Facile and Rapid Synthesis of a Dithiol-Protected Ag₇ Quantum Cluster for Selective Adsorption of Cationic Dyes

M. S. Bootharaju and T. Pradeep*

DST Unit of Nanoscience (DST UNS), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

Supporting Information

ABSTRACT: We report a facile and rapid (less than 15 min) synthesis of atomically precise, dithiol-protected, silver quantum cluster, $Ag_7(DMSA)_4$ (DMSA: meso-2,3-dimercaptosuccinic acid), through a modified solid state route. The assynthesized cluster exhibits molecular optical absorption features with a prominent λ_{max} at ~500 nm. Composition of the cluster was confirmed using various spectroscopic and microscopic techniques such as electrospray ionization mass spectrometry (ESI MS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (SEM),



transmission electron microscopy (TEM), and energy dispersive analysis of X-rays (EDAX). Clusters supported on neutral alumina have been shown as better adsorbents for selective adsorption of cationic dyes (over anionic dyes) from water. This selectivity for cationic dyes was evaluated by zeta potential (ζ) measurements. The efficiency of clusters for removal of dyes is very high when compared to nanoparticles (NPs) protected with ligands (citrate and mercaptosuccinic acid (MSA)) possessing similar chemical structures as that of DMSA. The higher efficiency of clusters for the removal of dyes is attributed to their smaller size and large surface area compared to the NPs in addition to favorable electrostatic interactions between the clusters and cationic dyes. Adsorption of dyes (cationic and anionic) was enhanced when dye molecules contain hydrogen bond forming functional groups. Supported clusters have been reused up to five cycles without the loss of activity once the adsorbed dye is extracted using suitable solvents.

■ INTRODUCTION

Research on monolayer-protected noble metal (Au, Ag, Cu, Pt, and Pd) quantum clusters is progressively increasing due to their unique and unusual optical, physical, and chemical properties.¹⁻⁶ These nanosystems are falling (in length scale) in-between molecules and quantum dots/NPs. The typical cluster size regime is less than 2 nm. Clusters of gold, protected with both water- and organic-soluble ligands, are extensively studied compared to silver analogues. Crystal structures of some of the gold clusters, $Au_{25}(SC_2H_4Ph)_{18}$ ^{7,8} $Au_{36}(SPh-tBu)_{24}$,⁹ $Au_{38}(SC_2H_4Ph)_{24}$,¹⁰ $Au_{102}(p-MBA)_{44}$,¹¹ and { $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$ },¹² have been solved. The crystallization of silver clusters is difficult as they are usually less stable compared to the gold ones. However, the crystal structure of Ag₁₄(SC₆H₃F₂)₁₂(PPh₃)₈ has been obtained recently.¹³ Silver and gold clusters exhibit applications in a variety of fields such as catalysis,¹⁴ sensing,^{15,16} biology,^{17,18} and electrochemistry.¹⁹ There are numerous methods in the literature for the synthesis of these systems which include interfacial etching,²⁰ core etching,²¹ galvanic exchange,²² microwave irradiation,²³ sonochemical methods,²⁴ sunlightassisted methods²⁵ and reactions in gel media.²⁶ Protein-²⁷ and polymer-coated²³ metal clusters have also been reported. The important and desirable aspects to be considered in the synthesis of clusters are easiness to handle the reaction, short synthesis time and high yield of the product. One of the simple methods to synthesize silver clusters is grinding the precursors of metal and ligand in the solid state, followed by reduction with a reducing agent. Using this method, $Ag_9(MSA)_7^4$ and $Ag_{152}(SC_2H_4Ph)_{60}^{28}$ clusters have been synthesized. This method is also extended for the synthesis of NPs of C_{60} by grinding C_{60} powder using mortar and pestle.²⁹

One of the important aspects of synthesis of clusters is utilizing them for various applications. The luminescence and absorption features of the clusters are very sensitive to metal ions and molecules. This sensitivity is relevant to the environment, particularly water. The luminescence of clusters may be quenched or enhanced depending on the nature of interaction with an analyte.^{30–32} Certain clusters exhibit unusual reactivity with ions owing to their small size and large surface area.³³ In this paper, we use this emerging category of materials for an application of relevance to developing societies.

Organic dyes³⁴ used in textiles, leather, printing, cosmetics, and other industries^{34–36} are main water contaminants in industrial areas. Presence of dyes in environment to a degree

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greater than the tolerable levels causes undesirable effects not only on the environment but also on human health. The potential toxicity of various azo dyes has been known for a long time. Certain azo dyes are not being used since they are carcinogens.³⁷ Disazo dyes, based on benzidine, are also found to cause cancer.³⁸ The presence of these coloring materials in water bodies adversely affects the photosynthetic activity of aquatic life. Also, it reduces the light penetration and increases the chemical oxygen demand (COD).³⁹ Therefore, it is important to remove them from wastewater. There are two types of dyes, namely, cationic (D^+) and anionic (D^-) . Removal of dyes is not a simple task due to the resistance of dyes to aerobic digestion and to biodegradability. Their resistance is due to the presence of stable aromatic rings in their structures. The most commonly used methods to decontaminate wastewater from dyes are coagulation,⁴⁰ adsorption,^{41,42} oxidation,⁴³ membrane filtration,⁴⁴ photocatalysis,^{34,45} biological treatment,⁴⁶ etc. Among these, all except adsorption are expensive methods. There are many advantages in adsorption which include simplicity of operation and flexibility in design, high efficiency, recyclability, and insensitivity to toxic substances. Adsorption is prominent when the surface area of the adsorbent is large.

Nanomaterials are important in the purification of water as they exhibit high surface area with a large number of active adsorption sites.⁴⁷ In the recent past, several nanomaterials were explored in this context. Importantly, carbon-based materials, such as graphene, graphene–metal/metal oxide composites, carbon nanospheres (CNS), carbon nanotubes (CNT), and activated carbon, show promising adsorption capacities toward dyes.^{47,48} Other materials such as polymerbased adsorbents, iron oxide NPs, bimetallic nanosystems, clays, and zeolites are also used for the adsorption of dyes.^{36,49} When magnetic NPs are used as adsorbents, the separation of dye-adsorbed NPs from water is achieved simply by using a bar magnet. Noble metal nanoparticles (NPs) are shown to have applications in water purification.^{50,51} As clusters are smaller in size compared to NPs, they are expected to exhibit higher surface area and reactivity.

In this paper, we report the facile synthesis and application of atomically precise Ag₇ cluster protected with meso-2,3dimercaptosuccinic acid (DMSA), having the formula $Ag_7(DMSA_4)$. It is prepared according to the method originally reported for $Ag_9(MSA)_{77}^4$ with some modifications in synthesis conditions. Molecular formula of the cluster is obtained by mass spectrometric analysis. The cluster was characterized using various spectroscopic tools. The cluster was synthesized in the solution phase previously by Z. Wu et al.,⁵² wherein, synthesis was completed in 12 h. In our method, we achieved it in less than 15 min. As-prepared clusters are supported on neutral alumina and tested for the removal of rhodamine 6G (R6G), methylene blue (MB) and malachite green (MG) [which are cationic] and eriochrome black T (EBT), methyl orange (MO) and methyl red (MR) [which are anionic]. We found that our material shows selectivity toward cationic dyes probably due to favorable electrostatic interactions. The effect of substrate, alumina, was also evaluated. The efficiency of clusters for the removal of dyes is compared with that of Ag NPs protected with (i) trisodium citrate and (ii) mercaptosuccinic acid. Although silver is expensive than carbon and ironbased materials for the removal of dyes, percentage loading of cluster is very less (0.4 wt %). Synthesis of this cluster is easier than other materials in terms of time, easy loading and other

factors. The material was found to be recyclable for large number of cycles which makes the present clusters important for this application.

EXPERIMENTAL SECTION

Materials. Silver nitrate (AgNO₃; CDH, India), trisodium citrate (TSC, Qualigens), mercaptosuccinic acid (MSA), meso-2,3-dimercaptosuccinic acid (DMSA), sodium borohydride (Sigma Aldrich), and methyl alcohol were received from various laboratories and used as such without further purification. Neutral alumina (60–325 mesh, BSS) was supplied by SRL, India. The BET surface area of alumina was 80.4 m²/g, and the mean particle size was 0.13 mm. Pore size distribution was 50–60 Å. Dye molecules, rhodamine 6G chloride (R6G), methylene blue (MB), malachite green (MG), eriochrome black T (EBT), methyl orange (MO), and methyl red (MR) were obtained from Sigma Aldrich and used as-received with no further purification.

Synthesis of Ag₇(DMSA)₄. The Ag₇(DMSA)₄ cluster was synthesized according to the method used for synthesis of Ag₉(MSA)₇,⁴ with some modifications. Briefly, 23 mg AgNO₃ and 25 mg DMSA (1:1 mol ratio) were ground to get a reddish brown thiolate (within 2–3 min.). After that, 25 mg NaBH₄ powder was added and grinding was continued for 3–4 min. A quantity of 6 mL ice-cold water was added dropwise to the above mixture along with grinding. The resultant black solution was poured into excess methyl alcohol (nearly 15 mL) which was kept at 0–5 °C. The reddish brown precipitate formed was washed 3–4 times by dispersion and centrifugation using methyl alcohol to remove excess ligand and excess reducing agent. Methyl alcohol was evaporated using a rotary evaporator to get the cluster in powder form.

Preparation of Supported Clusters. A known quantity of cluster in powder form was dissolved in a known volume of water which gives a reddish brown solution. To this, a known amount of neutral alumina was added followed by gentle shaking. This leads to the adsorption of clusters on alumina surface which could be visually observed as the intensity of the brown color of the supernatant decreases while the colorless alumina becomes increasingly colored. At a certain stage of alumina addition, the color of the solution disappeared completely. The absence of cluster in the supernatant was ensured using UV/vis absorption spectroscopy. At the point of surface saturation of alumina, 4 mg of cluster was adsorbed per 1 g of alumina (0.4 wt %).

Synthesis of Ag@citrate and Ag@MSA NPs. Citrate-⁵³ and MSA-protected²⁰ Ag NPs were synthesized according to previously reported protocols: (1) To a boiling aqueous solution of AgNO₃, trisodium citrate solution was added. Boiling was continued till the solution turned yellow in color. A solution of Ag@citrate was cooled under tap water. (2) The Ag@MSA NPs were synthesized by reducing methyl alcoholic Ag(I)MSA thiolate with aqueous sodium borohydride solution. The resulting black precipitate was washed several times with methyl alcohol to remove excess ligand, and finally methyl alcohol was evaporated to get NPs in powder form. Alumina-supported NPs were prepared as described earlier (at a loading of ~0.5 wt %). The ligand, DMSA was supported on alumina (500 mg) by stirring a 5 mL solution of DMSA (12 mg/mL, pH 10) at 500 rpm for 15 min. After that, alumina was washed 4 times with distilled water to remove excess DMSA. The presence of DMSA on alumina was confirmed using FTIR spectroscopy.

Adsorption of Dyes onto Supported Clusters/NPs. For this study, 500 mg of supported nanomaterial was separately treated with 3 mL of 5 ppm cationic and anionic dyes. These mixtures were subjected to gentle shaking using a mechanical shaker for the required duration, at room temperature (25 °C). For reuse of the used material, adsorbed dyes were extracted into acetone/ethanol (three times, 4 mL each time). Extraction of dyes was evident by the appearance of color of the dye in the solvent. After extraction of the dye, the adsorbent material was dried in ambience for about 1 min and used for successive adsorption and desorption cycles. The capacity of adsorption (q_e) of dye was calculated using the equation $q_e = (C_0 - C_e)V/m$ mg/g. Here, q_e is the adsorption capacity in mg of dye per gram of cluster excluding

the mass of alumina, C_0 and C_e are initial and equilibrium concentrations, respectively, in the supernatant of dye solution expressed in mg per liter, V is the volume of solution in mL, and m is the mass of adsorbent in mg.

Instrumentation. UV/vis absorption spectra were recorded using a PerkinElmer Lambda 25 instrument in the spectral range of 200 to 1100 nm. HRTEM of the samples was carried out using a JEOL 3010 instrument with a UHR pole piece. Specimens for TEM analysis were prepared by placing one or two drops of aqueous solution on carboncoated copper grids and allowing them to dry at room temperature overnight. All measurements were done at 200 kV in order to minimize the damage to the sample by the high energy electron beam. SEM images and EDAX studies were carried out using a FEI QUANTA-200 SEM. For SEM measurements, samples were dropcasted on an indium tin oxide (ITO)-coated conducting glass followed by drying in ambience. The FTIR spectra were recorded using a PerkinElmer Spectrum One instrument. KBr crystals were used as the matrix for preparing the samples. XPS measurements were done using an Omicron ESCA Probe spectrometer with polychromatic Al K α Xrays ($h\nu$ = 1486.6 eV). The X-ray power applied was 300 W. The pass energy was 50 eV for survey scans and 20 eV for specific regions. The sample solution was spotted on a molybdenum plate and dried in vacuum. Supported cluster powder was pressed as pellets and pasted on the sample plate using conducting carbon tape. The base pressure of the instrument was 5.0×10^{-10} mbar. The binding energy was calibrated with respect to the adventitious C 1s feature at 285.0 eV. Most of the spectra were deconvoluted to their component peaks, using the software CASA-XPS. XRD data were obtained with a Shimadzu XD-D1 diffractometer using Cu K α (λ = 1.54 Å) radiation. The samples were scanned in the 2θ range of 10 to 90°. The ESI mass spectrometric measurements were done in the negative mode using LTQ XL instrument, with m/z = 150-4000. Here, the spray and the extraction are orthogonal to each other. The clusters obtained were dispersed in 1:1 water-methanol solution and used for the measurements. The samples were electrosprayed at a flow rate of 10 μ L/min at a temperature of 150 °C. The spectra were averaged for 75 scans. BET surface areas of alumina and supported clusters were measured on the basis of N2 adsorption-desorption isotherms using MICROMERITICS ASAP 2020 Porosimeter. Zeta potential (ζ) measurements were performed with a HORIBA instrument.

RESULTS AND DISCUSSION

Characterization of As-Prepared Material. As-synthesized material was characterized by various analytical tools. The absorption spectrum of Ag@DMSA in water shows a sharp peak at 500 nm with a shoulder around 620 nm as shown in Figure 1. These features indicate the absence of plasmonic NPs which generally exhibit surface plasmon resonance around 400 nm.⁵³ The photographs of as-prepared clusters in powder and in solution form (a and b, respectively) are shown as insets of Figure 1. Inset c is a cartoonic representation of the silver cluster protected by DMSA ligand.

As-obtained Ag@DMSA was subjected to electrospray ionization mass spectrometry (ESI MS). Negative mode ESI MS of the cluster in a 1:1 water-methanol mixture, up to m/z= 4000, is shown in Figure 2. It consists of only two major sets of peaks around m/z = 720-800 and 480-540. After careful analysis, these were assigned to doubly and triply charged Ag₇(DMSA)₄ ions, respectively, as shown in Figure 2. Expanded view of the spectrum of the doubly charged ion is shown as inset a. On top of graph (a), expected positions for the addition of 0-6 sodium ions are depicted. The MS consists of a series of peaks separated by m/z = 11. This observation confirms the presence of sodium (mass 23) in the doubly charged ions, which substitutes hydrogen, explaining the mass difference (Na-H, 22/2 = 11). Presence of sodium is due to sodium borohydride used in the synthesis. As the DMSA ligand Article



Figure 1. UV/vis absorption spectrum of as-synthesized Ag@DMSA cluster. Insets are photographs of the as-prepared cluster in powder and aqueous solution forms (a and b, respectively). Schematic representation of the cluster is shown in inset c.



Figure 2. ESI MS of as-synthesized silver clusters (in 1:1 watermethanol volume ratio) in –ve mode. Insets are expanded views of the spectrum of doubly charged species along with sodium adducts. Inset a: Expanded view in m/z = 730-810 range corresponding to the addition of 0–6 Na. Inset b: Expanded view in m/z = 745-752 range corresponding to one sodium addition, $[Ag_7(DMSA)_4H_5Na]^2$. Each peak in the m/z = 730-810 window shows similar isotope distribution.

is a dicarboxylic acid, carboxylic groups can interact with sodium ions. Since there are 8 ligands in the cluster, we can see 6 sodiums added and the remaining two carboxylates are contributing to overall charge. To confirm the chemical formula for this ion, the mass spectrum was calculated for the formula $[Ag_7(DMSA)_4H_5Na]^{2-}$ and compared with the experimental spectrum (inset b). Experimentally observed peaks match well with the calculated peaks confirming the validity of peak assignments.

The spectrum of triply charged ion is expanded and shown in Supporting Information, Figure S1A. The separation of peaks is at a mass of 7.3 which corresponds to the mass of sodium (7.3 \times 3 = 22, substitution of Na in place of H corresponds to the mass difference 22). Similar to the spectrum of the doubly charged ion, there are five peaks corresponding to the five added sodium ions. The remaining three carboxylate groups (out of eight) are contributing to the charge on the ion. For further confirmation, the calculated mass spectrum for the formula $[Ag_7(DMSA)_4H_5]^{3-}$ is compared with the experimental mass spectrum. The peaks match very well (inset of Figure S1B). For additional confirmation, one can go for MS² of a particular ion. MS^2 of the species at m/z = 747.4, corresponding to the mono sodium salt of the doubly charged species [Ag₇(DMSA)₄H₅Na]²⁻ is shown in Figure S1B at a nominal collision energy of 15 eV. The major peak is at m/z =673.4, corresponding to the loss of one DMSA ligand without sulfur [74 = (180-32)/2]. This confirms the assignment. The MS² of other species also shows the loss of ligand minus the bonded sulfur, as observed in the previous report.⁵² Formation of cluster composition is proved using other spectroscopic tools. Comparison of the FTIR data (Figure S2) of the cluster and the lignad shows the absence of S-H stretching frequency (at 2550 $\rm cm^{-1}$ in parent DMSA) in the cluster, indicating the binding of Ag with the ligand through the S atom. The other characteristic peaks of the ligand are also present, but they are shifted and broadened with respect to that of the parent ligand. This shift and the broadening again confirm the protection of the cluster by the DMSA ligand. SEM-EDAX analysis of the cluster confirms the presence of main elements, Ag, S, and Na, as shown in Figure S3. A large aggregate of clusters was mapped using EDAX. The quantification table of elements suggests the atomic ratio between Ag and S as 0.90 which is close to the composition obtained from MS analysis (0.88). An XPS survey spectrum of the cluster clearly shows the presence of the expected elements, C, S, O, Ag, and Na (Figure 3A). Ag 3d_{5/2} is at 368.0 eV (Figure 3B) which is in between that expected for Ag⁺ and bulk Ag^0 (367.5 and 368.2 eV, respectively).²² This shows silver to have more reduced character (Ag⁰). Insets of Figure 3A are C 1s and S 2p regions. The C 1s peaks appearing at 285.0, 288.0, and 290.0 eV are assigned to C in <u>C</u>-C, $-\underline{C}OO$, and possibly, $-\underline{C}OONa$, respectively. The S $2p_{3/2}$ peak, appearing at 162.0 eV, confirms the presence of S in the thiolate form. Although, MS analysis suggests the presence of a free S-H, we detect in XPS only one type of S. The atomic ratio between Ag and S is found to be 0.91 which is also close to the ratio obtained from MS analysis. TEM (Figure S4A) of cluster confirms the absence of NPs. However, after electron beam irradiation, there was growth of clusters to form aggregates (inset of Figure S4B). This sensitivity to electron beam is common for several silver clusters. XRD also confirms the absence of diffraction peaks corresponding to the NPs or bulk silver (Figure S4B). From all of these observations, formation of clusters in pure form is confirmed.

Application of Clusters in Removal of Dyes. For this study, $Ag_7(DMSA)_4$ clusters were supported on neutral alumina. The advantage of supported clusters is their recyclability. The supported clusters were characterized using SEM-EDAX and XPS techniques. SEM-EDAX analysis shows the presence of the elements in the cluster, Ag and S (Figure S5). The XPS data show the presence of Ag in the zerovalent state as that of parent clusters. Visual inspection of the parent alumina and supported clusters (photographs in Figure 4) support the adsorption of clusters. Nearly 500 mg of supported clusters was treated with 3 mL of 5 ppm R6G for 10 and 15 min. The absorption spectra of residual R6G were recorded and



Figure 3. (A) XPS survey spectrum of silver clusters in which the various features are labeled. Insets are C 1s and S 2p regions. (B) Expanded spectrum in the Ag 3d region.

the data are shown in Figure 4F. Effect of bare alumina on adsorption of dye was also checked under the same experimental conditions (Figure 4F). In 10 min, clusters adsorb more than 80%, and in 15 min, it is 99.7%, whereas, bare alumina adsorbs only about 23% in 15 min. This clearly confirms the favorable capacity of supported clusters for R6G removal. The photographs of R6G-adsorbed supported cluster, 5 ppm R6G solution, and R6G solution with supported cluster are shown in Figure 4, panels C, D, and E, respectively. The colors of the materials confirm the adsorption of clusters and R6G. The other confirmation for adsorption of R6G is the observation of luminescence from R6G under UV lamp (inset of Figure 4C).

The zeta potentials (ζ) of as-prepared clusters (unsupported), R6G (1 ppm), and R6G-treated clusters were measured to understand the nature of the interaction between the cluster and R6G at equilibrium at pH (6.3). As Ag₇(DMSA)₄ clusters possess carboxylate groups, they exhibit negative zeta potential (-75.7 mV), whereas R6G appears almost neutral ($\zeta = -0.1$ mV). After addition of R6G to the cluster, a decrease in the zeta potential of the cluster (-56.6)mV) was observed at room temperature, indicating charge neutralization due to electrostatic attraction between two oppositely charged ions (inset of Figure 4F). XPS analysis of R6G-treated supported clusters was done to check the change in oxidation state of silver after interaction with the dye (Figure 5). Survey spectra of supported clusters before and after treatment of R6G show the presence of expected elements, Al, C, O, S, and Ag from clusters (Figure 5A). The Ag $3d_{5/2}$ peak



Figure 4. Photographs of bare alumina (A), cluster-loaded alumina (B), 5 ppm R6G adsorbed on supported clusters (C), 3 mL of 5 ppm R6G (D), and D + 500 mg of supported clusters (E). Inset of C is the photograph of material in C under UV lamp. Scale bar is 1 cm. (F) UV/vis absorption spectra of residual R6G solutions treated with 500 mg of various materials for 10 and 15 min. Inset of F is a of table of zeta potentials (ζ) of the unsupported cluster and the cluster treated with R6G at an equilibrium pH of 6.3.

observed at 368.1 eV (assigned to Ag^0 in supported clusters) was not changed after R6G uptake (Figure 5B). This clearly indicates that the uptake of R6G is due to adsorption. Another proof of adsorption is the UV/vis absorption spectrum of adsorbed dye, after extraction with acetone. The spectrum is the same as that of the parent dye (inset of Figure 5A). The spectrum further proves that no cluster is released back into the solution.

Kinetics of Adsorption. For this study, adsorption of 5 mL of 1 ppm R6G on 100 mg of supported cluster was monitored with time in batch. The residual concentrations of R6G in solution after treatment for different time intervals were determined by knowing the absorption intensity at 526.8 nm with reference to a standard calibration curve of R6G. The kinetics of R6G adsorption could be fitted to pseudo first order and pseudo second order equations (Figure S6). For determining the adsorption capacity of clusters for R6G, MB, MR, and MO, 250 mg of loaded cluster was treated with 5 mL of 5 ppm dye solutions for 45 min. The adsorption capacities of R6G, MB, MR, and MO are found to be 17.2, 16.4, 3.2, and 0.2 mg/g of cluster, respectively. The efficiency of supported clusters for R6G adsorption was compared with that of alumina alone, DMSA on alumina, and alumina supported NPs of Ag@ citrate and Ag@MSA (sizes of Ag NPs were 30-60 and 15-25 nm, respectively, and loading of these materials on alumina was

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Figure 5. (A) Survey spectra of supported silver clusters before and after R6G adsorption (black and red traces, respectively). (B) Comparison of Ag 3d region. Inset of A is the UV/vis absorption spectrum of extracted R6G from supported clusters. Extraction was done using acetone.

 ~ 0.5 wt %, comparable to that of clusters) under the same experimental conditions (500 mg material was treated with 3 mL of 5 ppm R6G for 15 min.). Under these conditions, the percent removal of R6G by (i) alumina, (ii) cluster, (iii) Ag@ MSA, (iv) Ag@citrate, and (v) DMSA (ii, iii, iv, and v being supported on alumina; presence of DMSA on alumina was confirmed by FTIR analysis) were 22.4, 99.7, 30.0, 29.6, and 29.8%, respectively (Figure S7). These results clearly highlight the importance of clusters for nearly complete adsorption of dye. The reasons for the large adsorption by clusters are their smaller particle size and large surface area which were confirmed by BET surface area measurements. The BET surface areas of alumina and supported clusters were 80.4 and 99.2 m^2/g , respectively. The other reason may be the increased number of functional groups in the cluster (due to small size) compared to nanoparticles for a given quantity of material. The increased reactivity and adsorption capacity of smaller clusters $[Ag_9(MSA)_7]$ compared to nanoparticles are observed in reaction with halocarbons.⁵⁴ The higher efficiency of a supported cluster than a supported ligand may be due to the difference in density of functional groups on the alumina surface. For supported clusters, there is possibility for a large number of functional groups per adsorption site due to threedimensional arrangements of ligands on the cluster (see below in Scheme 1). In the case of ligand alone, there is a maximum of two functional groups per adsorption site.

Recycling of Supported Clusters. About 500 mg of supported cluster (0.4 wt % loading) and 3 mL of 5 ppm R6G were shaken in a conical flask for 15 min using a mechanical

Scheme 1. Schematic Representation of the Interaction of Cationic and Anionic Dyes with $Ag_7(MDSA)_4$ Clusters Supported on Alumina^{*a*}



^aCationic dyes interact with carboxylate groups of DMSA through electrostatic interaction. Anionic dyes do not show a strong tendency for adsorption. Adsorbed dyes can be extracted using acetone/ethanol, and the supported adsorbent could be used for the next cycle. For clarity, only two ligands per cluster are shown. The sizes of cluster and ligands in the scheme are not to scale.

shaker. After that, the mixture was centrifuged for 5 min at 5000 rpm. Absorbance of the supernatant was measured, and the concentration of R6G in it was calculated using a calibration curve (Figure S8). After centrifuging, the solid material was rinsed 3 times with 3 mL portions of acetone/ethanol. The progress of extraction of R6G into the solvent could be seen by the color change. After removing all of the solvent, the material was used for next cycle of dye adsorption. All of these steps were followed for 6 cycles. In each cycle, the % of R6G removal was calculated using the absorbance at 526.8 nm (Figure 6A). The removal capacity decreases in successive cycles (Figure 6B). Nevertheless, the removal capacity is 92.2% even in the sixth cycle.

Selectivity of Dye Removal. We found that the clusters are selective toward cationic dyes, whereas they poorly adsorb anionic dyes. For testing the selectivity, we have chosen three cationic (R6G, MB, and MG) and three anionic (EBT, MR, and MO) dyes, the chemical structures of which are shown in Figure 7A. For selectivity studies, we treated 500 mg of loaded cluster with 3 mL of 5 ppm solution of each dye separately. After 15 min, the residual concentration of dye left behind was determined using absorption spectroscopy. A calibration curve was constructed for each dye. Interestingly, only cationic dyes are adsorbed in contrast to anionic dyes. To know the reason for selectivity, zeta potentials were measured. We found that, after the addition of cationic dyes into clusters (unsupported), the negative charge of the cluster gradually decreased, whereas the zeta potential increased slightly on addition of anionic dyes. The decrease of the negative charge on cluster is due to the electrostatic attraction of the positively charged cationic dye with the anionic cluster. In the case of anionic dyes, repulsion between negative charges of carboxylate groups of the cluster and of dyes operates against effective adsorption. The adsorption behavior of the system was also tested in tap water, and the efficiencies were found to be similar (99.7 and 99.3% in distilled water and tap water, respectively, for R6G). Monitoring the adsorption of a mixture of cationic dyes was



Figure 6. (A) UV/vis absorption spectra of residual R6G left in the supernatant after treating the dye solution with supported clusters at different cycles (1-6). (B) Histogram of percent removal of 5 ppm R6G in different cycles. Error in the evaluation of adsorption efficiency is less than 1%.

difficult by absorption spectroscopy as their absorption maxima are similar.

Among the cationic dyes, R6G and MB are prominently adsorbed whereas MG shows ~50% adsorption (Figure 7B). Data suggest that, besides ionic interactions, functional groups are also important in deciding the extent of adsorption. R6G possesses ester and other oxygen functionalities which can form hydrogen bonding with carboxylate groups of the cluster. In the case of MB, the sulfur atom (Figure 7A) shows affinity toward the Ag cluster. However, in MG, there are no such functionalities except the positive charge. These are possible reasons for the varying adsorption capacities of R6G, MB, and MG. EBT and MR are negatively charged dyes, and they show small but definite adsorption. EBT has two -OH groups and MR has one carboxylate group which would form hydrogen bonding³⁹ with the cluster functionalities. MO has one sulfonic group which also can form hydrogen bonds but shows poor adsorption. The most probable reason for the poorest adsorption of MO is strong electrostatic repulsion between clusters and MO than in the case of MR. In the case of MO, negative charge can be delocalized on three oxygen atoms, whereas in MR it is on only two oxygens. It is also well-known that the sulfonic group has a higher electronegative center due to its strong electron withdrawing nature than carboxylic groups. These are the probable factors that are responsible for adsorption of the two (EBT and MR) anionic dyes. Above observations are depicted in Scheme 1. Adsorption capacities (q_{ad}) of silver clusters for R6G, MB, MR, and MO are 17.2, 16.4, 3.2, and 0.2 mg/g of cluster, respectively. These values suggest that $q_{ad}(D^+) \gg q_{ad}(D^-)$. Cationic dyes were efficiently adsorbed by anionic clusters, whereas anionic dyes were not. Adsorption of both cationic and anionic dyes was enhanced by the presence of hydrogen bonding functional groups.



Figure 7. (A) Chemical structures of cationic and anionic dyes (R6G, MG, MB, EBT, MR, and MO) used in the experiment. (B) Histogram representing percent removal of dyes (3 mL of a solution of 5 ppm concentration of each dye was treated with 500 mg quantities of supported clusters for 15 min). Error in the evaluation of adsorption efficiency is less than 1%.

SUMMARY AND CONCLUSIONS

We have synthesized atomically precise silver quantum clusters protected with the dithiol, $Ag_7(DMSA)_4$, using a modified solid state route which takes just about 15 min. The cluster was characterized using several spectroscopic and microscopic analytical tools. The chemical formula of the cluster, Ag₇(DMSA)₄ was determined by ESI MS and was confirmed by MS/MS. These clusters, after supporting on alumina, selectively remove cationic dyes. The capacities for the removal of R6G and MB are 17.2 and 16.4 mg/g, respectively. The large capacity of clusters for the removal of dyes, compared to NPs, is attributed to the smaller size and the larger surface area. Possible reason for the preferred adsorption of cationic dyes is electrostatic attraction between the clusters and dyes. Hydrogen bond formation may enhance the adsorption of cationic and anionic dyes when they contain hydrogen bond forming functional groups such as -OH. The supported cluster based adsorbent is reusable after simple extraction of the adsorbed dyes with solvents. Although silver is expensive, the cluster loading is only 0.4 wt %. Small quantities of the material and recyclability make the system useful for water purification applications.

ASSOCIATED CONTENT

S Supporting Information

ESI MS, ESI MS/MS, FTIR, TEM, XRD, and SEM-EDAX of unsupported and supported clusters, calibration curve for R6G, comparison of efficiencies of the cluster, and NPs for R6G removal. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pradeep@iitm.ac.in. Fax: 91-44-2257-0545/0509.

Notes

The authors declare no competing financial interest.

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Article

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