Synthesis of thermally stable monodispersed Au@SnO$_2$ core–shell structure nanoparticles by a sonochemical technique for detection and degradation of acetaldehyde$^+$

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A simple ultrasound assisted chemical precipitation technique for the synthesis of Au@SnO$_2$ core–shell structure nanoparticles is reported. Au nanoparticles were synthesized via chemical reduction of metal salt followed by sonochemical deposition of a tin dioxide shell with controlled shell thickness. The phase and morphology have been investigated by an X-ray diffraction technique (XRD) and transmission electron microscopy (TEM) respectively. Au@SnO$_2$ core–shell nanocomposites have shown a distinct surface plasmon peak in the UV–visible spectrum at 540 nm. The core–shell morphology is confirmed from the TEM images. XRD patterns have suggested the formation of gold and tin dioxide in the face-centered cubic and Cassiterite form respectively. Our investigations suggested that the formation of a core–shell structure results in the enhanced thermal stability of the system. The synthesized material is used for the detection and oxidation of acetaldehyde gas. Our investigations suggest the potential application of sonochemically synthesized Au@SnO$_2$ nanoparticles for realization of a sense and shoot device for indoor air purification.

**Introduction**

The ability to engineer materials at a nanometer length scale has sparked interest across many scientific disciplines and has enabled direct investigation into the fundamental size-dependent properties of matter. Of the wide range of nanomaterials currently under investigation, core–shell nanocomposite particles with a metal core and metal oxide shells have potential applications in optical information storage, advanced coatings, and catalysis.$^{+,*}$ The major benefits of materials with core–shell morphology can be summarized as: (1) metal nanoparticles can be protected against aggregation and can be transferred from a liquid phase to a solid phase while retaining the size dependent properties, (2) very small metal oxide nanoparticles can be formed on a metal nanoparticle surface, and (3) the crystal size and structure of the metal oxide shell can be retained at high temperature.$^5$ Thus, researchers have tried to use various metal oxides such as SiO$_2$, TiO$_2$, and Fe$_2$O$_3$ as the shell materials since they offer a range of refractive indices and dielectric constants.

Recently, metal@SnO$_2$ core–shell structure nanoparticles have received considerable attention. Mulvaney et al. have reported the concept of a nanocapacitor based on the Au@SnO$_2$ core–shell structure nanoparticles.$^6$ Tripathy et al. have demonstrated that the surface plasmon based optical property of the noble metal nanoparticles can be preserved in core–shell nanoparticle films.$^{7,8}$ The same group has also investigated the gas-phase photocatalytic efficiency of the metal@SnO$_2$ core–shell nanocomposites.$^{10}$ However, the most exciting possible application for such materials will be in gas-sensing devices. The conventional gas-sensors use SnO$_2$ with surface doped noble metal particles. Usually, the nanoparticles aggregate at a higher operating temperature required for the operation of oxide based gas-sensors and hence leads to the decrease in the efficiency of the device.$^{5,11}$ Encapsulation of noble metals with a tin oxide shell can protect the former against aggregation and particle growth.$^{5,7,8,10}$ In addition to this, formation of a core–shell structure is expected to preserve the phase and crystalline size of SnO$_2$ nanoparticles at higher temperatures.$^{5,12}$ The sensitivity is expected to depend on the formation of well dispersed and
uniform composite nanoparticles with higher crystallinity. However, the conventional precipitation technique employed for the synthesis of metal@SnO$_2$ core-shell nanostructures could not provide sufficiently crystalline materials required for device applications. In addition to this the scale up of the process was also another challenging issue. Thus it became necessary to develop alternative synthetic protocols to obtain tailor made core-shell materials. Recently, Yu and Dutta have reported the microwave assisted process for the synthesis of crystalline Au@SnO$_2$ core-shell nanocomposites which have shown a superior CO-sensing property.$^{13,14}$ However, none of these techniques produced monodispersed core-shell particles. The simultaneous nucleation and growth of small metal oxide particles on the surface of the metal nanoparticles make the formation of monodispersed core-shell particles a challenging issue. An increase in the reaction temperature (as in the case of microwave processing) to coat the metal nanoparticles with oxide shells leads to aggregation and growth of the particles.$^1$ Thus it is not only necessary to investigate alternative synthetic protocols to obtain the monodispersed metal@SnO$_2$ core-shell nanostructures but also to check the potential of such materials for sensing of gases particularly volatile organic compounds (VOCs). Recently, sonochemical techniques have been used extensively to obtain well dispersed and highly crystalline nanomaterials.$^{15}$ Ultrasound assisted techniques are considered to be eco-friendly routes which are more effective in the synthesis of porous metal oxides with sufficient crystallinity.$^{15,16}$ However, to the best of our knowledge, such techniques have never been exploited for the synthesis of metal@SnO$_2$ core-shell nanoparticles. As discussed earlier the most promising application of such materials would be as gas-sensors and maybe as photocatalysts.

In the present paper, we demonstrate an ultrasound assisted method for the synthesis of monodispersed Au@SnO$_2$ core-shell nanoparticles. The structure and morphology of the materials are investigated by XRD and TEM. The crystal phase and core-shell morphology are found to be thermally stable at 400 °C. The material is investigated for acetaldehyde sensing and showed higher sensing than that of Au/SnO$_2$ nanocomposites without the core-shell structure. Additionally we have investigated the photocatalytic oxidation of acetaldehyde by using these materials. We have selected acetaldehyde as the target VOC because it is a common indoor pollutant generated by cigarette smoke, burning of fossil fuels, and also originates from old wooden furniture, cloths, and rotten biowaste. It is a carcinogen for humans and can cause adverse health consequences such as delirium, hallucinations and loss of intelligence.$^{17}$ So, it is very important to identify and eliminate it from the indoor atmosphere. Our investigations suggest the potential application of sonochemically synthesized Au@SnO$_2$ nanoparticles for realization of a sense and shoot device for acetaldehyde.

**Experimental**

Gold colloid was synthesized by a chemical reduction technique. HAuCl$_4$·4H$_2$O (Sigma Aldrich) and tri-sodium citrate dehydrate (Sigma Aldrich) were used as the starting material and reductant, respectively.$^{2,3,9}$ A schematic of the reaction system is shown in Fig. S1.$^†$ In a typical synthesis, 0.1 g of gold salt was added to 500 mL of de-ionized water and heated to boiling. The initial color of the gold salt solution was yellow. At 99 °C, 28 mL of 1 wt% tri-sodium citrate dehydrate was added under constant stirring to the above solution. The color of the solution changed from faint yellow to wine red which indicated the formation of citrate stabilized gold nanoparticles. The controlled deposition of tin dioxide nanoparticles on metal nanoparticles was achieved by an ultrasound assisted chemical process. The exact synthesis technique is as follows. The pH of the gold colloid was increased to ~10 by addition of 0.1 mM of NaOH solution. This colloid was placed in a sonochemical bath. Then sodium hexahydroxostannate (Sigma Aldrich) was added. 10 mL of sodium hexahydroxostannate was added at various concentrations ranging from 20 mM to 60 mM. The reaction was allowed to continue for 0.5 to 2 h. Then the solution was allowed to cool by a natural process. The composite nanoparticles were then collected by centrifugation (at 12 000 rpm) and dried at 80 °C for 12 h. During centrifugation nanoparticles were washed with de-ionized water (three times) to remove the water soluble sodium chloride and other impurities.

**Fabrication of a thick film based sensing device and sensing tests**

Au@SnO$_2$ paste was prepared by dispersing the nanoparticles in isopropyl alcohol with hydroxypropyl cellulose (HPC) of one half of the material weight using an ultrasonic disperser for 20 min. The paste was deposited on the commercial Al$_2$O$_3$ substrate (15 mm × 15 mm) with previously screen printed gold electrodes (10 mm × 10 mm) by a doctor blade technique and dried at 200 °C for 1 h followed by baking in a furnace at 400 °C for 1 h. The gas-sensing activity of the device was investigated by using a homemade gas-sensing evaluation system (ESI, Fig. S2†) equipped with digital mass flow controllers, a rapid heating system with programmed temperature controllers, and a quartz reactor for carrying out the sensing reactions. The change in resistance of the device due to the presence of target gas was measured using a high resistance meter (Keithley source meter 2400). The device was tested in the temperature range of 25-400 °C at various concentrations of the target gas (5-500 ppm) in a temperature-controlled environment. The background gas was N$_2$, mixed with atmospheric air to have 10% of oxygen content. The flow of gas (100 mL min$^{-1}$) over the sensor device was altered between the sample gas and dry air to record the sensor response in terms of electric resistance. The sensor response was represented as the relative change in the resistance of the device in the presence of air and target gas according to the following equation:

$$\text{Sensor response} = \frac{(R_{air} - R_{gas})}{R_{gas}}$$

where $R_{air}$ and $R_{gas}$ are the resistance of the device in the presence of dry air and the target gas, respectively.

**Evaluation of photocatalytic activity**

Photocatalytic tests were carried out by using a gas chromatography technique (Shimadzu GC-2010 series). A sketch of the
gas-chromatography arrangement for the evaluation of photocatalytic activity is shown in the ESI (Fig. S3a).† Au@SnO₂ nanoparticles were deposited onto porous ceramic foam and heated at 400 °C (ESI, Fig. S3b†). Acetaldehyde gas (500 ppm) was used to investigate the photocatalytic activity of the samples. Irradiation was carried out using two UV-365 nm lamps (15 W). Prior to evaluation, blank experiments were carried out (with only ceramic foam and UV-light) to confirm the possible reactions occurring in the absence of catalyst or UV-light.

Results and discussion

Formation of the SnO₂ shell on the gold nanoparticles is monitored by UV-visible spectroscopy. Time dependent UV-visible spectra of the nanocomposite particle formation process are shown in Fig. 1. The gold colloid showed a clear and distinct surface plasmon (SP) resonance band at 518 nm. The color of the Au nanoparticle dispersion changed from ruby red to purple after the formation of a tin oxide shell (inset in Fig. 1). Upon the addition of sodium hexahydroxostannate, the SP band exhibited an immediate red-shift of ≈ 20 nm which is attributed to the increased refractive index around the colloid particles after SnO₂ deposition (the refractive index of SnO₂ is 2.0 which is much higher than that of water).† It can be observed that the shift in the SP band was more pronounced in the initial 90 min, after which the shift was very small. This suggests that the formation of the oxide shell is almost completed in this time.

The core-shell morphology of the as-synthesized materials was investigated by TEM studies. Fig. 2 shows the TEM images of the gold and Au@SnO₂ nanocomposite particles at different reaction times. As shown in Fig. 2(d) and (e), tin dioxide undergoes nucleation on the gold nanoparticle surface at a pH > 9. With an increase in the reaction time, growth and crystallization of the tin dioxide take place which results in the formation of stable Au@SnO₂ core-shell nanoparticles [Fig. 2(g) and (h)]. The composite particles have a metallic core of 10 to 12 nm in size and have a uniform shell of 10 nm in thickness after 90 min of the reaction. The metal core was found to have an interplanar spacing of ≈ 0.235 nm which corresponds to the (111) plane of the metallic gold with the face-centered cubic structure [Fig. 2(e) and (h)]. The oxide shell was found to have an interplanar spacing of 0.265 nm which corresponds to the (101) plane of the Cassiterite SnO₂ with a tetragonal geometry. Unlike the previously reported papers free tin dioxide nanoclusters were not observed.‡ The Au nanoparticle dispersion changed from ruby red to purple after the addition of sodium hexahydroxostannate, the SP band exhibited an immediate red-shift of ≈ 20 nm which is attributed to the increased refractive index around the colloid particles after SnO₂ deposition (the refractive index of SnO₂ is 2.0 which is much higher than that of water).† It can be observed that the shift in the SP band was more pronounced in the initial 90 min, after which the shift was very small. This suggests that the formation of the oxide shell is almost completed in this time.

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core–shell structure have better stability against grain growth induced at higher temperature required for the operation of gas-sensors. To support the above concept, we have investigated the microstructure of materials with core–shell and without core-shell morphology before and after heat treatment at 400 °C. As seen in Fig. 5, although heat treatment of the core-shell

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**Fig. 2** TEM images showing the Au nanoparticles (a–c), and formation of Au@SnO₂ core–shell structure nanoparticles at 30 min (d–f), and 90 min (g–i) by a sonochemical synthesis process. (j–l) The TEM images of the particles synthesized at 90 min over a larger area to confirm the formation of monodispersed core–shell structures.

**Fig. 3** TEM images of the Au@SnO₂ core–shell nanoparticle synthesized by the sonochemical technique by addition of (a) 20, (b) 40, (c) 60 mM Na₂SnO₃, and (d) the corresponding UV-visible spectrum.
nanoparticles has resulted in slight aggregation, the size of the Au nanoparticles did not change remarkably. However, in the case of materials without the core–shell structure, the size of the metal particles is increased significantly (ESI, Fig. S5b†). In addition to this severe particle aggregation is also observed. The TEM analysis has supported the previous results obtained from XRD investigation.

The Au@SnO2 nanoparticles with a core–shell structure have been investigated for a gas sensing property. Thick film based gas sensing devices are fabricated and tested for sensing of four different gases (acetaldehyde, carbon monoxide, ethanol, and pyridine). The sensor response of the films towards acetaldehyde is shown in Fig. 6(a). The sensor response for all the gases was measured at 5, 10, 25, 50, 100, 200, and 500 ppm concentrations. The highest sensitivity (for 200 ppm of acetaldehyde) of 64.5 per ppm was observed at 300 °C in the linear range.

Fig. 6(b) explains the sigmoidal behavior of the sensor response in the form of a calibration curve at 300 °C. The sensor had a response time of ≈18 s, a linear detection range (y = 0.331x + 1.898, R² = 0.94302) between 5 and 200 ppm (Fig. 6b) (comparable with previous literature19,20) and an experimentally calculated limit of detection (LOD) of 2.5 ppm for acetaldehyde (LOD was calculated as over three times the standard deviation of sensor response for minimum detectable concentration). The interfering gases such as carbon monoxide (ESI, Fig. S6a†) and...
ethanol (ESI, Fig. S6b)) also produced a detectable sensor response at an equivalent concentration to acetaldehyde, yet, the sensor response was temperature specific (Fig. 6c). It is a well known fact that gas sensors\(^*\) such as CO\(_2\) sensor based fire alarms) do have cross-reactivity towards various other gases, however, if set under optimum operational conditions, they perform adequately in the test conditions.\(^*\) However, the exact mechanism still remains unclear. In addition to gas-sensing, Au@SnO\(_2\) nanoparticles with core-shell morphology are expected to have interesting photocatalytic properties.\(^*\) Thus, we investigated the photocatalytic activity of our device on acetaldehyde samples with the aim of developing a sense and shoot strategy for indoor air purification, keeping in view the health hazards posed by this common indoor pollutant. The photocatalytic oxidation of acetaldehyde was monitored using the gas-chromatography technique. The results are shown in Fig. 7(a). It was observed that acetaldehyde gas was almost completely oxidized to carbon dioxide within 90 to 120 min SnO\(_2\) with a band gap energy of 3.8 eV (close to that of TiO\(_2\)); theoretically it can be excited by the photons with the wavelengths under 490 nm. However, pure tin dioxide is known to have less photocatalytic activity. This is probably due to the faster recombination of the photogenerated electron–hole pairs in SnO\(_2\).\(^*\) However, in the case of noble metal-anchored (Au in the present case) SnO\(_2\), the following situation is expected. Since SnO\(_2\) (similar to TiO\(_2\)) undergoes charge separation under UV-irradiation, the photogenerated electrons are expected to be transferred to noble metal nanoparticles as both systems undergo charge equilibration. The transfer of electrons from the excited semiconductor to the metal is an important aspect that dictates the overall energy of the composite and hence the efficiency of the photocatalytic reduction process. The photoactive SnO\(_2\) thus plays an important role in absorption of incident photons and injection of electrons into the noble metal surfaces. The processes that led to storage of electrons in the noble metal core are summarized below (reaction 2–4) and in Fig. 7(b).

$$\text{SnO}_2 \rightarrow \text{SnO}_2 (e^- + h^+) \quad (2)$$

$$\text{SnO}_2 (h^+) + \text{acetaldehyde} \rightarrow \text{products} \quad (3)$$

$$\text{SnO}_2 (e^-) + \text{metal} \rightarrow \text{SnO}_2 + \text{metal (e^-)} \quad (4)$$

Under UV excitation, SnO\(_2\) undergoes charge separation followed by charge recombination and interfacial charge-transfer processes. As the photogenerated holes are scavenged by acetaldehyde, the electrons accumulate within the SnO\(_2\) particles. Since metal particles such as gold with a favorable Fermi level are good electron acceptors, we expect a facile electron transfer from excited SnO\(_2\). This property of charge equilibration between the semiconductor and metal nanoparticles has been suggested by Kamat et al. by the addition of metal colloids to preirradiated TiO\(_2\) colloids in ethanol. In the present case the mechanism is expected to be similar to that suggested by Kamat and Hirakawa.\(^*\) Thus, the presence of the smaller noble metal core is expected to enhance the photocatalytic activity of the tin dioxide.

Therefore, the results above provide an interesting opportunity for the design of a sense and shoot kind of device for indoor purification. The first reports on such kinds of systems in aqueous and gaseous media have been proposed by Kamat et al. and Tripathy et al., respectively.\(^*\)\(^*\) Our investigations provide an initial approach to the realization of such a system for detection and degradation of acetaldehyde. Apart from that, it can be used to sense ethanol and CO however at lower sensitivity than for acetaldehyde.

**Conclusion**

In summary, an ultrasound assisted precipitation technique was reported for synthesis of Au@SnO\(_2\) core-shell structure nanoparticles. XRD analysis has showed that Au and tin dioxide are in the face-centered cubic and tetragonal structure respectively. TEM has confirmed the formation of a tin dioxide shell on gold nanoparticles. The material has shown thermal stability.
up to 400 °C which makes it suitable for gas-sensor applications. The materials have shown the highest acetaldehyde-sensing at 300 °C. Additionally the materials have shown good photocatalytic activity for the oxidation of acetaldehyde.

References