Transactions of the Materials Research Society of Japan VOL.29 33-36 (2004)

Fluorescent Nanobubbles

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Degradation of halocarbons using silver and gold nanoparticles has been utilised for the synthesis of empty nanoshells or nanobubbles starting from coreshell particles. The studies conducted were mainly on zirconia and silica nanoshells. Removal of the metal core was followed by UV-visible spectroscopy. The properties of nanoshells were further modified by incorporating molecules namely ciprofloxacin and aniline inside the shell. The new materials obtained were characterized using UV-Visible spectroscopy, emission spectroscopy and transmission electron microscopy. Aniline@SiO_2 was found to have pH sensing property with complete reversibility. When confined inside the silica shell, aniline shows an additional red shifted peak apart from the usual fluorescence peak. This additional peak is attributed to the emission from excimers of aniline.

Key words: Halocarbons, core-shell nanoparticles, nanobubbles, ciprofloxacin and aniline

1.INTRODUCTION

In recent years, there has been renewed interest in the fabrication of core-shell particles with unique and tailored properties[1]. The properties of such composite particles are governed by the characteristics of the shell. Some of these properties (e.g. electrical, optical, magnetic, catalytic, mechanical) have extensive scientific and technological interest. Several approaches have been used recently to make silica[2], titania[3] and zirconia[4] covered noble metal nanoparticles. We have made zirconia and silica protected gold and silver core-shell nanoparticles[2,5]. The reactivity towards halocarbons has been used to remove the metal core while the shells can be preserved intact leading to oxide nanobubbles of varying thicknesses[6]. Since the synthesis of silica core-shell particles requires two-step[2], molecules of interest can be incorporated inside the coreshell structure and the core can be leached out to get silica bubbles containing molecules. We have tried to incorporate two molecules, aniline and ciprofloxacin inside the silica nanoshell. Aniline shows pH dependent emission characteristics, while ciprofloxacin is an important fluoroquinolone antibacterial agent.

2. EXPERIMENTAL SECTION

2.1 Materials

$AgNO_3$ was purchased from Qualigens chemicals; India. Tetrachloroauric acid trihydrate, trisodium citrate, and aniline were purchased from CDH fine chemicals; India. Aniline was used after distillation from zinc dust. (3-amino) propyl methyl diethoxysilane (APS), tetrabutyl ammonium hexafluorophosphate, zirconium (IV) propoxide and tetra methoxysilane (TMS) were purchased from Aldrich and were used as received. Ciprofloxacin was purchased from Fluka. Carbon tetrachloride was purchased from Ranbaxy chemicals, India and was used as received. Nano pure water was used for all the experiments.

2.2 Synthesis of different nanosystems and nanobubble formation

Bare gold and silver nanoparticles in the 10-15 nm range were prepared by the citrate reduction route[7]. Zirconia coated silver and gold nanoparticles were prepared by a one-pot synthesis[5] reported in the literature. 30 mg $AgNO_3$ (tetrachloroauric acid trihydrate in the case of Au@SiO_2) was dissolved in a mixture of 15 ml dimethylformamide (DMF) and 5 ml H_2O. Another solution containing 200-μl acetyl acetone and 250 μl of zirconium (IV) propoxide in 40 ml 2-propanol was prepared. The two solutions were mixed and refluxed for 45 minutes at 90°C till a greenish-black colour appeared. This solution consists of core shell particles of ~30-60 nm core diameter and ~3 nm shell thickness[5]. For synthesizing nanobubbles, a newly found reaction between nanoparticles and halocarbons was used[6]. 4 ml of the above prepared cluster solution was mixed with 1 ml CCl_4. The reaction was monitored in a time dependent manner by UV-visible spectroscopy. Silver nanoparticles were leached out as ions and got precipitated as AgCl, whereas Au got transformed into $AuCl_3$ during the reaction. The same kind of reaction was found in the case of other halocarbons like benzyl chloride also.

2.3 Synthesis of Au@SiO_2, formation of silica bubbles and incorporation of aniline and ciprofloxacin

In order to coat gold nanoparticles with silica, a method developed by Makarova *et al.*[8] was followed. Briefly

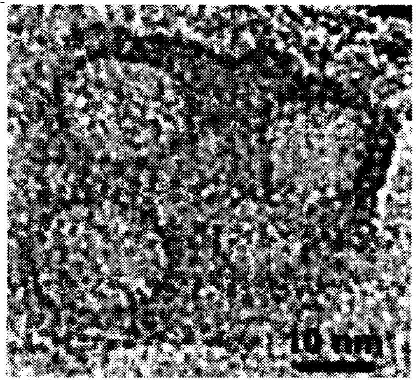

Fig. 3 TEM image of ciprofloxacin@SiO_2

3.4 Fluorescence studies

Since aniline and ciprofloxacin are fluorescent in nature, emission spectroscopy was used to characterize aniline@SiO_2 and ciprofloxacin@SiO_2. Free ciprofloxacin shows an emission peak around 448 nm[10] while ciprofloxacin@SiO_2 shows a red shifted peak around 458 nm . This red shift in the emission wavelength may be due to changes in the environment. of the molecule, such as changes in polarity.

Free aniline has an emission maximum around 340 nm[11] and for aniline@SiO_2, there are two broad emission peaks, one having emission maximum around 355 nm with low intensity and the other around 408 nm with high intensity. The second peak, which is broad, shows a maximum around 408 nm. Pyrene, when adsorbed on silica gel in higher concentrations, shows an additional 'excimer–like' peak.[12] In the case of pyrene adsorbed on silica even for concentrations far below the monolayer coverage, this broad emission is observed. Here in this case also, aniline molecules are present inside a small confined cavity of silica which gives rise to this red shifted emission. In another study, it was found that the time resolved fluorescence and excitation spectra of both pyrene and naphthalene adsorbed on silica gel shows 'excimer like' emission.[13] The associated complexes formed in the ground state are responsible for this excimer-like emission. Since pure physically adsorbed pyrene molecule cannot form ground-state complex, this kind of pyrene-pyrene complex formation is characteristic of silica gel and porous glass. The probability of this bimolecular associations and the intensity of the broad-band excimer like emission was found to increase with increase in surface coverage. This kind of slight red shift in emission, in comparison with monomer emission and appearance of a new broad shifted spectrum, are similar to the behaviour of a sandwich dimer observed by Mataga and co-workers.[14] Present study of aniline@SiO_2 also shows similar kind of emission characteristics, indicating that the same kind of ground state dimers are formed inside the silica nanobubble.

We looked at the applications of this material especially as a sensor in the solution state. For this purpose, we monitored the fluorescence by adding micromolar quantities of acids and bases. As said earlier, this new material gives two emission peaks, one at 340 mm and another at 408 nm (Figure 4A) in the intensity ratio of 1:17.

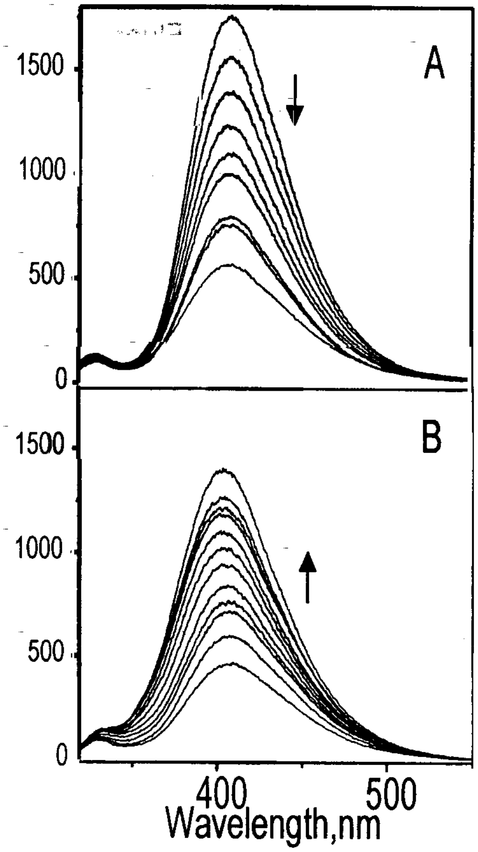

Fig. 4 (A) Quenching of fluorescence of aniline@SiO_2 by the addition of micromolar acetic acid in aqueous medium. (B) Recovery of fluorescence of aniline@SiO_2 by the addition of micromolar ammonium hydroxide to the aqueous medium.

Since the emission at 408 nm is very much higher in intensity than the one at 340 nm, we concentrated on the change in intensity of the former peak. It may be pointed out that the change in intensity of both the peaks is similar upon the addition of acid and alkali. In order to check the behaviour of aniline in acidic medium, we added micromolar quantities of acetic acid to the solution containing aniline@SiO_2. It showed progressive quenching of florescence intensity, as the addition continued. The system was found to have excellent reversibility. We could get the fluorescence back almost quantitatively by adding micromolar ammonium hydroxide (Figure 4B), thus making it an efficient pH sensor.

4. CONCLUSIONS

The halocarbon reactivity of core-shell nanoparticles has been investigated. While bare metal nanoparticles completely degrade halocarbons, core-shell particles give metal oxide nanobubbles by the selective leaching of the metal core. Incorporation of aniline and ciprofloxacin molecules into the bubbles gives new systems with interesting properties. The reactivity of halocarbons with coreshell particles and the nanoshells incorporated with the method involves the following procedure: A millimolar solution of aniline and ciprofloxacin were added separately to Au@citrate and stirred for one hour, so that the molecule gets adsorbed on the surface of the nanoparticles, followed by APS and sodium silicate solution to get silica coated gold nanoparticles. Au@aniline@SiO_2 and Au@ciprofloxacin@SiO_2 thus obtained were treated with CCl_4 under mild stirring to remove the gold core. The reaction between gold core and CCl_4 was monitored by UV-visible spectroscopy. The removal of gold and the formation of bubbles were confirmed by the time dependent disappearance of the plasmon excitation peak. The bubbles thus obtained were centrifuged for about six hours, and the product collected was washed with 2-propanol and water and re-dispersed in water to get aniline@SiO_2 and ciprofloxacin@SiO_2. The bubble samples were also prepared by a core removal procedure using CN^-.

The samples were characterized by UV-visible spectroscopy (Perkin Elmer Lambda 25), transmission electron microscopy (TEM, Philips CM20, 200 KeV) and optical emission spectroscopy (F- 4500 Hitachi Spectroflourimeter).

3. RESULTS AND DISCUSSION

3.1 UV-visible studies showing the halocarbon reactivity of core-shell nanoparticles

It has been reported that the metal nanoparticles reacts with halocarbons producing metal halides and amorphous carbon[6]. Here we have extended this study, for coreshell particles leading to the formation of nanoshells. Figure 1 shows the time dependent UV-visible spectra of the Ag@ZrO_2 solution as a function of reaction time with CCl_4. The traces were recorded at an interval of 30 minutes after the addition of CCl_4. The intensity of the plasmon absorption band decreases with the passage of time, which implies the selective leaching of the Ag core. Finally the plasmon absorption is lost completely indicating the completion of selective leaching of the core or the formation of freely suspendable ZrO_2 nanobubbles.

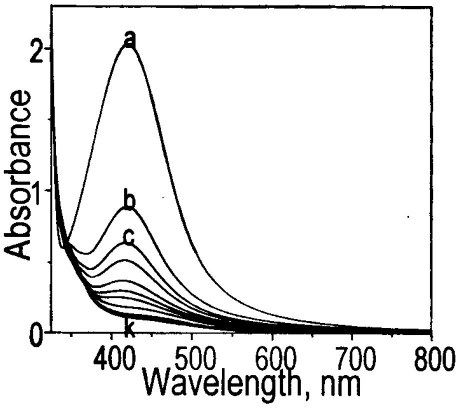

Fig. 1 Time dependent UV-visible spectra of the reaction of Ag@ZrO_2 with CCl_4.

3.2 UV-Visible studies of the aniline@SiO_2 and ciprofloxacin@SiO_2.

The absorption spectra of free cirpofloxacin, Au@ciprofloxacin@SiO_2 and ciprofloxacin@SiO_2 in the propanolic medium are shown in figure 2. Free ciprofloxacin shows three characteristic peaks around 225, 283 and 326 nm in alkaline media[9] (trace a). The absorption spectrum of Au@ciprofloxacin@SiO_2 (trace b) shows the characteristic plasmon absorption band of gold nanoparticles apart from the three ciprofloxacin peaks. As can be seen from the trace, there is a red shift in the plasmon absorption from 521 nm (bare nanoparticles) to 526 nm. We attribute this to the the adsorption of ciprofloxacin on the nanoparticle surface and the subsequent silica cover on it, the latter being more significant[2].

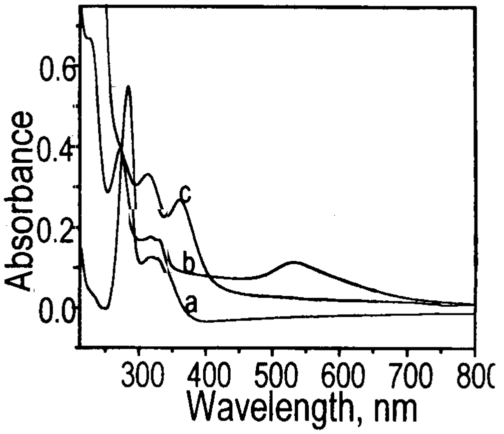

Fig. 2 UV/Vis spectra of a) free ciprofloxacin, b) Au@ciprofloxacin@SiO_2 and c) ciprofloxacin@SiO_2, in propanolic solution.

The spectrum c is that of ciprofloxacin@SiO_2 which shows only the peaks due to ciprofloxacin. The red shift seen in the case of ciprofloxacin@SiO_2 is very much expected since many ciprofloxacin molecules are present inside the confined volume of the nanoshell (as the surface of gold is covered by several molecules). A similar kind of study has been done for aniline@SiO_2 also. Au@aniline@SiO_2 showed two peaks at 280 nm and 528 nm due to aniline and gold surface plasmon respectively. Aniline@SiO_2 showed a peak a single 280 nm due to $\pi \rightarrow \pi^*$ transitions.

3.3 Transmission electron microscopic studies

TEM image of the ciprofloxacin@SiO_2 nanobubbles are shown in the figure 3. We can see particles of average shell diameter of around 15 nm, in agreement with the gold nanoparticles used in the synthesis. The shell morphology is largely spherical as expected. The particles are extremely beam-sensitive and they collapse upon prolonged exposure. A similar kind of image was obtained for aniline@SiO_2 also.

molecules inside were studied by UV-visible spectroscopy, transmission electron microscopy and emission spectroscopy. Aniline incorporated nanobubble was found to have pH sensing property with complete reversibility.

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(Received Dec. 1, 2003; Accepted March 15, 2004)