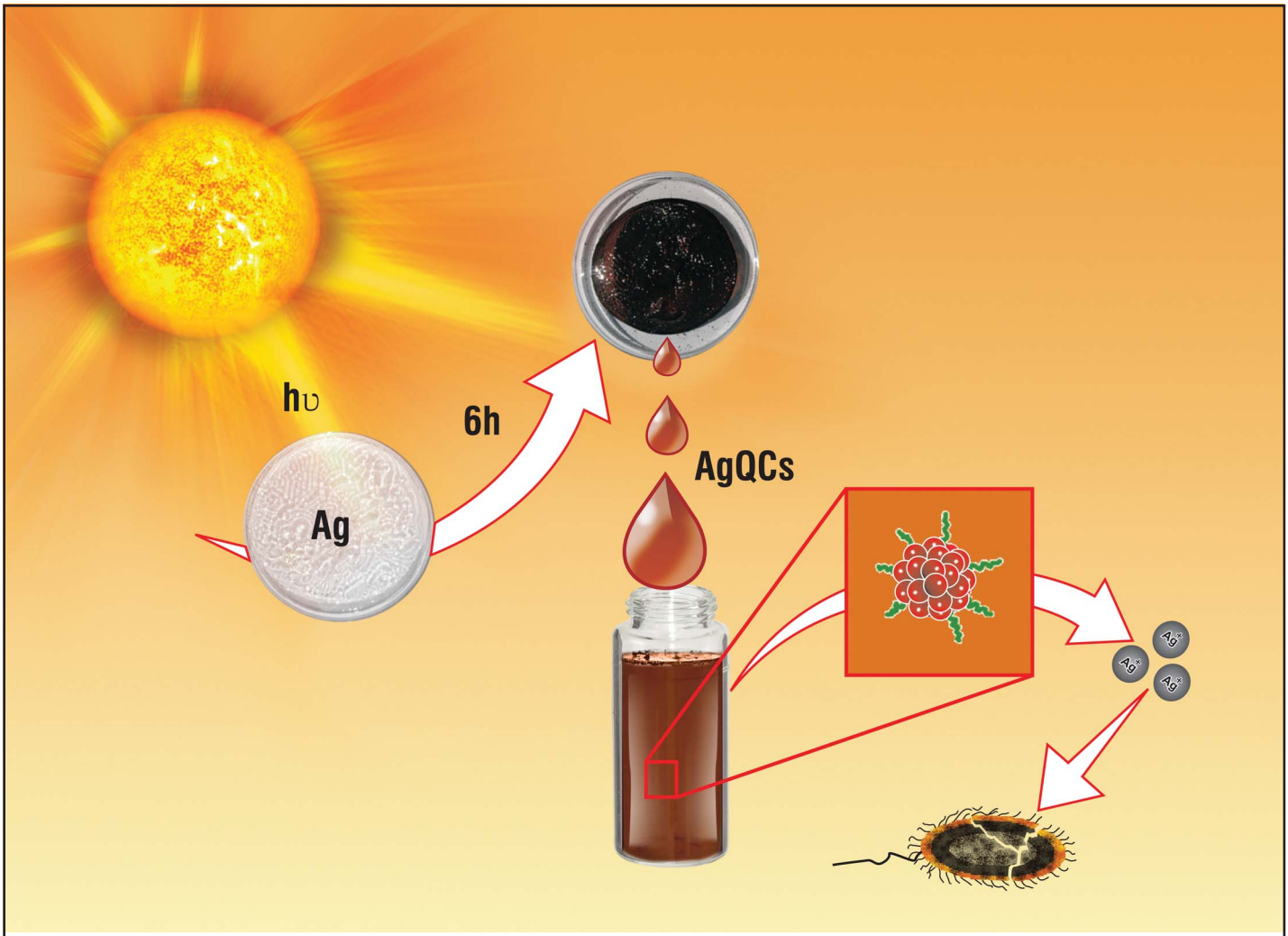

Showcasing research from Prof. T. Pradeep's laboratory at IIT Madras, Chennai, India.

Title: Sunlight mediated synthesis and antibacterial properties of monolayer protected silver clusters

Details of the research undertaken in our laboratory can be found at http://www.dstuns.iitm.ac.in/pradeep-research-group.php. A green route to synthesise glutathione protected atomically precise silver clusters by sunlight irradiation of silver thiolates confined in gel cavities, and the antibacterial properties of the as-synthesized clusters against gram-negative and gram-positive bacteria.

As featured in:

See I. Chakraborty *et al.*,
J. Mater. Chem. B, 2013, **1**, 4059.

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Sunlight mediated synthesis and antibacterial properties of monolayer protected silver clusters†

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Received 26th April 2013
Accepted 17th June 2013

DOI: 10.1039/c3tb20603c

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Glutathione protected, silver clusters were synthesized within gel cavities, using sunlight. Compared to the conventional chemical reduction process, this method is cheaper and environmentally friendly as it involves the use of natural resources. The as-synthesized silver quantum clusters in aqueous medium show a distinct step-like behavior in their absorption profile. They have been characterized with various spectroscopic and microscopic techniques such as UV/Vis Spectroscopy, Luminescence Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), High Resolution Transmission Electron Microscopy (HRTEM), and X-ray Photoelectron Spectroscopy (XPS). Polyacrylamide gel cavities seemingly control the growth of the particles. The cluster synthesis is scalable by increasing the amount of reagents yielding hundreds of milligrams in a single step. The antibacterial properties of the as-synthesized Ag clusters were studied against a Gram negative and Gram positive organism, *Escherichia coli* and *Staphylococcus aureus*, respectively.

Introduction

Few-atom noble metal clusters (or quantum clusters, QCs) with discrete electronic structures, exhibiting distinct HOMO–LUMO transitions in optical absorption,[1–4] intrinsic magnetism,[5,6] enhanced photoluminescence,[7–12] and modified redox properties[13–18] are interesting new materials. These properties are fundamentally different from the larger metallic nanoparticles which exhibit surface plasmon resonance arising from the coherent oscillations of free electrons in the conduction band.[19] QCs are good candidates for applications in areas such as catalysis,[20,21] nanoelectronics,[14] sensing,[22,23] *etc.* Several such clusters of noble metals have been synthesized using various templates such as peptides,[24,25] thiols,[26–29] dendrimers,[31] and proteins.[31–34] Among them, the thiol protected ones are more intensely studied with diverse techniques as well-defined compositions can be obtained.[10,16,27–29,31,35–38]

A variety of chemical and physical methods have been developed to produce them and most of the synthetic routes are limited to gold QCs. Although gold and silver belong to the same group, because of differences in their chemical reactivity, the area of silver QCs has not expanded significantly.[39] It is expected that silver may be a better system for sensor applications due to the high extinction coefficient.[40] In our group, we have demonstrated the possibility to synthesize thiol protected silver clusters using interfacial[41] and solid state routes.[29] Glutathione protected clusters may be made through a high temperature nucleation route as well.[24] Jin *et al.* reported dimercaptosuccinic acid protected Ag_7 quantum clusters.[42] Kitaev and Cathcart, reported glutathione (SG) protected silver clusters in a single step.[27] In all of the cases, synthesis involves the use of chemical reducing agents such as $NaBH_4$,[29,43] HCOOH,[24] *etc.* However, it's a challenge to material chemists to synthesize the desired materials using natural resources.[44] To the best of our knowledge, no reports are available on the synthesis of GSH protected silver QCs using sunlight, although several reports are available to make plasmonic nanoparticles using natural sources such as light irradiation[45,46] and by using materials of plant origin.[47] There are also other methods such as microwave irradiation.[48] Some reports are also available for visible light photoactivated clusters.[49–51] Herein we report the synthesis of luminescent ($QY = 5 \times 10^{-3}$) silver QCs protected by glutathione using sunlight, without a chemical reducing agent. The products have been isolated, characterized and applied.

Results and discussion

Initially, the silver thiolate containing polymerized gel appears transparent. Upon exposure to sunlight, there is a gradual color change from colorless to light yellow and finally to brown-black (Fig. 1). At the same time, the softness of the gel decreases and it becomes harder, due to evaporation of water. The conversion to brown-black color indicates the completion of the reaction and formation of clusters, as observed in other methods of cluster synthesis.[22,27] In traditional synthesis, the initially turbid metal thiolates become dark brown or black upon addition of an

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† Electronic supplementary information (ESI) available: Details of the phase transfer procedure, photographs of large scale synthesis, ESI MS, XPS, FT-IR and PL of AgQCs and other control experiments. See DOI: 10.1039/c3tb20603c

‡ These authors contributed equally.

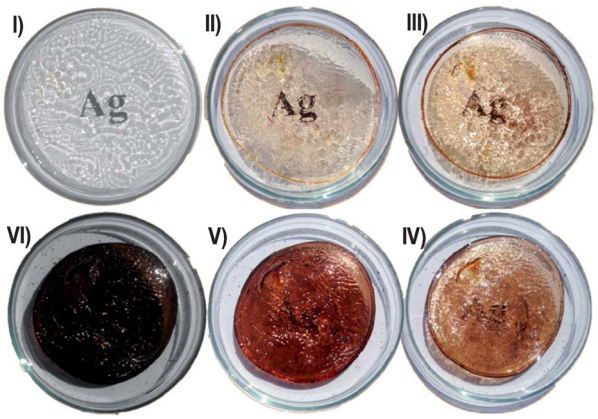

Fig. 1 (I) Photograph of the polymerized form of acrylamide gel along with oligomeric Ag(I)SG, taken in a Petri dish. (II), (III), (IV), (V) and (VI) are photographs corresponding to the exposure to sunlight at different time intervals of 5 min, 30 min, 1 h, 3 h, and 6 h, respectively. The Petri dish was placed on white paper with the label, 'Ag' printed on it. Note the change in transparency from (I) to (VI). The gel shrinks upon irradiation as water evaporates and the dry gel is detached from the Petri dish.

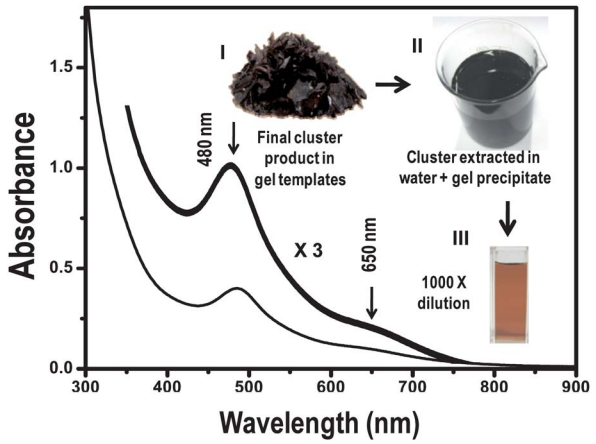

Fig. 2 UV/Vis spectrum of as-synthesized AgQC. Dominant spectral peaks at 480 nm and 650 nm are marked on the enlarged optical spectrum. Insets: (I) photograph of the gel templates containing silver clusters after exposure to sunlight for 6 h. (II) Extracted clusters which are readily soluble in water whereas the gel was insoluble and the solution appears dark brown in color. (III) Upon dilution 1000 times, the solution appears reddish brown and the spectrum is shown as the main figure.

external reducing agent such as sodium borohydride, due to the formation of clusters or nanoparticles. Fig. 1 shows the evolution of cluster formation with the duration of light exposure as manifested by the change in color of the gel. All the images were collected from the same Petri dish. During the progress of the reaction, the transparency of the gel was reduced and finally the gel became opaque due to cluster formation (Fig. 1). In a typical synthesis, we make about 70 mg of the cluster powder following the procedure outlined in the Experimental section.

This method was scalable to make hundreds of milligram quantities of AgQCs in a single step, by increasing the amount of reagents used in the reaction. For larger scale synthesis, 50 mL of the acrylamide gel solution was used and the reagents necessary for polymerization along with Ag(I)SG were taken in a 3 ft × 2 ft glass tray and the polymerization was started. The tray was irradiated to make the clusters. Photographs of the process are given in Fig. S2.†

When the cluster formation is complete, a flake-like gel appears as shown in Fig. 2 (inset I). For extraction of the clusters, 50 mL of water was added to the final hard gel and the solution was kept at 20 °C for 1 hour (Fig. S3†). Clusters were extracted with water while a colorless gel residue settled at the bottom. A peak at 480 nm (2.58 eV) and a shoulder at 650 nm (1.9 eV) were observed in the UV/Vis spectrum of the cluster (Fig. 2). The cluster in water showed a dominant step-like behavior, typical of this size regime, indicating that the material was composed of a few atoms. Note that the silver cluster synthesized by Kitaev and Cathcart[27] shows similar absorption peaks and they had suggested the possibility of a 25 atom core. The absorption profile also matches that of the cluster (band 6) reported by the Bigioni group.[43] Our group has also reported a silver cluster (GSH protected) with similar absorption features.[22,29] As the plasmon resonance feature around 400 nm is absent in the spectrum, it is clear that larger silver nanoparticles are absent and the spectrum is similar to that of molecules.[29] This is also supported by TEM measurements (see later). The cluster in water is stable for several months without change in its absorption peaks. Clusters in high concentrations appear to have a brown-black color (Fig. 2II) but upon 1000 times dilution, the color becomes reddish brown (Fig. 2III). Time dependent profiles show that the process of reduction is slow and it takes nearly 6 h to get AgQCs. In the initial stages of the reaction, a broad peak at 480 nm appeared (1 h), which became narrow with time and increases in intensity. No observable changes in absorption profiles and peak intensities were seen even after 6 h of irradiation time. The evolution of peaks within 6 h indicates that it is a slow reaction. Time dependent UV/Vis for the evolution of cluster is given in Fig. S4.† Clusters appear as tiny dots in the TEM image (Fig. S5†). Smaller clusters coalesce upon high energy electron beam exposure and nanoparticles of larger dimension are observed. In view of this, a large size distribution (Fig. S5†) from 0.5 to 3 nm was found with an average size distribution of 1.6 nm. This kind of electron-beam induced coalescence was seen earlier.[52] Such coalescence is reduced when the protection is better, for example with a silica coating.[53]

The cluster exhibits luminescence at 710 nm at all (395, 440 and 518 nm) excitation wavelengths (Fig. 3I). The emission and excitation is comparable with the cluster reported by our group.[22] In view of the specific optical absorption and emission features and due to the fact that no nanoparticles are seen in the TEM image, we conclude that monolayer protected silver clusters are formed in the synthesis.

The thiolate form of the glutathione being attached to cluster core is supported by XPS (Fig. 3II). The XPS survey spectrum of the clusters shows all the expected elements (Fig. S6†). Ag $3d_{5/2}$ (BE of 368.1 eV) supports the Ag(0) state (Fig. 3II). Note that there is not much difference in BE between Ag(0) and Ag(I) states. The S $2p_{3/2}$ BE is thiolate-like and a value of 162.0 eV is observed (Fig. S7†). An additional S $2p_{3/2}$ peak at 164.1 eV observed upon peak fitting may be due to other ligand

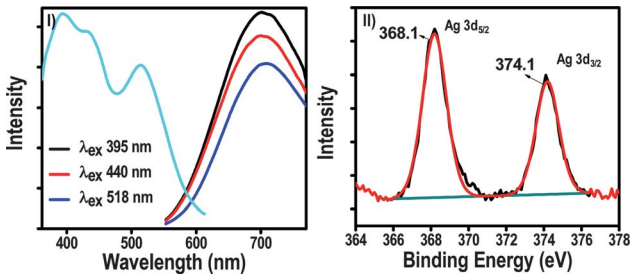

Fig. 3 (I) Luminescence spectra of the as-synthesized cluster, which show three excitation wavelengths and all of these give emission at the same wavelength. (II) X-ray photoelectron spectrum of the cluster in the Ag 3d region. The corresponding peaks are assigned. The peaks are fitted with spin–orbit split components.

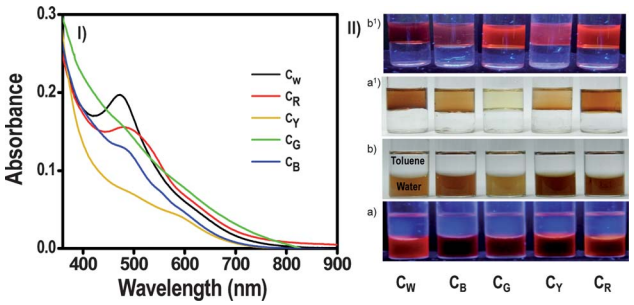

Fig. 4 (I) UV-Vis spectrum of the AgQCs synthesized using various filters: without filter (C_W), blue (C_B), red (C_R), yellow (C_Y) and green (C_G). (II) Photographs of AgQC clusters under visible light (b and a1) and UV light (a and b1), before (a and b) and after (a1 and b1) phase transfer.

binding sites or X-ray induced damage of the monolayer.[54] IR spectrum of the cluster shows that the cluster is connected to glutathione through the thiolate link (Fig. S8†). The S–H stretching at 2552 cm^{-1} of glutathione is absent in the case of the cluster. Electrospray ionization mass spectrometry (ESI MS) analysis (in negative mode) was performed to discover the composition of the cluster but we could see only some fragmented ions with good isotopic distribution (Fig. S9†). The peaks corresponding to *m*/*z* 933 and 1443 were assigned to $Ag_3(SG)_2^+$ and $Ag_4(SG)_3^+$. Upon a closer view, another peak with a difference of *m*/*z* 22 was seen for both the cases which could be attributed to replacement of Na in place of H. Matrix assisted laser desorption ionization mass spectrometry (MALDI MS) did not yield molecular ion signatures, similar to the glutathione protected clusters reported before.[39] Efforts are in progress to find the composition of the cluster. The tiny quantities of the polymeric gel remaining with the cluster seem to prevent it from creating intact ions in the gas phase. ESI MS analysis of silver cluster has been difficult in a number of cases.[39]

We also performed several experiments by exposing the sample to sunlight under different filters. Red, blue, green and yellow filters were used to allow specific light to be exposed to the sample. Depending on the filter used in the synthesis, these clusters are labeled C_W, C_R, C_B, C_G and C_Y (W, R, B, G and Y refer to without filter, with red, blue, green and yellow filters, respectively). The clusters formed were extracted into water. Variation in the absorption profiles were observed by varying the filter as shown in Fig. 4. At the same time, some similarities were also there, like the 480 nm peaks appeared for both the C_W and C_R cluster, but with different width. All these clusters show luminescence in the red region. Their QY is of the order of 10^{-3}. Clusters exhibit significant differences in their excitation and emission profiles. Excitation and emission spectra for C_W, C_R, C_B, C_Y, C_G clusters are given in Fig. S10.† As these clusters are protected with glutathione which is a dicarboxylic acid, it is possible to connect the polar end of the quaternary ammonium salts so that the resultant cluster is soluble in organic solvents. This kind of phase transfer helps in the exploration of properties of the clusters in both organic and aqueous phases.[55] The procedure for phase transfer is given in the ESI.† The absorption profiles of phase transferred clusters are not changed. Luminescence still remained as in the case of the parent clusters indicating that the cluster core is intact even after phase transfer. Photographs of the C_W, C_R, C_B, C_Y and C_G clusters in water and toluene before and after phase transfer in both ambient and UV light are given in Fig. 4II(a, a1, b and b1). These results confirm the fact that the cluster formation is highly dependent on the photon energy.

Several control experiments were done to understand the formation and to improve the yield of the cluster. The same reaction in the absence of sunlight does not produce clusters, showing the importance of light exposure for the synthesis (Fig. S11†). A Petri dish containing polymerized acrylamide gel with Ag(I)SG was kept in sunlight but covered with aluminum foil so that there was no light penetration while there was heat input. After 6 h of exposure, there was no observable color change during the reaction (Fig. S12†). This ruled out the possibility of any thermal effect in cluster synthesis. Upon exposure of aqueous oligomeric Ag(I) SG to sunlight, (Fig. S13†) silver clusters were not formed. It shows featureless UV/Vis spectra which resembled the spectrum of oligomeric Ag(I)SG (figure not shown). In the absence of gel polymerizing agent (APS and TEMED), clusters were formed but optical features were not prominent. The photographs and UV/Vis spectra of cluster, synthesized without gel precursors are given in Fig. 5I.

In another experiment, Ag(I)SG was placed in acetonitrile and exposed to sunlight for 8 h (Fig. S14†). A color change from blackish powder to reddish brown powder occurred indicating the reduction of silver. The final powder was insoluble in

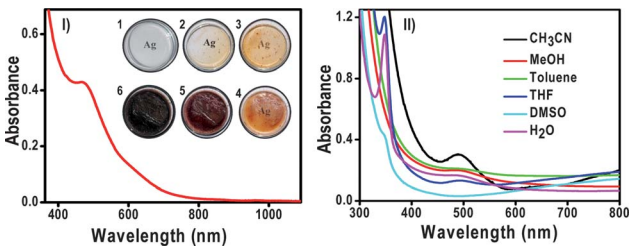

Fig. 5 (I) Inset (1 to 6) are photographs of AgQC synthesized without gel precursors (APS and TEMED) at different time intervals of exposure to sunlight, starting form initial to 6 h. UV/Vis spectrum of AgQC cluster extracted from 4. (II) UV/Vis spectra of AgQC synthesized in different media. Among them, acetonitrile shows enhanced intensity. The presence of gel as impurity in the product leads to increased background in some samples.

acetonitrile but dispersible in water. UV/Vis spectrum of the sample in aqueous medium showed a surface plasmon resonance at 400 nm indicating the formation of silver nanoparticles (Fig. S14†). In the case of acetonitrile, the growth step was not controlled so it produces nanoparticles, whereas in the gel system the growth of clusters was controlled within the gel templates.

A possible mechanism for the formation of the Ag@SG cluster is similar to that reported by Harada and Katagiri[56] where the process involves three main steps, namely photon induced reduction, autocatalytic nucleation and a subsequent growth process (Scheme 1, ESI†). The final growth is controlled by the ligand as well as the gel cavity available. Several other aspects such as temperature and photon energy will also have an influence on the cluster formation. It is known that the quantum efficiency of absorption (number of photons absorbed/total number of photons) is an important factor in the conversion of Ag(I) to Ag(0). This can be improved by choosing a given solvent in the photochemical reaction so that the liquid phase proceeds under the influence of the solvent cage.[57] So, the mechanism of photoreduction by using a solvent as a cage is assumed to be electron transfer from the solvent molecule to the silver ion: $(Ag^+, ROH/NH_2/CN)_{cage} + h\nu \rightarrow (Ag, ROH^+/NH_2^+/CN^+)_{cage}$.[57] Cluster formation is initiated by the photons of sunlight, through the influence of the solvent cage and then through a autocatalytic nucleation process,[58] further growth happens as described above.

Various solvents such as toluene, acetonitrile, tetrahydrofuran and dimethyl formamide were taken on top of the reaction medium (polymerized gel + Ag(I)SG) and exposed to sunlight (Fig. S15†). This was to check the effect of solvent properties on cluster synthesis. Variations in their absorption profile were observed as the extent of cluster formation was different for each solvent (Fig. 5II). The product obtained in acetonitrile shows better intensity compared to all other solvents. This supports our earlier argument that CH_3CN can facilitate the photochemical reduction of silver. This synthetic method is extendable to get clusters protected with other ligands such as mercaptosuccinic acid (Fig. S16†) and cysteine (Fig. S17†). The possibility of obtaining gold clusters was also checked (Fig. S18†).

The antibacterial activity of monolayer protected AgQCs was evaluated against a Gram negative organism, *Escherichia coli* (Fig. 6) and Gram positive organism, *Staphylococcus aureus* (Fig. S19I†). The result shows that the AgQCs were more active against *E. coli* than towards *S. aureus*. The average diameter of the zone of inhibition for *E. coli* was about 12, 14, 16 and 19 mm, respectively for 10, 20, 30 and 40 μL of synthesized AgQCs. For *S. aureus* (Fig. S19I†), the inhibitory effect was mild when compared to *E. coli*. Here, the diameter of the zone of inhibition was found to be 11, 12, 14 and 16 mm for the 10, 20, 30 and 40 μL of AgQCs, respectively. A solution-based study (Fig. S19II and III†) also shows similar results to those we got for the diffusion method where we could see that AgQCs are much more effective against Gram negative bacteria compared to Gram positive ones. With an increase in cluster concentration, the antibacterial effect also increases, so it is a concentration

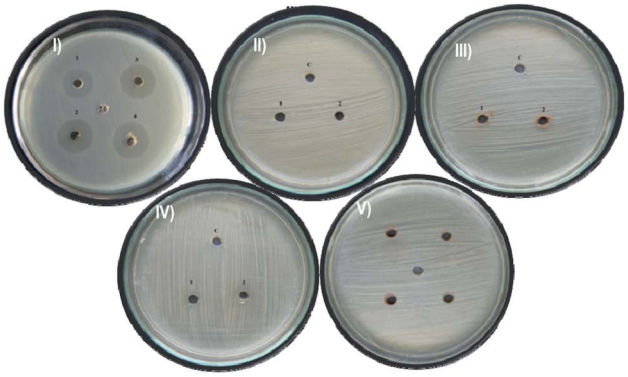

Fig. 6 The antibacterial activity of (I) monolayer protected AgQCs compared with (II) glutathione, (III) Ag(I)@SG, (IV) Au_{25}@SG and (V) Ag@SG nanoparticle. In all the cases, Petri dishes of 2.5 cm diameter and *Escherichia coli* bacteria (ATCC 8739) were used.

dependent phenomenon. Experiments using glutathione, Ag(I) SG complex and $Au_{25}(SG)_{18}$ clusters do not show any zone of inhibition which confirms that the antibacterial activity is due to the AgQCs alone. The mechanism of the antibacterial properties can be understood from a recent report of Alvarez *et al.*[59] The fast internalization of silver nanoclusters may be one of the reasons for this activity. The other possibility is the enhanced release of silver ions from the clusters which happens as a result of the following equations.

$$4Ag(0) + O_2 \rightarrow 2Ag_2O \quad (1)$$

$$2Ag_2O + 4H^+ \rightarrow 4Ag^+ + 2H_2O \quad (2)$$

The consequent antibacterial action makes the structural changes which result in cell death.[60,61] It is also known that Ag nanoclusters interact with sulfur containing proteins which in turn affects the cell viability.[62] Glutathione protected nanoparticles does not show any antibacterial effect which proves the earlier argument of fast silver ion release from clusters in comparison to nanoparticles.[59]

Conclusion

In summary, we have demonstrated sunlight-induced formation of silver clusters starting from silver thiolate complexes, in suitable gel templates. The as-synthesized AgQCs were extracted into water and made into fine powders using freeze drying. Gel templates were chosen in such a way that they were insoluble in water. AgQCs show step-like features in optical absorption spectrum as well as intense emission in the luminescence spectrum. The cluster formation is sensitive to solvents and ligands. We have demonstrated cluster formation with glutathione as the ligand. A similar method can also be used for gold clusters. These clusters can be phase transferred from aqueous to organic medium. The clusters show enhanced antibacterial action in comparison to plasmonic nanoparticles protected with glutathione.

Experimental section

Chemicals

All the chemicals were commercially available and were used without further purification. Silver nitrate ($AgNO_3$, 99%), glutathione (GSH, 97%), methanol (GR grade), acrylamide (AR grade), *N*,*N*′-methylenebisacrylamide (BIS) (AR grade), ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED) were purchased from SRL Chemical Co. Ltd., India. Solvents, ethanol (HPLC grade, 99.9%, Aldrich), methanol (HPLC grade, Aldrich), dichloromethane (HPLC grade, 99.9%, Aldrich) were used as received.

Synthesis

A well-known gel, acrylamide:bisacrylamide was used to control the growth of AgQCs. Gel solutions were synthesized similar to the method reported from our group[22] with slight modification in the concentrations of the thiol. In a typical synthesis, 10 g of acrylamide and 0.75 g of bisacrylamide were dissolved in 50 mL of water and sonicated to get a clear solution (which was stored at 10 °C and used as stock solution). 47 mg of silver nitrate and 110 mg of GSH were added to 1 mL of 1 M NaOH; the resultant mixture was sonicated until the solution color changes from turbid to clear pale yellow which is due to the formation of oligomeric silver thiolate. 3 mL of the former solution was poured into a Petri dish which contains 1 mL of silver thiolate and the two were mixed well to form a uniform solution. Then 30 μL of APS (0.1%) and 20 μL TEMED were added to initiate the polymerization. Upon keeping the sample without disturbance, polymerization and formation of the gel was visible after 15–20 min. The sample was kept under sunlight for 6 hours (starting at 9 am, in open air) to yield AgQCs. Chennai, during the period of the experiment (June–December 2011), was sunny for most of the days (average temperature 28 °C). Formation of AgQCs was visible by a change of color from colorless to black-brown. Addition of 10 mL water to the gel results in the extraction of the cluster selectively, leaving gel pieces at the bottom. These were separated from the cluster solution through filtration, followed by centrifugation. The final cluster solution was subjected to freeze drying to yield a powder sample. The cluster was phase transferred to the organic medium to observe its enhanced luminescence properties (ESI, Fig. S1†).

Ag@SG nanoparticles were made with $AgNO_3$ (47 mg) and GSH (110 mg in 50 mL water) followed by rapid addition of $NaBH_4$ (90 mg in 12.5 mL water). It was further purified by ethanol washing and dried in Rotavapor.

Instrumentation

UV/Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200–1100 nm. Luminescence measurements were carried out on a Jobin Yvon NanoLog instrument. The band pass for excitation and emission was set as 2 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA Probe spectrometer with polychromatic MgKα X-rays ($h\nu = 1253.6$ eV). The samples were spotted as drop-cast films on a sample stub. Constant analyzer energy of 20 eV was used for the measurements. High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The samples were drop cast on carbon-coated copper grids and allowed to dry under ambient conditions. FT-IR spectra were measured with a Perkin Elmer Spectrum One instrument. KBr crystals were used as the matrix for preparing samples.

The bacterial strain, *Escherichia coli* (Gram-negative rod) and *Staphylococcus aureus* (Gram positive) were obtained from the Culture Collection Center (strains used were, ATCC 8739 & MTCC96). The antibacterial activity of the Ag nanoclusters against the organisms were measured using the well-diffusion method. Pure cultures of bacteria were grown in Mueller–Hinton broth (HiMedia, Mumbai, India) at 27 °C on a rotary shaker at 200 rpm. Wells that were 6 mm in diameter were made on the Mueller–Hinton LB plates using a gel puncture. The cultures were swabbed on test media with sterile cotton swabs. About 10, 20, 30 and 40 μL of synthesized Ag nanoclusters were added to the well, and then the plates were incubated in an incubator at 37 °C for 12 h. After incubation, the diameter of the inhibition zone was measured. To compare the antibacterial activity, the experiment was repeated using glutathione, Ag(I)@SG, Au_{25}@SG and Ag@SG nanoparticles instead of AgQCs. Sterile distilled water was put in the control well. For the solution phase antibacterial test, sterile test tubes, each containing 2 mL of nutrient broth medium and the desired amount of Ag nanocluster solutions were inoculated with 10 μL of freshly prepared bacterial suspension. The tubes were incubated at 37 °C in a rotary shaker at 200 rpm. The bacterial growth was evaluated by measuring the increase of the absorbance at 600 nm at regular intervals for 24 hours in a spectrophotometer.

Acknowledgements

We thank the Department of Science and Technology, Government of India for constantly supporting our research program on nanomaterials. I. C. Thanks IITM for a research fellowship.

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