



Rosemary, M.J. and Suryanarayanan, V. and MacLaren, I. and Pradeep, T. (2006) *Aniline incorporated silica nanobubbles*. *Journal of Chemical Sciences*, 118 (5). pp. 375-384. ISSN 0253-4134

<http://eprints.gla.ac.uk/4870/>

Deposited on: 16 January 2009

# Functionalized, fluorescent and pH sensing nanobubbles: aniline@SiO<sub>2</sub>

M. J. Rosemary<sup>1</sup>, V. Suryanarayanan<sup>1</sup>, Ian MacLaren<sup>2†</sup> and T. Pradeep<sup>1\*</sup>

<sup>1</sup>Department of Chemistry and Sophisticated Analytical Instrument Facility  
Indian Institute of Technology Madras  
Chennai 600 036, India.

<sup>2</sup>Institute for Materials Science  
Darmstadt University of Technology  
Petersenstr. 23  
64287 Darmstadt, Germany.

We report the synthesis of monolayer functionalized nanobubbles of SiO<sub>2</sub> with aniline inside, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>@SiO<sub>2</sub>@stearate, exhibiting fluorescence and 'excimer-like' emission which behaves as a nanoscopic pH sensor, with reversibility. Stearic acid functionalization allows the materials to be handled just as free molecules; for dissolution, precipitation, storage, etc. The methodology adopted involves adsorbing aniline on the surface of gold nanoparticles with subsequent growth of a silica shell through monolayers, followed by the selective removal of the metal core either using sodium cyanide or a new reaction involving halocarbons. The material is stable and could be stored for extended periods without loss of fluorescence. Spectroscopic and voltammetric properties of the system were studied in order to understand the fluorescence probe as well as the monolayer, whilst transmission electron microscopy has been used to study the silica shell.

\*For correspondence, Email: pradeep@iitm.ac.in Fax: 00-91-44-2257-0509 or 0545

† Now at Department of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ, UK

## Introduction

Incorporation of organic molecules, mainly dye molecules, inside solid matrices is an attractive topic of research because of the wide range of properties<sup>1, 2</sup> such as increased photostability and fluorescence quantum yield<sup>3-5</sup> of the modified materials. An approach in this regard is to incorporate molecules inside solid matrices such as silica spheres.<sup>6, 7</sup> Advantage of this kind of nanoscopic container is that it can be used to control the environment of the molecule. The molecule can be

protected from unwanted chemical reactions and the cavity provides a rigid environment for adsorbed molecules. Colloidal dispersions of silica shells are optically transparent, providing an opportunity to study the behavior of the molecules incorporated without excessive light scattering problems. Imhof *et al.* have studied the incorporation of fluorescein isothiocyanate inside silica spheres where the main objective was to increase the photostability of the dye molecule. Results of this study seemed to suggest an inhomogeneous distribution of the molecules inside the shell.<sup>8</sup> Studies have been performed on the excited state reactions of the photochemically important molecule, ruthenium tris(bipyridyl) dye inside silica shells, where the excited Ru(II) shows significant enhancement of phosphorescence yield and lifetime.<sup>9</sup> Moreover, the dye reacts with molecules such as methylviologen. Bosma *et al.* have synthesized colloidal poly (methyl) methacrylate (PMMA) particles where fluorescent dyes are incorporated into the polymer network.<sup>10</sup> There are some other interesting studies as well on molecules such as pyrene adsorbed on silica gel, where the molecule shows 'excimer like' emission in addition to the monomer emission for different surface coverages.<sup>11</sup>

The synthetic approach followed in all these studies was to allow the dye molecules to react with a silane coupling agent such as 3-(aminopropyl) triethoxysilane (APS) followed by the addition of another silane containing reagent, which undergoes hydrolysis/condensation incorporating the dye inside a silica shell. But in a different approach, Makarova *et al.* introduced a new method where fluorescein isothiocyanate molecule was adsorbed on a nanoparticle surface after which silica was grown on it, thereby allowing the molecule to remain inside the shell.<sup>12</sup> Recently Ostafin *et al.* has studied the encapsulation of cascade blue dye at high concentrations and has shown that the fluorescence intensity of the dye trapped inside the nano-sized silica shells can be higher than that observed in their free solution under comparable conditions.<sup>13</sup>

There has, in these studies, been a significant focus on the photochemistry and spectroscopy of the adsorbed molecules, possibly to the neglect of other interesting properties of the incorporated molecules. Since these molecules are isolated, they may show different properties in contrast to the free ones when confined within a shell. Many of the materials are widely used as sensors and fluorescence intensity-based sensors are also made.<sup>14-16</sup> We have incorporated a simple molecule, namely aniline, and investigated the pH dependant properties of the new material. Free aniline is fluorescent and its fluorescent intensity decreases linearly with decreasing pH.<sup>17</sup> By incorporating aniline into the shell, we were able to make a nanoscopic pH sensor, which

has reversibility. Aniline, when confined inside the silica shell, shows an additional red shifted peak in addition to the usual fluorescence peak. This additional peak is attributed to the emission from excimers of aniline. The presence of the molecule inside the shell was further confirmed by cyclic voltammetric measurements. The external surface of the shell was modified with a monolayer cover of stearic acid so that this material can be dispersed in diverse media. We undertook these studies as an extension of our work on monolayer protected clusters<sup>18-22</sup>, core-shell nanomaterials<sup>23</sup>, and nanobubbles.<sup>24</sup>

## **Experimental**

### **Materials**

Chloroauric acid, trisodium citrate, aniline and stearic acid were purchased from CDH fine chemicals, India. Aniline was used after distillation from zinc dust. (3-amino) propyl methyl diethoxysilane (APS) and tetra methoxysilane (TMS) were purchased from Aldrich and were used without additional purification. Ethanol and 2-propanol were purchased from E.Merck. Carbon tetrachloride was purchased from Ranbaxy Chemicals, India. Ultra pure water was used for all the experiments.

### **Synthetic Procedure**

Gold nanoparticles of size 15 nm were prepared using the Turkevich reduction method.<sup>25</sup> In order to cover this gold particle with silica, a method adopted by Makarova *et al.*<sup>12</sup> was followed. To 200 ml of the gold sol, 1 ml of millimolar aqueous solution of aniline was added under vigorous stirring and the solution was allowed to stand for 15 minutes so that complete complexation of aniline on gold surface took place. Next, 1.5 ml of millimolar solution of freshly prepared solution of APS was added to it with vigorous stirring. This mixture of gold particles with APS was again allowed to stand for around 15 minutes 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. 10 ml of active silica thus prepared was added to 200 ml of the surface modified gold sol. The resulting mixture was allowed to stand for one day, so that the active silica polymerized on the surface of the gold particle to form Au@SiO<sub>2</sub>. Further growth of the silica shell was achieved by following the Stober<sup>26</sup> method and the particle obtained by this method was of the size around 90 nm.

The solution thus obtained was centrifuged for around 1 hour and the particles were collected which were repeatedly washed with 2-propanol to make sure that no aniline was present on the surface of silica. This material was re-dispersed in about 100 ml of 2-propanol. To this solution, 2 M sodium cyanide solution was added to remove the gold core and stirred for around 48 hours. The reaction between the gold cores and the sodium cyanide was monitored by UV/VIS spectroscopy. The dissolution of gold was confirmed by the disappearance of the gold plasmon peak. The formation of bubbles was confirmed from TEM images. By using carbon tetrachloride<sup>27</sup> instead of sodium cyanide to remove the gold core, we observed carbon onion structures inside the silica shell in the TEM pictures. Later when we extended this study for trapping other molecules such as ciprofloxacin, there also we could see the same kind of carbon onion structures inside the silica nanoshell (a detailed study of the microscopy of these onion materials will be published separately). The bubbles thus obtained were centrifuged at 2000 rpm for around six hours, and the product collected was washed with 2-propanol and water and re-dispersed in water to yield aniline@SiO<sub>2</sub> and such other materials.

To disperse this material in organic solvents and also for easy storage and handling, we functionalized the bubbles by adding 1 mM solution of stearic acid to the aqueous dispersion of aniline@SiO<sub>2</sub>. We designate this monolayer protected material as aniline@SiO<sub>2</sub>@stearate. The material can be freely dispersed, precipitated and stored.<sup>28</sup>

## Techniques

**Optical Absorption and Emission Spectroscopy.** UV/VIS absorption spectra were recorded using Perkin Elmer Lambda 5 spectrometer and Emission spectra were measured using an F- 4500 Hitachi spectrofluorimeter.

**Infrared Spectroscopy.** FT-IR spectrum was recorded with a Perkin Elmer Spectrum One instrument using 5% (by weight) KBr pellets.

**Transmission Electron Microscopy.** Suspensions of the particles were dropped onto copper grid supported carbon-films and allowed to dry leaving particles dispersed on the carbon film. These were then imaged using transmission electron microscopy with a JEOL 3010 UHR TEM equipped with a Gatan Imaging Filter.

**Cyclic Voltammetry.** Cyclic voltammetry data were obtained from an electrochemical analyzer (CH Instruments Model 600A) in a standard three-electrode cell comprising of a Pt disk

(area = 0.8 mm<sup>2</sup>) as the working electrode, a platinum foil as the counter electrode and Ag/AgCl as the reference electrode.

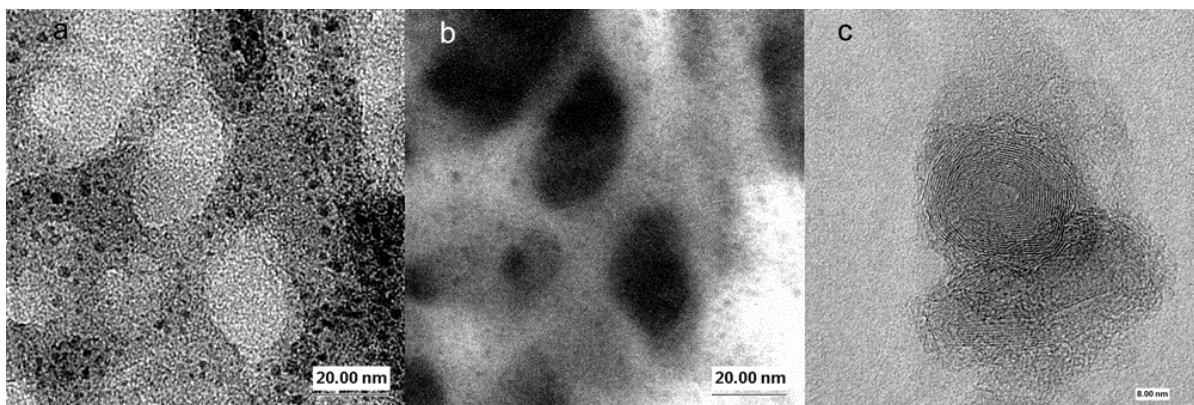
**Mass Spectrometry.** The mass spectrometric studies were conducted using a Voyager DE-PRO Biospectrometry Workstation (Applied Biosystems) MALDI–TOF MS instrument.

## Results and Discussion

As the oxide-protected nanoparticles have been adequately characterized, we present data only on the new materials. The hollow nanospheres formed by the CN<sup>-</sup> removal method (Figure 1a and b), have an average shell diameter of around 10-20 nm in agreement with the gold nanoparticles used in the synthesis. They are surrounded by roughly spherical amorphous silica shells, although it was difficult to determine the exact thickness since the shells were usually found in small clusters as here. Figure 1a shows a conventional bright field HRTEM image of the shells surrounded by the darker SiO<sub>2</sub> shell material, the background comes from the C support film. Figure 1b shows an image of the same area recorded using the Gatan Image Filter to select electrons which have lost  $15 \pm 2.5$  eV. This has been shown in core-shell nanoparticles with SiO<sub>2</sub> shells to highlight the SiO<sub>2</sub> shell rather well (supporting information 1) and appears to correspond to a surface plasmon of amorphous silica.<sup>29</sup>

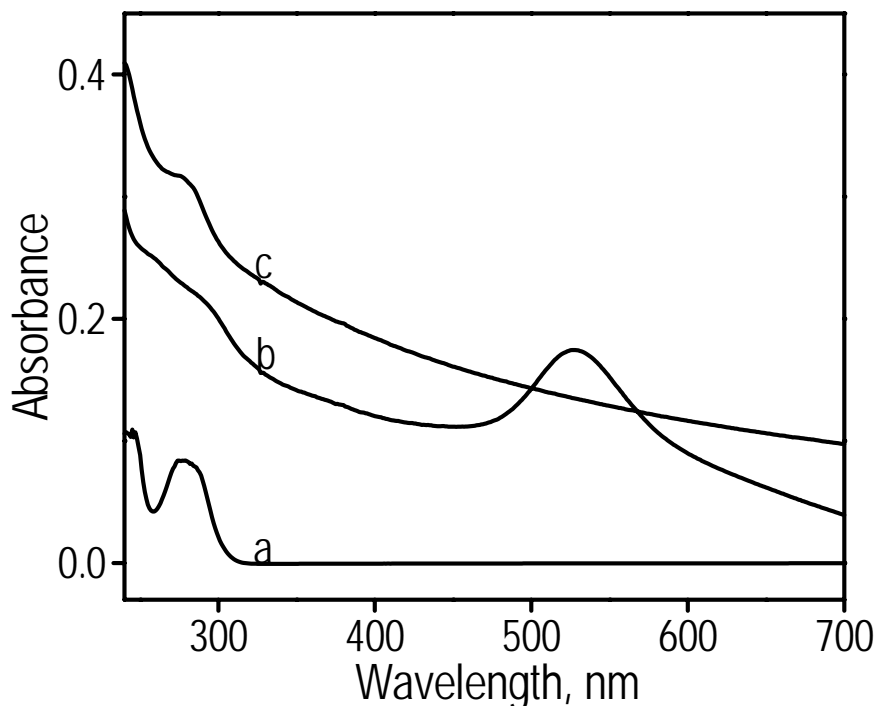
Different studies of dye incorporation inside the silica shell by the same method has also reported nano bubbles of the same dimensions.<sup>12</sup> As the material collected is pure white and the solution is transparent in the visible region we do not expect metal particles or adsorbed metal ions on the silica surface. No gold was detected in any of the analysis performed indicating that the ions were completely leached out from the particles.

We have analyzed the sample, aniline@SiO<sub>2</sub> made by the CCl<sub>4</sub> removal method also. In this process<sup>24, 27</sup>, nanoparticles of Au and Ag react with CCl<sub>4</sub> forming Au<sup>3+</sup> and Ag<sup>+</sup>, respectively. Amorphous carbon deposits in the process with formation of Cl<sup>-</sup> in solution. The TEM Image of the formed material showed carbon onion-like structures inside silica shells (Figure 1c). The formation of carbon onions is probably due to the deposition of amorphous carbon within the shells, which transforms to onions within the confinement of the nanocavity. A detailed investigation of the onion structures will be published separately.



**Fig. 1** TEM images of bubbles. a) Bright-field HRTEM image of a cluster of bubbles in aniline@SiO<sub>2</sub>. b) Energy filtered image of the same area using the SiO<sub>2</sub> surface plasmon loss of 15 eV showing the SiO<sub>2</sub> shells very clearly. c) Carbon onion structures inside the silica nanobubbles after CCl<sub>4</sub> was used to remove the gold core for aniline@SiO<sub>2</sub>.

The absorption spectra of free aniline, Au@aniline@SiO<sub>2</sub> and aniline@SiO<sub>2</sub> are shown in Figure 2. Free aniline (trace a) has an absorption maximum around 280 nm due to  $\pi \rightarrow \pi^*$  transitions.<sup>30</sup> Spectrum (b) shows the absorption spectrum of Au@aniline@SiO<sub>2</sub>. It shows a red shift in the surface plasmon resonance band from the typical value of 521 nm to 528 nm due to the modification of the gold surface, both due to aniline adsorption and due to the silica cover; the latter being more significant.<sup>31</sup> The position and intensity of the gold surface plasmon depends on the particle size, and the optical and electronic properties of the system surrounding it.<sup>32</sup> For Au@SiO<sub>2</sub> core-shell structures, it is known that as the thickness of the silica cover increases; there is an increase in the absorption intensity and a red shift in the absorption maximum. This red shift in plasmon absorption is attributed to the fact that aniline and APS are adsorbed on the gold surface. The encapsulated aniline molecules inside the silica shell after removing the gold core show absorption at 280 nm (trace c), which is same as that of free aniline. We removed the bubbles from aqueous solution by centrifugation, after redispersion the absorption spectrum shows the same spectral characteristics proving that aniline is indeed inside the silica shell. The intensity and the peak position remained the same indicating that there is no change in the chemical state or loss of material indicating that the shell is a stable container for this molecule. The supernatant did not show aniline absorption.



**Fig. 2** Absorption spectra of (a) free aniline (b) Au@aniline@SiO<sub>2</sub> and (c) aniline@SiO<sub>2</sub> in aqueous medium. The background present in (b) and (c) can be attributed to the formation of the thick shell and also due to the difference in refractive index between the medium and the silica shell.

We have also studied the fluorescence spectrum of aniline@SiO<sub>2</sub> (Figure 3). Free aniline has an emission maximum around 340 nm<sup>33</sup> and for aniline@SiO<sub>2</sub>, 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. When dye molecules are present inside the silica particles, there can be a red shift in the fluorescence peak, attributed to the fact that there may be energy transfer between the molecules. Ostafin *et al.* has shown that cascade blue dye molecule inside the silica nanobubble shows a decrease in intensity as well as red shift in the emission spectrum compared to the free solution.<sup>13</sup>



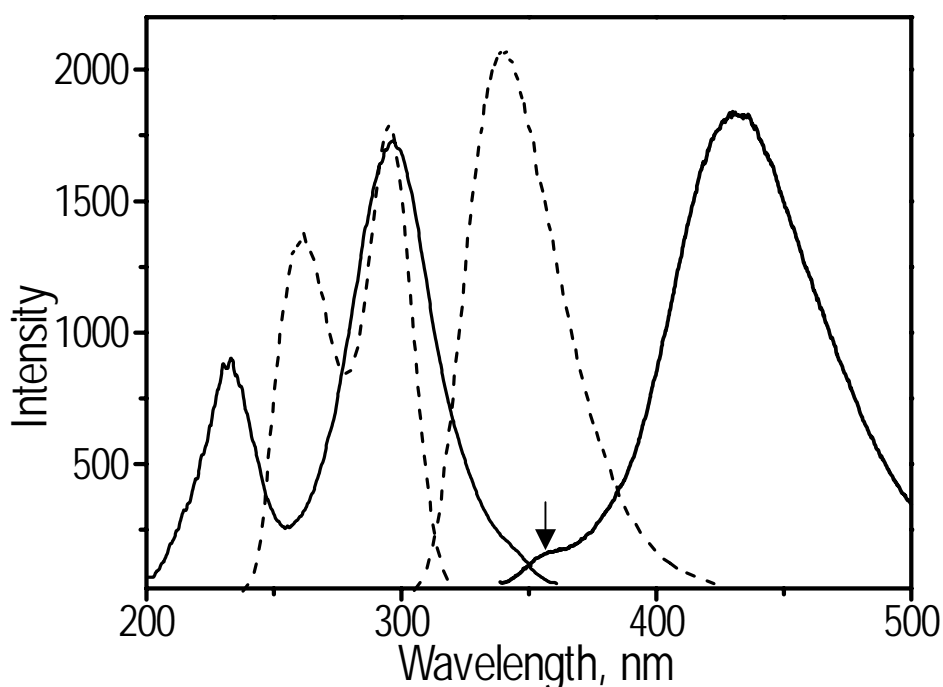


Fig. 3 Excitation and emission spectrum of aniline@SiO<sub>2</sub> (solid line) and free aniline in aqueous medium (dotted line).

In the case of aniline@SiO<sub>2</sub> (Figure 3) there is one more peak apart from the usual peak at 340 nm. Note that the first peak is at 355 nm, significantly reduced in intensity and red shifted by 15 nm compared to the free molecule. The second peak is broad and shows a maximum around 408 nm. Pyrene, when adsorbed on silica gel in higher concentrations, shows an additional 'excimer-like' peak.<sup>11</sup> In the case of pyrene adsorbed on silica even at concentrations far below the monolayer coverage, this broad emission is observed. 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.<sup>34</sup> The associated complexes formed in the ground state are responsible for this excimer like emission. Since pure physically adsorbed pyrene molecule cannot form a 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 shifted emission, compared to monomer emission, and appearance of a new broad shifted spectrum, are similar to the behavior of a sandwich dimer observed by Mataga and co-workers.<sup>35</sup> The same type of behavior was found in the case of anthracene also.<sup>36, 37</sup> The

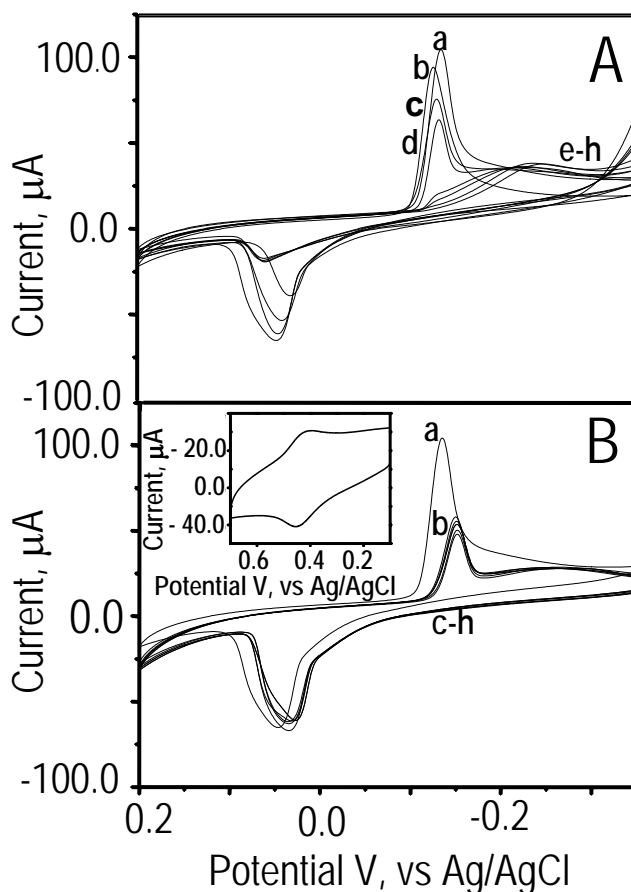
present study of aniline@SiO<sub>2</sub> also shows similar emission characteristics, indicating that similar ground state dimers may be formed inside the silica nanobubble.

To make sure that aniline molecule is indeed inside the bubble, we measured the emission spectrum of the supernatant solution obtained after centrifuging the bubble solution for around six hours. The bubbles were precipitated. The supernatant did not show any fluorescence, confirming the fact that the molecule is indeed inside. Note that while preparing the nanobubble, i.e. before the reaction with CCl<sub>4</sub> and cyanide, we washed the precipitated gold@SiO<sub>2</sub> with propanol many times and it is unlikely that there is adsorbed aniline on the silica surface.

We have characterized this material using cyclic voltammetry. The addition reaction between aniline and cupric chloride solution<sup>38</sup> was used to study the presence of aniline inside (or outside) the silica shell. Aqueous aniline forms an addition compound when added to cupric chloride solution, and the complex shows different electrochemical characteristics with respect to Cu when compared to free Cu<sup>2+</sup> solutions. This reaction was monitored by cyclic voltammetry on Pt electrode in perchloric acid medium with varying intervals of time. Curve a of Figure 4A shows the voltammogram of pure aqueous cupric chloride solution (10<sup>-4</sup> M) and curves b-d show the time dependant voltammograms obtained subsequently by the addition of aqueous aniline (10<sup>-4</sup> M) to the above at a time interval of five minutes. Cu shows a quasi-reversible redox couple Cu<sup>2+</sup>/Cu<sup>0</sup> at the cathodic and anodic potentials of - 0.135 and 0.046 V, respectively with a peak separation of 0.180 V.<sup>39</sup> With the addition of aniline solution (10<sup>-4</sup> M), the peak current decreases (curve b-d) and after some time, both the characteristic anodic and cathodic peak potentials shift further. The peak separation also increases to 0.300 V and with further time interval (curve e-h), the voltammograms become stable indicating the completion of the reaction. The shift of potential and the change in peak separation may be attributed to the distortion of the symmetry of Cu<sup>2+</sup> of the molecular species upon addition to aniline.<sup>40</sup>

A different voltammetric behaviour was observed, when the same quantity of cupric chloride solution was added to bubble aniline solution under identical experimental conditions. Curve a in Figure 4B represents CV of pure cupric chloride solution (10<sup>-4</sup> M) and curve b shows the voltammograms after the addition of bubble aniline solution (10<sup>-4</sup> M) in which an initial decrease in the peak current was noticed (Figure 4B, curve b); this phenomenon may be due to an effective deposition of Cu on the electrode surface catalyzed by the presence of other additives in solution. However, no considerable shift of characteristic anodic and cathodic peak potentials is noted with

time (curves c-h) indicating the absence of the reaction found in the case of free aniline. The CV taken after five days did not show any shift in peak potential confirming the stability of the system and it further shows that the absence of the reaction is not due to the time required for ion diffusion through the shell. The inset in Figure 4B shows CV of bubble aniline solution taken at a slow sweep rate of  $20 \text{ mV s}^{-1}$ . The observed  $E_{1/2}$  value for aniline@SiO<sub>2</sub> is  $0.425 \text{ V}$  and for the free aniline<sup>42,43</sup>, it is at  $0.406 \text{ V}$  in the acid medium. It may be noted that the redox



**Fig. 4** Time dependant cyclic voltammograms of (A) indicating the addition reaction between aqueous cupric chloride and free-aniline solution, (concentration -  $10^{-4} \text{ M}$ ) and (B), the absence of such reaction between aqueous cupric chloride and bubble aniline solution taken on Pt electrode in  $0.1 \text{ M}$  perchloric acid medium at a sweep rate of  $0.3 \text{ V s}^{-1}$ . Curve a and curves b-h (taken at a time interval of five minutes) show CV in the absence and presence of aniline, respectively. The inset shows the cyclic voltammogram of the bubble aniline solution at a sweep rate of  $0.02 \text{ V s}^{-1}$ .

accessibility of aniline is achieved through pores of the  $\text{SiO}_2$  shell, very similar to that of the oxide coated Au and Ag nanomaterial.<sup>23</sup> The study showed that while free aniline is capable of binding to  $\text{Cu}^{2+}$ , aniline inside the bubble is unavailable for binding.

After confirming the presence of the fluorescing molecule inside the silica shell using absorption and emission spectroscopic studies and voltammetry, we thought of looking at some other parameters such as the solubility of this material in organic solvents. In order to increase its solubility in organic solvents, we functionalized the silica nanoparticle surface using stearic

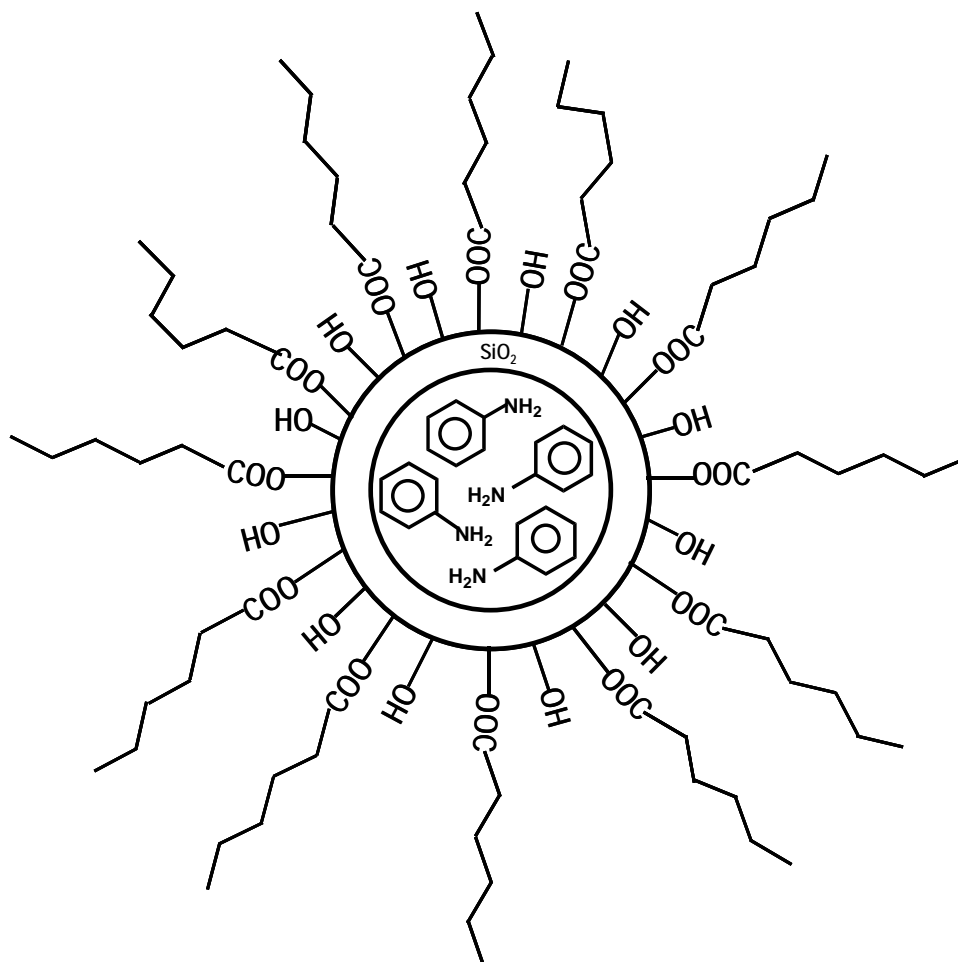


Fig.5 Schematic representation of aniline@ $\text{SiO}_2$ @stearate.

acid. The product obtained after adding millimolar solution of stearic acid to the solution containing aniline@ $\text{SiO}_2$  was centrifuged and the precipitate collected was dispersed in 2-propanol. This solution was also found to be fluorescent confirming the fact that aniline is inside the bubble. This material is labeled as aniline@ $\text{SiO}_2$ @stearate.

Infrared spectra of the dry material reveals features due to the long alkyl chain and carbonyl group showing that the material is covered with stearate groups<sup>20</sup> (supporting information 2). It doesn't show any features due to aniline. The spectrum shows a peak at around 1650  $\text{cm}^{-1}$  due to carbonyl group present in the stearic acid.<sup>42</sup> Methylene modes ( $\text{d}_+$  and  $\text{d}_-$ ) appear at 2852 and 2925  $\text{cm}^{-1}$  corresponding to a disordered methylene chain.<sup>18</sup> The methyl modes ( $\text{r}_+$  and  $\text{r}_-$ ) show that there is free rotation possible for the chains.<sup>20</sup> The spectrum does not show the characteristic progression bands showing that long range order is absent in the chains. The laser desorption mass spectrum of aniline@SiO<sub>2</sub>@stearate shows a peak at 283 due to stearate (supporting information 3). Keeping all these information we have schematically represented the new material aniline@SiO<sub>2</sub>@stearate as in Figure 5. It shows that aniline molecules are inside the bubble, surrounded by silica, which in turn is protected with stearate groups, having disordered alkyl chains. We have shown earlier that the alkyl chains on core-shell nanomaterials are disordered<sup>28</sup>.

We looked at the applications of this material aniline@SiO<sub>2</sub> especially as a sensor in the solution state. There are related studies of this type where the encapsulated dye molecule's fluorescence has been quenched by a diffusing analyte. The open pores of the shell allows the diffusion of molecules inside. Rhodamine dye systems are found to sense SO<sub>2</sub> this way.<sup>16</sup> It is known that while aniline is fluorescent, its protonated form, the anilinium ion, is nonfluorescent.<sup>44</sup> This made us to explore the possibility of using this material as a pH sensor. 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 nm and another at 408 nm (Figure 6 A) in the intensity ratio of 1:17. 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 behavior of aniline in acidic media we added micromolar quantities of acetic acid to the solution containing aniline@SiO<sub>2</sub>. This resulted in progressive quenching of fluorescence intensity, as the addition continued. After adding a definite quantity of the acid, the solution was allowed to stand till there was no more quenching, and the additions were repeated a few times. The observed quenching is attributed to the formation of anilinium ion. The rate of formation of anilinium ion was found to depend on the diffusion rate of proton through the silica pore confirming the fact that aniline is present inside the molecule, which is clear from the slow decrease of

fluorescence intensity (took more than an hour to decrease the intensity to one-third of the original value). The system was found to have excellent reversibility. The fluorescence could be recovered almost quantitatively by adding micromolar ammonium hydroxide (Figure 6B), thus making it an efficient pH sensor.

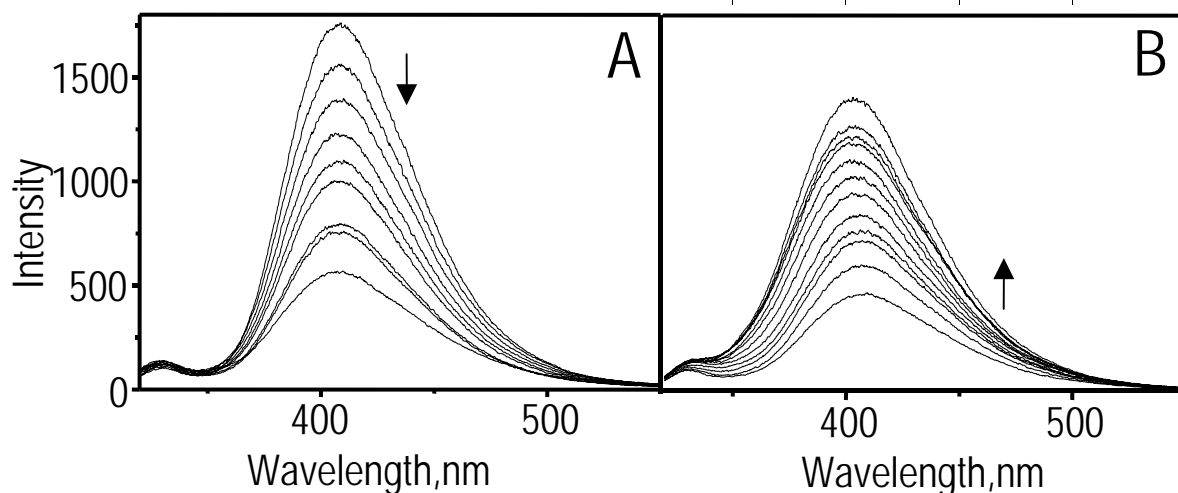


Fig. 6 (A) Quenching of fluorescence of aniline@SiO<sub>2</sub> by the addition of micromolar acetic acid in aqueous medium. (B) Recovery of fluorescence of aniline@SiO<sub>2</sub> by the addition of micromolar ammonium hydroxide to the aqueous medium. The difference between any two curves shows a difference of around 200 in the fluorescence intensity and the time gap given is around 10 minutes. The excitation wavelength was 280 nm. Acid/alkali was added if there was no shift in the spectrum after 10 minutes.

## Conclusions

In this paper we have reported a novel material, aniline@SiO<sub>2</sub> and used it in aqueous solution as a pH sensor. It was characterized using UV/VIS absorption spectroscopy, TEM, cyclic voltammetry, and emission spectroscopy. The presence of the molecule inside the bubble was confirmed by the reaction between cupric chloride and aniline, apart from other studies. This material was modified by functionalization with stearic acid, so that the product is soluble in organic media and can be stored in the dry state. It was characterized using infrared spectroscopy and laser desorption ionization spectroscopy. Apart from fluorescence, the aniline@SiO<sub>2</sub> material was found to show an 'excimer like' emission inside the silica shell. It was found that the new material shows change in fluorescence intensity upon addition of micromolar acetic acid and recovers it by adding the same concentration of ammonium hydroxide. Thus, a nanoscopic pH-sensing device is made of silica nanobubbles containing aniline molecules within.

## Acknowledgements

T. P. thanks the Ministry of Information Technology for financial support. Department of Science and Technology is thanked for equipment support through the nanotechnology initiative. V.S. thanks the Council of Scientific and Industrial Research for a research associateship. I.M. would like to provide Prof. Hartmut Fuess for the provision of laboratory facilities.

**Supporting information available:** An energy filtered TEM image of Au@SiO<sub>2</sub>, imaged using 15 eV loss electrons, LDI spectra and infrared spectra of Au@SiO<sub>2</sub>@stearate. This material is available free of charge at <http://www.rsc.org>.

## References

1. F. Bentivegna, M. Canva, P. Georges, A. Brun, F. Chaput, L. Malier and J. P. Boilot, *Appl.phys.Lett.*, 1993, **62**, 1721.
2. R. Reisfeld, R. Zusman, Y. Cohen and M. Eyal, *Chem. Phys. Lett.*, 1998, **147**, 142.
3. J. M. McKiernan, S. A. Yamanaka, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1990, **94**, 5652.
4. C. R. Viteri, J. W. Gilliland and W. T. Yip, *J. Am. Chem. Soc.*, 2003, **125**, 1980.
5. T. Suratwala, Z. Gardlund, K. Davidson, D. R. Uhlmann, J. Watson, S. Bonilla and N. Peyghambarian, *Chem. Mater.*, 1998, **10**,190.
6. A. Van Blaaderen and A. Vrij, *Langmuir*, 1992, **8**, 2921.
7. N. A. M. Verhaegh and A. Van Blaaderen, *Langmuir*, 1994, **10**, 1427.
8. J. A. Imhof, M. Megens, J. J. Engelberts, D. T. N. De Lang, R. Sprik and W. L. Vos, *J. Phys.Chem. B*, 1999, **103**, 1408.
9. J. Wheeler and J. K. Thomas, *J. Phys. Chem.*, 1982, **86**, 4540.
10. G. Bosma, C. Pathmamanoharan, d. H. EHA, WK. Kegel, A. Van Blaaderen and HNW. Lekkerkerker, *J. Colloid Interface Sci.*, 2002, **245**, 292.
11. R. K. Bauer, P. D. Mayo, W. R. Ware and K. C. Wu, *J.Phys.Chem.*, 1982, **86**, 3781.
12. O.V. Makarova, A. E. Ostafin, H. Miyoshi, J. R. Jr. Norris and D. Meisel, *J. Phys.Chem. B*, 1999, **103**, 9080.

13. A. E. Ostafin, M. Siegel, Q. Wang and H. Mizukami, *Micropor. Mesopor. Mater.*, 2003, **57**, 47.
14. S. A. Yamanaka, D. H. Charych, D. A. Loy and D. Y. Sasaki, *Langmuir*, 1997, **13**, 5049.
15. A. Flamini and A. Panusa, *Sens. Actuators B*, 1997, **42**, 39.
16. A. Sharma and O. S. Wolfbeis, *Spectrochem. Acta*, 1987, **43A**, 1417.
17. M. Klessinger and J. Michl, *Excited states and photochemistry of organic molecules*; VCH: **1989**.
18. N. Sandhyarani and T. Pradeep, *Int. Rev. Phys. Chem.*, 2003, **22**, 221.
19. T. Pradeep and N. Sandhyarani, *Pure Appl. Chem.*, 2002, **74**, 1593.
20. N. Sandhyarani, G. P. Selvam, M. P. Antony and T. Pradeep, *J. Chem. Phys.*, 2000, **113**, 9794.
21. S. Mitra, B. Nair, T. Pradeep, P. S. Goyal and R. Mukhopadhyay, *J. Phys. Chem. B*, 2002, **106**, 3960.
22. N. Sandhyarani, M. R. Resmi, R. Unnikrishnan, K. Vidyasagar, M. Shuguang, M. P. Antony, G. Panneer Selvam, V. Visalakshi, N. Chandrakumar and T. Pradeep, *Chem. Mater.*, 2000, **12**, 104.
23. R. T. Tom, A. S. Nair, N. Singh, M. Aslam, C. L. Nagendra, R. Philip, K. Vijayamohan and T. Pradeep, *Langmuir*, 2003, **19**, 3439.
24. A. S. Nair, R. T. Tom, V. Suryanarayanan and T. Pradeep, *J. Mat. Chem.*, 2003, **13**, 297.
25. A. Enustun and B. V. Turkevich, *J. Am. Chem. Soc.*, 1963, **85**, 3317.
26. W. Stobber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **20**, 62.
27. A.S. Nair and T. Pradeep, *Curr. Sci.*, 2003, **84**, 1560.
28. A.S. Nair, I. MacLaren and T. Pradeep, *J. Mat. Chem.*, 2004, **14**, 857.
29. L.A.J. Garvie, P. Rez, J.R. Alvarez and P.R. Buseck, *Sol. Stat. Comm.*, 1998, **106**, 303.
30. J.G. Calvert, J.N. Jr. Pitts *Photochemistry*, John Wiley & Sons Inc: New York, **1966**.
31. L. M. Liz-Marazan, M. Giersig and P. Mulvaney, *Langmuir*, 1996, **12**, 4329.
32. A. N. Shipway, E. Katz and I. Wilner, *Chemphyschem.*, 2000, **1**, 18.
33. B. S. Neporent, *Elementary photo processes in molecules*, Consultants bureau: Newyork, **1968**.



34. K. Hara, P. de Mayo, W.R. Ware, W.R. Weedon, A. C. Wong and K. C. Wu, *Chem. Phys. Lett.*, 1980, **69**, 105.
35. N. Mataga and Y. Toriheshi, *Chem. Phys. Lett.*, 1967, **1**, 385.
36. E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, 1966, **45**, 3554.
37. E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, 1966, **45**, 3564.
38. M. Labanowska, K.R. Zurowski and E. Bidzinska, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1996, **115**, 297.
39. L. B. Israel, N. N. Kariuki, L. Han, M. M. Maye, J. Luo and C. J. Zhong, *J. Electroanal. Chem.*, 2001, **517**, 69.
40. J. Bacon and R. N. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 6596.
41. S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, 1967, **114**, 1025.
42. A. M. Diyas, J. A. Sang and K. Kwan, *Bull. Korean. Chem. Soc.*, 1996, **17**, 470.
43. J. U. Kim, W. K. Hartmann, H. J. Schock, B. Golding and D. G. Nocera, *Chem. Phys. Lett.*, 1997, **267**, 323.