

Applications of self-assembled monolayers in materials chemistry

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Abstract. Self-assembly provides a simple route to organise suitable organic molecules on noble metal and selected nanocluster surfaces by using monolayers of long chain organic molecules with various functionalities like –SH, –COOH, –NH₂, silanes etc. These surfaces can be effectively used to build-up interesting nano level architectures. Flexibility with respect to the terminal functionalities of the organic molecules allows the control of the hydrophobicity or hydrophilicity of metal surface, while the selection of length scale can be used to tune the distant-dependent electron transfer behaviour. Organo-inorganic materials tailored in this fashion are extremely important in nanotechnology to construct nanoelectronic devices, sensor arrays, supercapacitors, catalysts, rechargeable power sources etc. by virtue of their size and shape-dependent electrical, optical or magnetic properties. The interesting applications of monolayers and monolayer-protected clusters in materials chemistry are discussed using recent examples of size and shape control of the properties of several metallic and semiconducting nanoparticles. The potential benefits of using these nanostructured systems for molecular electronic components are illustrated using Au and Ag nanoclusters with suitable bifunctional SAMs.

Keywords. Self-assembled monolayer; monolayer protected clusters; molecular electronics; bio-mimetic synthesis; superlattice.

1. Introduction

Considerable attention has been drawn during the last few decades to modify noble metal surfaces by forming ordered organic films of few nanometers to several hundred nanometers thickness^{1–3}. One of the simplest means of forming these ultrathin films is by the mere immersion of the noble metal surface in a dilute solution (mM) of the organic molecule at ambient conditions and these unimolecular organic film is popularly known as self-assembled monolayers (SAM). Indeed, SAM formation provides one easy route towards surface functionalisation by organic molecules (both aliphatic and aromatic) containing suitable functional groups like –SH, –CN, –COOH, –NH₂ and silanes on selected metallic (Au, Cu, Ag, Pd, Pt, Hg and C) as well as semiconducting surfaces (Si, GaAs, indium coated tin oxide etc.)⁴. These type of SAM modified surfaces are highly useful for investigating several fundamental phenomena such as distance dependent electron transfer⁵, mechanism of single electron transfer⁶, observation of molecular event such as coulomb staircase⁷ etc. on artificially designed nanostructures. Due to the highly

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ordered nature and tight packing, these monolayers on metallic surfaces are also important for several practical applications such as chemical sensing⁸, control of surface properties like wettability and friction⁹ corrosion protection¹⁰, patterning¹¹, semiconductor passivation¹², and optical second harmonic generation¹³.

Molecular engineering is an interdisciplinary area where supramolecular systems are designed capable of electronic operations like switching, gating, rectification, amplification etc. The primary objective is to design and synthesize suitable building blocks with novel and potentially useful electronic properties. Aside from organising interesting molecules in two dimensions, development of nanotechnology also needs suitable size functional building blocks to continue the fabrication of nanoarchitectures. Colloidal particles or clusters of metal and semiconductors are immensely suitable as building blocks to tailor these types of nano devices due to their unique optical¹⁴ and electronic properties¹⁵. Flexibility in functionalising the terminal groups of SAM modified surfaces allows the build up of nanoarchitectures with these nanoparticles. If a single molecule can serve as a switch or a logic device its size allows to utilization of about 10^{13} units/cm² compared to the presently used level of 10^8 units/cm². For memory applications, "one bit per molecule" can give unprecedented storage density along with the other attendant advantages of size reduction. SAM is a simple way to organize 10^{13} molecules/cm² and hence is immensely suitable for achieving these objectives¹⁶. In addition, improved response time and low power, as observed in systems of biological electron transfer, are other benefits.

In this article, we describe the applications of SAM techniques in materials chemistry with special emphasis on the preparation of monolayer protected clusters and their utility in designing nanostructures for molecular electronics. Specific examples of monolayer-mediated synthesis (biomimetic material synthesis) and the organisation of monolayer protected clusters on SAM surfaces are illustrated with their unique features.

2. Self-assembled monolayers

The word SAM generally denotes a monomolecular thick film of organic compounds on flat (i.e., two-dimensional) metal or semiconductor surfaces. SAM formation provides one of the easiest ways to obtain ordered monolayers through strong chemisorption between the substrate head group of a desired compound and the metal surface leading to the preparation of thermodynamically stable monolayers¹⁻³ as compared to LB (Langmuir–Blodgett) and other techniques, where only physisorbed, thermally unstable mono/multilayer films are obtained. Several studies show that long-chain alkane thiols (containing more than six to seven methylene units) form more well-ordered defect-free monolayers than short-chain alkane thiols, disulphides or sulphides. Aromatic (π systems like benzene, naphthalene or diphenylene systems) or/and hydrogen-bonded molecules with multiple contacts, containing functional groups like thiols, amines, sulphides, selenides etc. provide improved stability¹⁷⁻²¹.

One of the important advantages of SAM is that they can be prepared in the laboratory by simply dipping the desired substrate in the required millimolar solution for a specified time followed by thorough washing with the same solvent and drying, often using a jet of dry argon. Gas-phase evaporation of the adsorbant can also form good monolayers, although structural control is difficult. Several factors affect the formation and packing density of monolayers, like nature and roughness of substrate, solvent used, nature of the adsorbate, temperature, concentration of adsorbate etc. Cleanliness and crystallinity of

the substrate also play a crucial role in determining the compactness, often quantitatively estimated by the pinhole distribution.

Electrochemical techniques like cyclic voltammetry (CV)²⁰, and impedance measurements^{17,22} are easy techniques for monitoring monolayer characteristics. These electrochemical studies also provide useful information about the distribution of defects like pinholes, redox property of attached groups (ferrocene, ruthenium bipyridine, and simple bipyridine molecules), kinetics and mechanism of monolayer formation, quantitative estimate of coverage etc. For example, figure 1 shows a comparison of the voltammograms of bare (curve A) and SAM modified (pentane dithiol) gold surfaces in 0.1 M aqueous KCl (curve B). Decrease in the double layer capacitance (at least one order of magnitude) confirms SAM formation on the gold surface while the lack of redox behaviour indicates surface passivation. If the SAM forming molecules are redox inactive

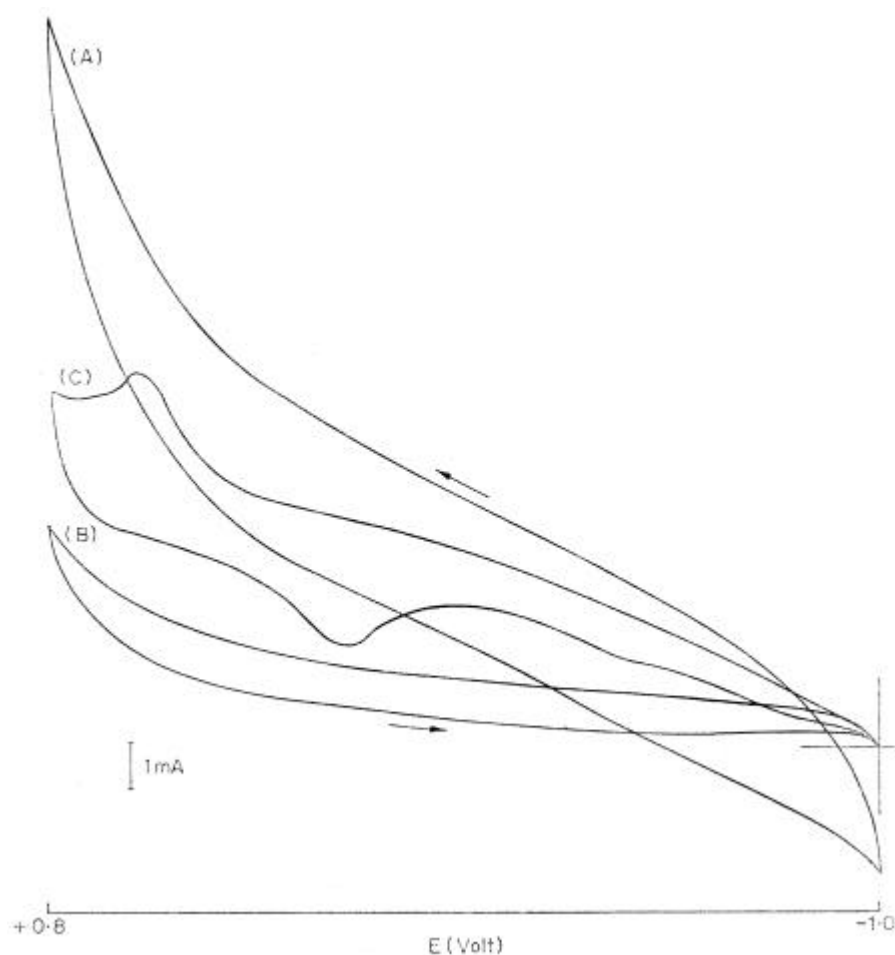


Figure 1. A comparison of cyclic voltammograms of bare (A) and SAM modified (B) (pentane dithiol) gold surfaces in 0.1 M aqueous KCl. Decrease in double layer capacitance from CV confirm the SAM formation on gold surface. (C) Redox couple arising after formation of ZrO_2 crystal on amino thiophenol surface on gold.

(e.g. simple thiols) the use of external redox probes like ferro/ferri cyanide or ferrocene is necessary to get pinhole distribution and other mechanistic details. For redox active SAM-forming molecules (like aminothiophenol, figure 1, curve C) voltammetry can give additional information about the kinetics and mechanism of monolayer formation and mode of surface confinement by careful analysis of the redox peaks. Similarly, impedance measurements can provide valuable information about the kinetics of monolayer formation, and a rough estimate of the dielectric constant of the film is also possible. Figure 2 shows a comparison of the impedance behaviour of naphthalene disulphide (a), and diphenyl disulphide (b) monolayers using 5-mM potassium ferro/ferri cyanide couple in 5 M aqueous KF solution. The Faradaic impedance plot shows the change in the diffusional behaviour of ferrocyanide ions through defects in the monolayer (microarray electrode) while the inset shows the potential dependence of differential

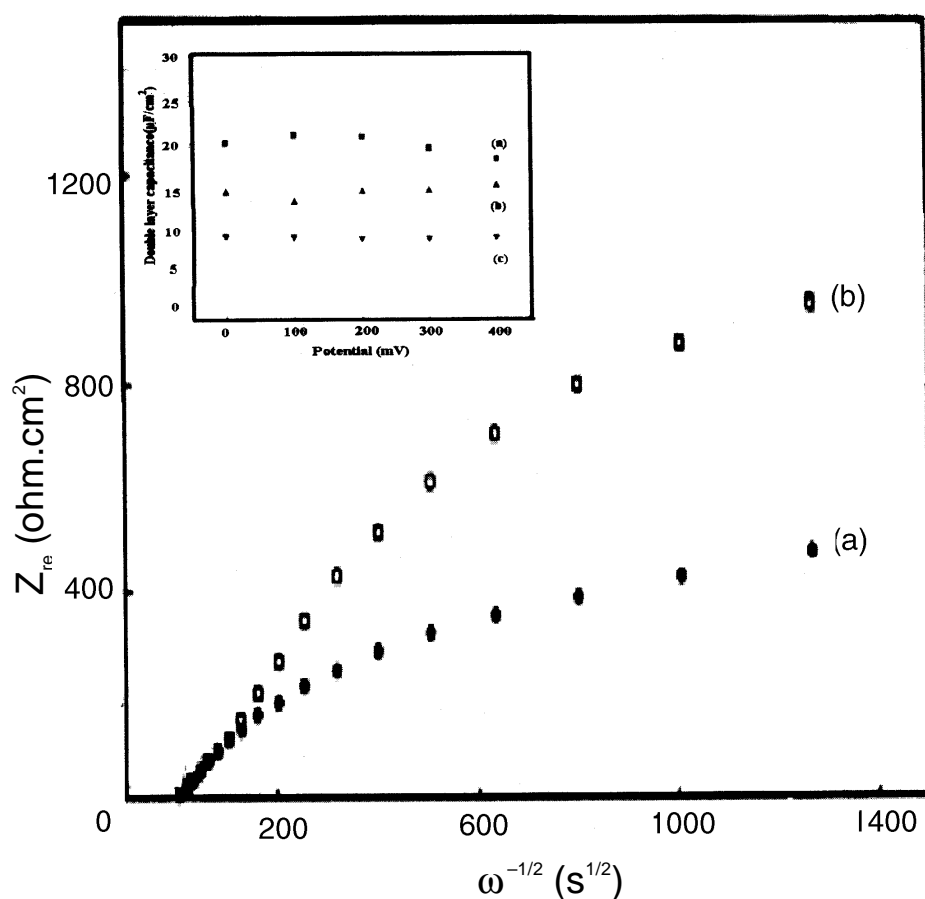


Figure 2. A comparison of the impedance behaviour of NDS monolayer (a) and DDS monolayer (b) using 5-mM potassium ferro/ferricyanide couple in 5 M aqueous KF solution. The Faradaic impedance plot shows features similar to those of a microarray electrode. The inset shows a plot of differential capacitance in a limited range versus applied potential in 0.1 M KF solution ($pH = 7$) for bare gold (a) and gold electrodes modified with NDS (b) and DDS (c).

capacitance in 0.1 M KF solution ($\text{pH}=7$) for bare (a) and gold (b and c) electrodes modified with NDS and DDS SAMs respectively.

The monolayers can be characterised by a variety of other methods including physical measurements like contact angle and wettability, spectroscopic techniques such as ellipsometry²³, X-ray photoelectron spectroscopy (XPS)²⁴, infrared spectroscopy (IR)²⁵, quartz crystal microbalance (QCM)¹⁸, surface enhanced Raman spectroscopy (SERS)²¹, scanning tunnelling spectroscopy (STM)²⁶, atomic force microscopy (AFM)²², fluorescence spectroscopy, surface plasmon resonance (SPR) etc., which provide valuable information about the structure and dynamics of SAMs. Due to their biological importance, several biomolecules such as enzymes or whole cells can be immobilised on SAM surfaces and their lipid-like microenvironment can be characterised specially for electrochemical sensing or biomolecular electronics^{27,28}. Several elegant discussions of the advantages and limitations of these methods are available¹⁻³.

Although SAM formation provides a simple strategy to form ultrathin organic films, several limitations, such as availability of substrate and organic molecules for monolayer formation, restrict their applications. Only some selected substrate surfaces like Au, Ag, Cu, GaAs, Si, ITO, carbon, Pt etc. are useful and there are also similar limitations about the choice of the anchoring group. In addition, limited solubility of some of the interesting organic molecule prevents SAM formation and certain bulky molecules cause large pinholes and other defects in monolayers. Limited thermal stability and oxidative stability are also responsible for curtailing their large scale use.

3. Monolayer protected clusters (MPCs)

Metallic or semiconducting nanoclusters have drawn much attention in the last decade due to their many applications in various areas of biology, physics, chemistry, colloidal science and material science due to the control of properties using well-defined size and shape²⁹⁻³¹. For example, Pd particles in the size range of 2–15 nm show size-dependent electronic specific heat as well as electronic susceptibility behaviour at very low temperatures³⁰. Similarly, impedance measurements on 1.4 nm Au₅₅ clusters, protected by a shell of PPh₃ ligand molecules show that particles of this particular size have mobile electrons which can be used for tunnelling processes between neighbouring clusters³². Effect of size on the properties of Pd and Au nanocrystals have been studied recently to elucidate the Coulomb staircase phenomenon³³.

The SAM method provides a unique opportunity to stabilise nanoparticles by isolating them from their environment, where particle growth and agglomeration by different mechanisms like Ostwald ripening, air oxidation etc. can be prevented. In contrast to the two-dimensional SAM on different structures as discussed above, these clusters can be viewed as three-dimensional SAM, formed on the curved surface of the metal or semiconductor nanoparticles, which gives them extra stability. Of particular interest is the assembly of these monolayer-protected nanoclusters of the same size, self-organised in crystalline arrays of one, two or three dimensions to form superlattice structures³⁴.

3.1 Preparation

One of the important general methods for preparing metallic nanoclusters is by the Brust synthesis, where the monolayers are organised *in situ*³⁵. In brief, the metal (Au, Ag, Cu, Pt etc.) salt in aqueous medium is reduced by NaBH₄, N₂H₄ etc., in the aqueous–non-

aqueous interface, in the presence of surface-passivating agent in non-aqueous medium. Vigorous stirring causes instantaneous transfer of the clusters to the organic phase through SAM formation with long chain organic thiols, amines, acids etc. present in the organic phase. Systematic variation of parameters like the nature and concentration of reducing agent, ratio of metal salt to capping agent, temperature, pH, and ionic strength can be used to control the size and shape.

Several groups have prepared various types of clusters of Au, Ag, Cu, Pd, Pt etc. by using Brust's method^{34,36}. We have recently prepared Au, Ag and Cu clusters with different capping agents like dodacane thiol (DDT), tridecyl amine, lauric acid etc. and the protective action of DDT was found to be superior. One example of such a nanocluster as revealed by the HRTEM image (figure 3) of a DDT-capped Cu cluster (15 nm) illustrates the faceting present.

3.2 Characterisation

Formation of these metal nanoclusters can be easily confirmed by the characteristic surface plasmon band, whereas similar semiconductor nanoparticles reveal characteristic excitonic bands in the UV-Vis absorption spectra. The electron transfer properties of these nanoclusters can be demonstrated by the redox features using cyclic voltammetry with standard redox markers like ferrocyanide/ferricyanide couple. This may not be needed for most of the metallic nanoclusters, as they are redox active. For example, silver, gold and copper clusters either in soluble form or as insoluble films, show reversible electrochemical behaviour on suitable electrolytes. HRTEM along with selected area electron diffraction is very important as most of the clusters show different structures with size in sharp contrast to their bulk analogues. Low-angle XRD and scanning probe microscopes (AFM and STM) are important to determine superlattice formation while these combined with other tools like XPS, IR, nuclear magnetic

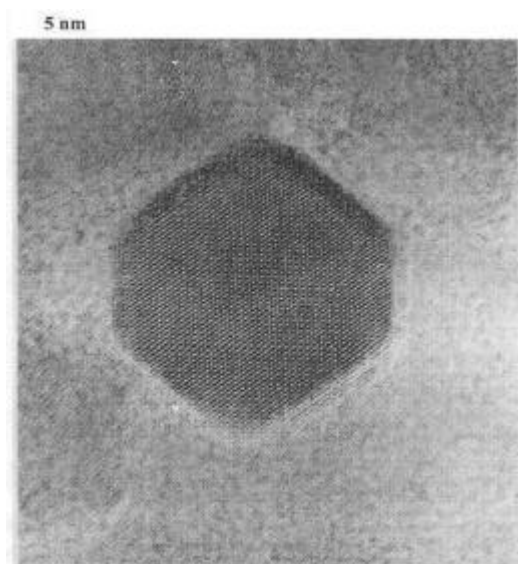


Figure 3. HRTEM image of DDT capped 15 nm Cu cluster.

resonance (NMR), fluorescence spectroscopy (FS) etc. provide structure, dynamics and molecular level information.

3.3 Applications

It is difficult to imagine an area in materials science and engineering, where these nanoclusters cannot have tremendous impact. For example, since nanoparticles of metals like Au and Ag have the unique ability to adsorb onto some proteins and antibiotics, suitable functionalisation on the nanoparticle surface with bioactive molecules, oligonucleotides, peptides, DNA etc., such as fluorophore attached nanoparticles, would help to label them. Consequently, these systems can be used for developing bioelectronics devices³¹. Electroactive or photoactive groups on nanoparticle surface can provide three-dimensional arrangements around the nanoparticles, which can have potential use in fluorescence patterning. Some of the nanoclusters, either alone or as composites (polymeric or semiconducting support), show very interesting chemical sensing applications. Similarly, the addition of an organic redox active centre bridged between two metal nanoclusters shows resonant tunnelling behaviour at room temperature as illustrated by 3 nm Au clusters interlined with an organic redox molecule like the bipyridinium moiety³⁷.

Nanocluster arrays organised by external driving forces such as temperature, electric field or magnetic field can be used in applications, where their collective properties can be utilised for electronic, optical or magnetic storage devices. For example, since charging of the nanoclusters (capacitance of a few attofarads, i.e. 10^{-18} F) occurs in increments of single electrons, giving rise to a series of equally spaced steps in the I - V spectrum, single-electron circuits can be designed for applications like transistors, molecular switches, resonant tunnelling diodes etc.³³. For a three-dimensional aggregation, if interparticle spacing is large compared to the cluster size, then the system is expected to behave like a Mott insulator with a Coulomb gap described by the charging energies of individual nanoparticle sites. On the other hand, spacing smaller than individual size can cause strong quantum mechanical exchange coupling leading to the disappearance of the Coulomb gap in the form of insulator to metallic transitions (IMT). Our recent temperature-dependent electrical measurements of dodecanethiol capped Cu, Ag, and Au nanoclusters show such IMT at low temperatures³⁸ and these studies are helpful in designing nanoelectronic devices.

4. SAM mediated solid state synthesis

The recent past has seen an increasing interest in the utilisation of functionalised interfaces for growing ceramic thin films at temperature below 100°C³⁹. Dense and highly adherent polycrystalline films of oxides, hydroxides and sulphides have been prepared on plastic, glass and other substrates, from aqueous as well as non-aqueous solutions using ω -functionalised SAMs as organic templates for controlled nucleation and growth³⁹. Due to the structural as well as functional similarities of SAM to protein surfaces, this type of preparation strategy is sometimes known as biomimetic synthesis as the monolayers play an important role by providing the suitable functionalities necessary to initiate the growth of the inorganic layers. For example, several studies have recently shown that by manipulation of surface energy through monolayer formation, nanophase

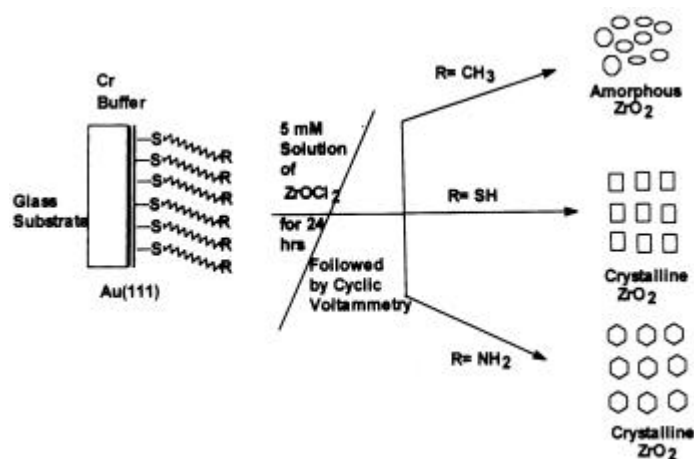
morphology, crystal growth habit, orientation and even chirality can be controlled in both aqueous and non-aqueous media.

4.1 Zirconia synthesis on SAM surface

As a typical example, we describe the effective use of SAM of 1,4-benzenedimethenethiol (BDMT) to link Zr^{4+} from an aqueous solution of appropriate zirconium salt to subsequently form microcrystalline, monoclinic zirconia at room temperature⁴⁰. As illustrated in scheme 1, first a quasi two-dimensional SAM surface is formed with different terminal functional groups as a general synthetic strategy before attaching Zr species from aqueous $ZrOCl_2$ solution. Potential cycling of this Zr attached samples as working electrodes in 1M aqueous KCl solution between -1.1 to 0.7 V vs saturated calomel electrode (SCE) gives microcrystalline zirconia. When the SAM surface is terminated with CH_3 (hydrophobic surface), amorphous ZrO_2 is formed while SH and NH_2 functional groups cause crystalline ZrO_2 albeit different morphological features. Figure 4 represents typical micrographs of such samples of zirconia formed on bare gold (a), DDT SAM surface (b), 1,5-pentane dithiol SAM surface (c) and amino-thiophenol SAM surface (d). Differences in nucleation and growth conditions are responsible for this remarkable variation as illustrated by the mechanistic investigations using current-time transients⁴⁰.

4.2 Other examples

Several other biomimetic synthesis of oxides, sulphides and other biocomposites have been reported based on such organic mono/multilayer as templates. For example, self-assembly of monolayers of thiols on gold (111) surfaces acts as a template for the crystallisation of $CaCO_3$ and $SrCO_3$ from the solution and different phases of $CaCO_3$ (calcite, vaterite and aragonite) can be controlled by pH , temperature, and the nature of the organic template⁴¹. Since monolayer protected clusters can provide initial nucleation sites, they can also be used for controlling crystallisation process⁴².



Scheme 1. General synthetic strategy for formation of microcrystalline ZrO_2 on SAM covered surfaces.

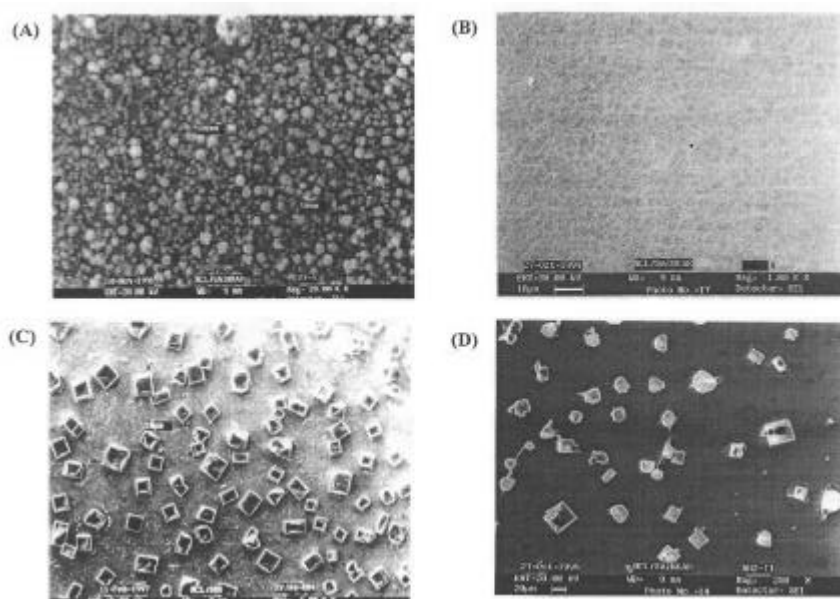
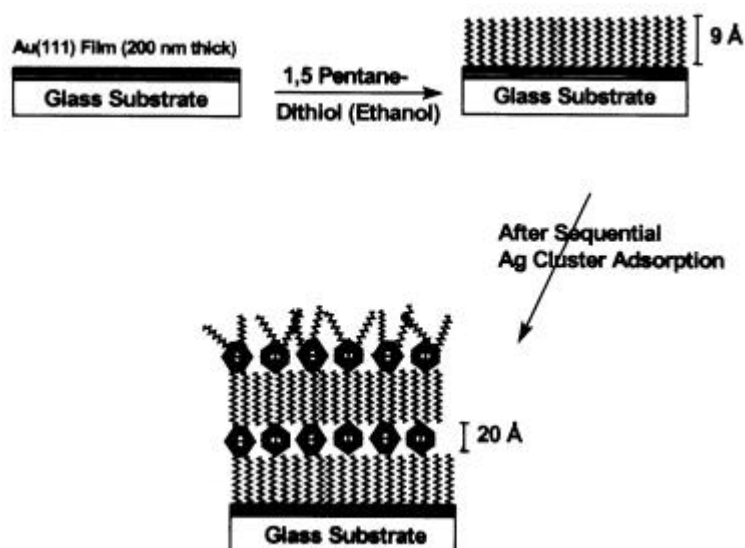


Figure 4. Micrographs of microcrystalline zirconia on (a) a bare gold substrate cycled for longer time, (b) a DDT SAM surface, (c) a 1,5-pentane dithiol SAM surface, and (d) a amino-thiophenol SAM (amine terminated) surface.



Scheme 2. Sequential multilayer growth of silver quantum dots on PDT SAM on gold surface.

5. Organisation of monolayer protected clusters on SAM surfaces

Another important application of self-assembled monolayers in materials chemistry is its utilisation for cluster organisation⁴³. Since the hydrophobic or hydrophilic nature of the

SAM can be easily tuned for organising metal or semiconductor nanoparticles, this type of organisation has several potential applications as mentioned earlier. For example, dithiol SAM on gold substrate can be suitable for organising metallic or semiconductor nanoparticles to form covalently linked two-dimensional superlattice^{44,45}. Heterometallic or multilayered superlattices can also be designed by sequential SAM formation (scheme 2) on the first metal or semiconductor monolayer as illustrated in a recent study of silver quantum dots^{46,47} using cyclic voltammetry (CV), photoluminescence (PL) and AFM measurements. Figure 5 represents the optical absorbance spectra of such silver clusters in aqueous solution: as prepared (a), and at two different time intervals of 150 min (b) and 270 min (c) respectively. The surface plasmon band change shows clear agglomeration with time, while the inset shows the complicated photoluminescent behaviour of such a superlattice.

Similar to the above case of covalent organisation using dithiol interconnects, electrostatic and hydrophobic organisation are also possible on suitable SAM surfaces. Amino or carboxyl terminated SAM surface at appropriate *pH* can be used for organising charged nanoparticles by the electrostatic interactions⁴⁸. Hydrophobic interactions

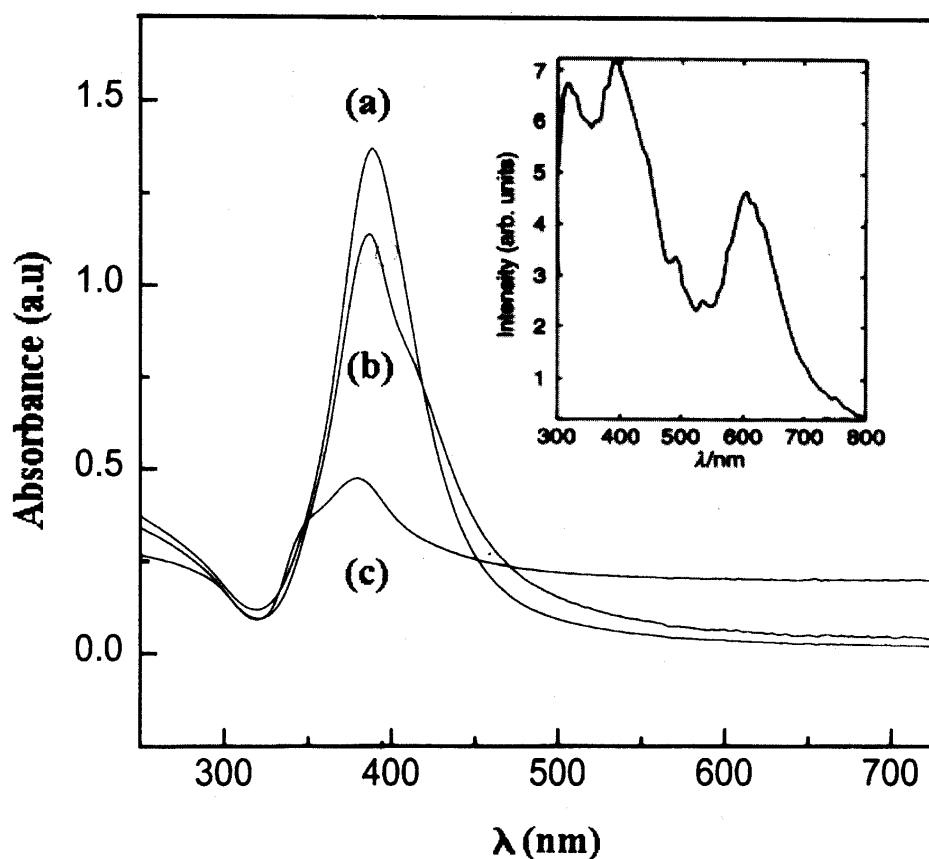


Figure 5. Optical absorbance spectra of silver clusters in aqueous solution before attachment to the SAM surface: (a) as prepared, (b) after 150 min, (c) after 270 min. Inset of the figure 5 shows the PL of the superlattice structure.

between the methyl terminated clusters and the SAM surface can be used to get more flexible and weak organisation⁴⁹. Recently we have been able to organise DDT capped gold clusters on a hydrophobic SAM surface, where nonlinearity in the I - V behaviour helped to correlate the electronic behaviour of nanoclusters before and after such an organisation⁵⁰.

6. Conclusions

The applications of self-assembled monolayers in materials chemistry are very diverse, ranging from the preparation of chiral surfaces for protein separation and devices for nanoelectronics to strategies for biomimetic material synthesis. Artificially designed SAM surfaces of metals and semiconductors using different molecules like the conjugated double-bond system, donor-acceptor complexes etc., are highly useful for performing selected catalytic reactions, molecular recognition and also for nanoelectronic applications. SAM linked heterostructures with nanoclusters have special technological importance due to their collective interactions as the cluster-cluster spacing can be tuned for the desired behaviour. Similarly, the biomimetic environment of SAM surface renders noble metal surfaces suitable substrates for the biomolecule immobilisation for biosensor and related bioelectronics applications.

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