JEOL 3010 UHR TEM equipped with a Gatan Imaging Filter using both High Resolution TEM imaging and energy filtered imaging with both plasmon-loss and core-loss electrons. The infrared spectrum was acquired with a Spectrum One infrared spectrometer from Perkin–Elmer. Mass spectra were recorded using a Voyager DE-PRO MALDI-TOF mass spectrometer of Applied Biosystems. UV/Vis spectra were taken with a Perkin–Elmer Lambda 25 UV/VIS spectrometer.

The starting Au@SiO₂ core–shell nanoparticles appear as shown in Fig. 1. Fig. 1a shows a zero energy loss

filtered HRTEM image of such a nanoparticle. Whilst the gold core is clearly visible, and closer inspection reveals this to be polycrystalline, the shell is faint and can only just be discerned. At higher magnifications and the minimum contrast defocus for the carbon support film, the shell can be a little better discerned (Fig. 1b).

An attempt was made to produce energy filtered images of such particles using the Si–L edge at 99 eV but this did not result in any clear image with reasonable signal to noise ratio, perhaps due to the fact that this edge usually shows a gradual onset, combined with the fact that the shell is very thin in comparison to the thick and heavy metal core. Energy filtered imaging using this edge has been found to be problematic in other materials too. However, if energy filtered images are recorded with inelastically scattered electrons from the low-loss regions, specifically using a plasmon energy loss of 15 eV with an energy selecting slit width of 5 eV, then the shell appears very bright in comparison to the core and the carbon support film. Such plasmon loss imaging has

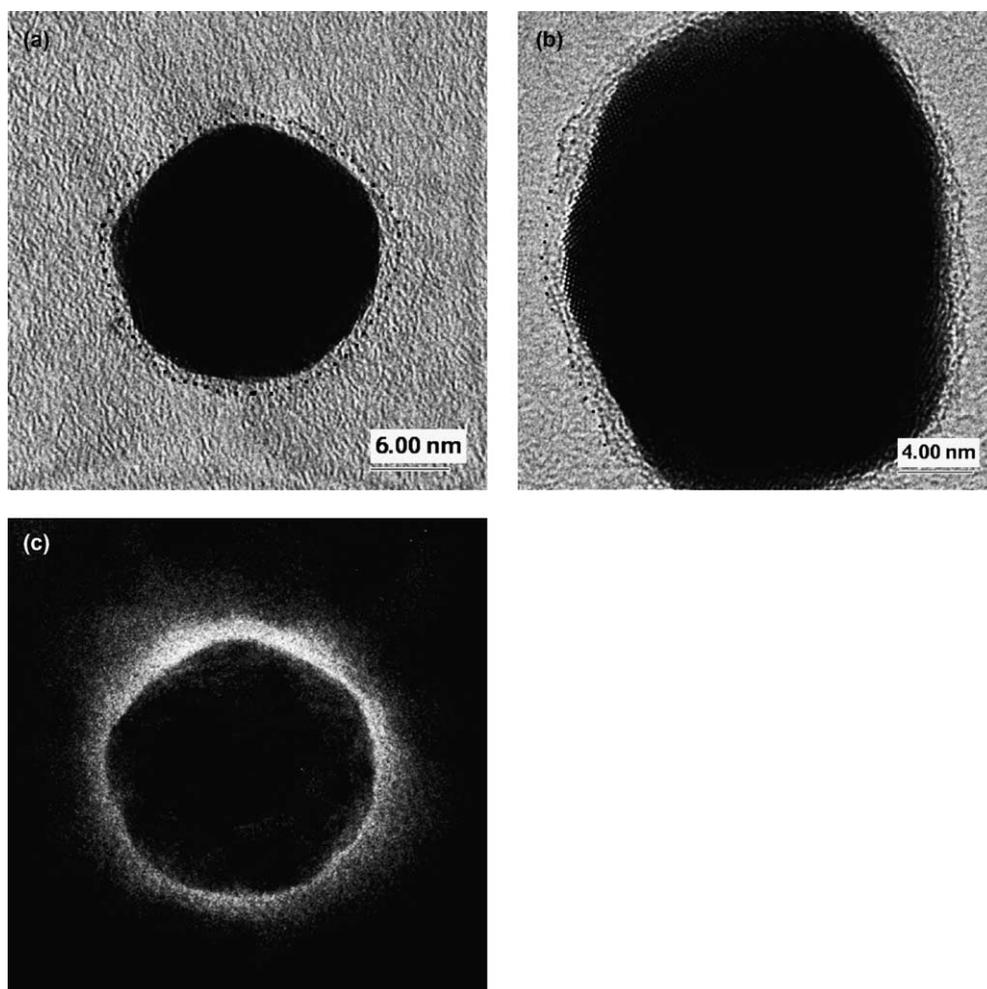


Fig. 1. Images of Au@SiO₂ core–shell nanoparticles: (a) zero loss image, the polycrystalline gold core is clearly visible but the thin SiO₂ shell is hardly discernable and its approximate boundary is shown with dotted lines; (b) image of a second core–shell particle recorded at higher magnification showing the shell more clearly; (c) image taken with an energy loss of 15 eV showing strong contrast from the shell and some weaker contrast outside, possibly from the tagged-on molecules, but little intensity from the gold core. (a) and (c) have the same scale.

previously been used to give image contrast between different phases in AlGe [13], Si [14], Y⁺ implanted Al₂O₃ [15], and Si–B–C–N ceramics [16]. An image of the particle of Fig. 1a taken using this method is shown in Fig. 1c. This 15 eV energy loss corresponds to a surface plasmon of amorphous SiO₂ [17], and at this energy, there is less plasmon intensity from Au; for bulk Au the plasmon peak appears at about 25.5 eV, whereas the surface plasmons appear at very low energies ≤ 6 eV [18,19]. Energy filtered images recorded with higher energies above 20 eV show increasing intensity from the gold core. In addition to the shell itself, some intensity is seen from outside the shell at 15 eV, possibly due to the organic molecules used in the growth process. In all images, the shell appears to be mostly of the order of 1 nm or at the thickest points 2 nm thick.

Fig. 2 shows high-resolution TEM images of bubbles after removal of the Au core using CCl₄. These appear to be typical of the sample and show certain distinct features. The outer portion of the shell is amorphous and a few nm thick, this is the SiO₂ shell. Within this, but in immediate contact with the shell, are concentric layers of graphitic carbon in a so-called “onion” structure. At least 20 layers are visible in each case. These structures were not formed by electron beam irradiation of amorphous carbon but were visible immediately on commencement of observations. In fact, they are somewhat beam sensitive themselves, and the SiO₂ parts, in particular, were prone to damage under extended exposure to the electron beam.

The amount of material synthesized is very small; in fact after centrifuging the solution containing the nanoshells, the quantity obtained in a normal synthesis is of the order of milligrams. As a result, bulk characterization such as XRD was not attempted. It would also not be expected to yield any additional information as the shell is known to be amorphous.

The formation of the onion structures inside the shells provides certain important information regarding the shell itself. It appears plastic in nature; hence it stretches and accommodates the carbon onions formed. Fig. 3 shows an elongated silica shell containing carbon onions inside. Probably this elongation happens as a result of the solution phase process, in which the shells are even more flexible. Energy filtered images were collected to ascertain the onion structure.

Even after the formation of the onion like structures inside the shell, it does not rupture immediately. The cavity left behind after the removal of gold is smaller than the dimension of the leached out metal implying that catalytic destruction of the halocarbon occurs and more carbon per metal ion is generated. The novelty of this work is that, it provides a room temperature solution phase method for generating carbon onions inside an inorganic matrix.

In order to make sure that the onion structures are formed as a result of the carbon deposited by the reaction, we studied the silica shells formed by the cyanide removal method [10], which creates clean shells of amorphous SiO₂ without any carbon deposition [20,21]. As such materials have been characterized earlier, we do not discuss such details here. It is possible to include molecules within these structures as well [20]. It may be noted that when the CCl₄ based metal core removal method was applied to core–shell particles like Au@ZrO₂ and Ag@ZrO₂ [22], clean shells were obtained [12]. This we believe is due to the fact that metal cores in them were much larger (30–60 nm) and could not force the reaction. No amorphous carbon was detected in infrared spectroscopic studies of the shells as they were leached out due to the increased porosity of the shells.

The shells show characteristic Si–O–Si asymmetric stretching at around 1100 cm⁻¹ in FT-IR spectroscopy and also Si–O–Si symmetric stretching at 801 cm⁻¹ [23]

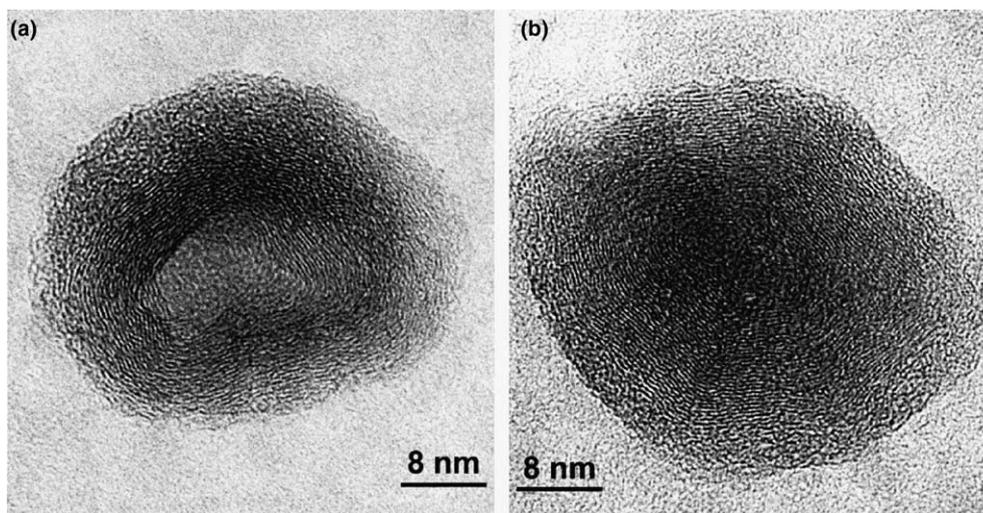


Fig. 2. High resolution TEM images of carbon onion containing shells. The outer few nm shows amorphous contrast and is the silica shell, inside this typical concentric ring structure of carbon onions is seen. In both cases more than 20 concentric graphitic planes are visible.

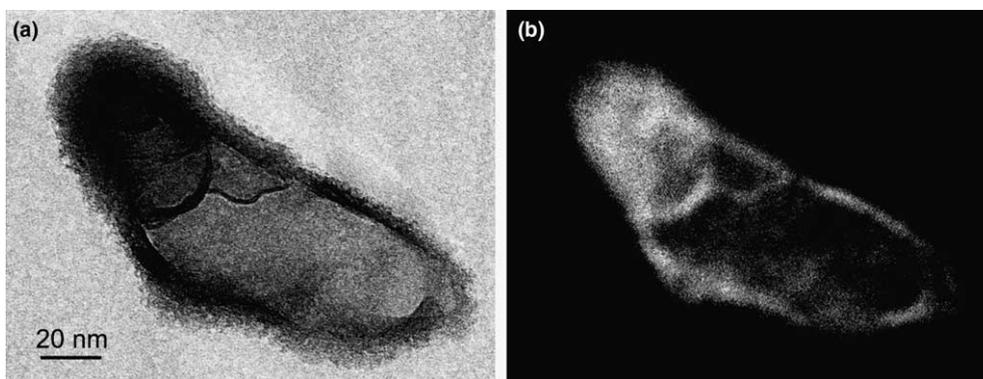


Fig. 3. TEM image showing (a) the silica shell and the carbon onion structures within of a particle formed from the merger of several shells. (b) An energy filtered image created using the C-K edge at around 284 eV, showing just the carbon structure.

(Fig. 4). The IR spectrum also shows a sharp feature at 1384 cm^{-1} showing the presence of amorphous carbon [7]. Thus not all of the carbon appears to be in the onion form. The fact that IR does not show any other features other than carbon and silica again confirms the formation of carbon material inside the silica shell. Laser desorption mass spectrum of the nanoshell shows characteristic signature of carbon clusters.

We present a novel solution phase process by which carbon onions can be formed within silica shells. It is believed that confinement of carbon formed within the nano shells forces its conversion to onions. The halo-carbon mineralization process is catalytic producing more carbon per metal ion removed. This appears to bring carbon atoms together leading to the formation of onions. This would imply that larger shells do not yield onions as confinement may not be adequate to force the reaction; it may be noted that free shells are seen with

bigger particles [12]. An alternate suggestion is that part of the carbon formed may leach out due to larger porosity of the shells. We believe that the method presented may be modified to create materials in which molecules are trapped within onions. Such trapping should be enduring as the molecules cannot leach out. The properties of coated onions could also be of significant interest.

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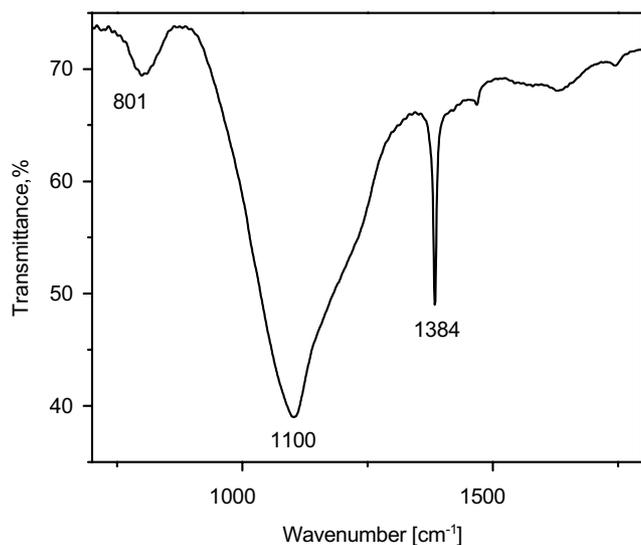


Fig. 4. FT-IR spectrum of the nanoshells dried at $350\text{ }^\circ\text{C}$ taken in KBr matrix showing the carbon feature at 1384 cm^{-1} and the Si–O–Si stretching modes at 801 and 1100 cm^{-1} .

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A new SiC/yttrium silicate/glass multi-layer oxidation protective coating for carbon/carbon composites

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Carbon/carbon (C/C) composites have potential uses as the key parts of engines in aircraft and aerospace due to their excellent high temperature mechanical properties and excellent thermal shock resistance. But the oxidation of these composites limits their use in oxygen containing atmospheres [1,2], which has led to research on the improvement of the oxidation resistance of C/C composites. An oxidation resistant coating is considered to be a reasonable choice for high temperature protection of C/C composites. In the design of oxidation resistant coatings, the physical and chemical adaptability of coating-to-matrix and bonding layer-to-outer layer is the crucial factor. During the investigations of many schol-

ars, a SiC coating has been found to be one of the best bonding layers between the C/C composite and the ceramic outer layer [3]. Therefore, the choice of the outer layer material becomes absolutely important. In our research, we have prepared ceramic outer layers such as MoSi₂, Al₂O₃–mullite and zircon [4–6]. In recent investigations, the yttrium silicates seem to be one of the best candidates for a coating material for carbon–carbon composites because of their excellent properties such an identical thermal expansion coefficient to SiC, low evaporation rate and oxygen permeation constant. This will result in a good bond to SiC materials [7]. However, the bonding of yttrium silicate coatings to SiC depends not only on the match of thermal expansion coefficients between the different layers, but also on the preparation technique. The yttrium silicate coating for C/SiC composites produced by Webster with a slurry dipping process showed a spallation of the outer coating after oxidation in air at 1873 K for approximately 50 h due to

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