

Coordination compounds on metallic surfaces

Rakesh Kumar and Sangeeta Obrai

Department of Chemistry, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar(Pb.) INDIA

ABSTRACT

Nanotechnology and Nanoscience has started a new era for Coordination Chemistry. It has attracted the attention of researchers to build coordination compounds on a metallic surface like flat surface, electrodes and nanoparticles. Due to this advancement it is possible to prepare nanoscale devices with novel properties. Bottom up approach is used to form the nanoscale functional architecture on a metal surface from the molecular components. Recent advances in this area also addresses the coordination multilayered structure on metal complexes. They are helpful due to their potential application in photo and electrochemical devices. Self assembled monolayers units proceed with the help of metal co-ordination and as a result formation of multilayered structures.

Key Words: Coordination compounds, nanoscience, metallic surface, self assembly, layer by layer.

INTRODUCTION

Coordination chemistry in supermolecular chemistry give rise to fast and spontaneous in corporation to nanosystems [1]. Preparation of coordination compounds on solid surfaces has made possible the development of nanoscale devices with novel properties. In addition to metal complexes the construction of coordination compounds is also possible on metal oxides, nanotubes and graphite. The formation of coordination compounds is possible on metal surfaces is possible by using two main approaches: first of all there is formation of complex and then self assemble it on the metal surface. The second one is to build the complex by using LBL procedure starting from the self assembly of a suitable ligand. Selection of suitable ligand is very important for the attachment of coordination compound to the metal surface [2]. Particularly the chemistry of surface modification by SAMs and LBL growth of multilayers is highly promising to construct two dimensional and three dimensional chemical systems on the surfaces [3, 4].

SAMs are extremely ordered molecular assemblies formed spontaneously by chemisorptions and self organization of long chain molecules on the surface of appropriate substrates. This is an interesting process for its biological relevance because it provides a novel approach to complex structure having nanoscale dimensions. These types of structures are difficult to prepare by traditional methods [5]. Alkanthiols self assembly onto gold is the most studied example of

SAMs which determine the strong gold sulphur and chain- chain interactions. SAMs have been applied in the development of sensors, [6,7] interfaces,[8] and microfabrication [9-13].

1. Self assembled Mono and multilayered on metal surfaces

One of the most common and simplest method to form the self assembly monolayers (SAM) is consist of to insert an extremely clean unoxidized gold sheet into an ethanol solution of the corresponding alkanethiols. Other type of volatile organic solvents can also be used. The concentration of thiol varies between 1mM and 1 μ M. In this process molecules are self assembled within first few seconds or minutes but complete formation of SAM occurs or take place in 12-18 hr of interaction at room temperature. Various researchers Ulamnn [14], Finkela [15], Whitesides and Coworkers [16] have discussed the factors which affect the SAMs formation in their earlier studies. SAMs have been built on silver, copper, nickel, Palladium and platinum [17]. But silver, copper and nickel are less insert and can easily oxidize, due to extremely oxidizing nature of Cu it is difficult to obtain the organised and compact SAM on this metal. A stable SAM on platinum surface can be obtained by using isocyanide [18]. In addition to a thiol group self assembled monolayer on the gold surface, other organic groups such as carboxylate, phosphonate and isocynide [19] are also recognized to act as suraface immobilized groups. In these organic anchoring groups differential reactivity towards Au, Pt and metal oxides which is often called orthogonal self assembly has been reported, thiol and disulphide groups are preferentially bound to gold substrate, [20] isocynide and pyridine groups are bound to the platinum surface and phosphonate and silanol group to indium tin oxide and metal oxide surface [21].

SAM of thiols and other sulphur containing molecules such as (Xanthates, dithiocarbamates, dithiocarboxylates) present a terminal functional group which constitute or permit the construction of a second monolayer through the formation of covalent bond. The most known reaction used for the formation of second monolayer corresponds to the formation of an amide group by the condensation between carboxylate and amine groups. The formation of second monolayer is also possible through electrostatically or by means of non-covlent interactions (vander waals forces, hydrogen bonding etc. or metal ligand bonding) [16]. The self assembly of mono and multilayers on metal can be carried out on flat surfaces, electrodes, nanoparticles and chemical or pores where as the metal electrodes can be present in the form of flat bead, disk like etc.

2. Self assembly of molecules on a flat surfaces and electrodes

2.1 Transition metal compounds

Construction of a first row transition metal compounds on a flat surface by using 11-mercaptoundecanoic and 16-mercaptoundecanoic acid as ligand and Cu(II) acting as coordinating linker. These ligand were used indistinctly to form base monolayer with the carboxylic moiety pointing outwards from the gold surface which served to Cu(II). A second monolayer was attached through coordination of the mercapto group to Cu(II) and upto six layers of mercaptocarboxylate were self assembled in this way [22]. Two approaches are generally remarked to build the coordination compounds on metal surfaces. Such as 4-piperidinethanethiol was synthesized and if assembled on a Au(111)surface. The NH group of piperidine moiety was then transformed into a dithiocarbamate group through condensation of CS₂, in this way an amphiphilic ligand with thiols and dithiocarbamate terminal anionic groups was formed. Amphiphilic ligand was able to make a flip and self assemble through the dithiocarmate group but less stability than the Au-thiollate interaction. Cu(II) was coordinated to free dithiocarbamate groups and its coordination sphere was completed with the addition of

morpholydithio carbamate anion. So, in this way bis(dithiocarbamato)Cu(II) complex was self assembled on a gold surface [23].

2.2 Bis (Phosphonates) and M (IV) of group four

A mercapto group from the base monolayers SAM on the gold surface which leaves the phosphonate terminal group to coordinate the M (IV) metal ions. 11-hydroxyundecanethiol was also reported [24]. There was a construction of coordination compounds on a solid surface in which Zr (IV) forming a base monolayer with decanphosphonate derivatives on a silicon wafer [25] was reported first time in this field. M (IV) links with two successive bis(alkanephosphonate) and also coordinates with the neighbouring chain. It gives rise to robust multilayer system. Here the M (IV) play the role of coordinating linker and it also reinforces the stability of the multilayer system term and resulting complex is neutral. This process was carried out by layer by layer (LBL) procedure.

2.3 Ruthenium Coordination compounds

Intermolecular interaction among the components of each monolayer is necessary to obtain a stable and compact system. According to coordination point of view, bulk terminal groups with donar atoms are practically indispensable to build a coordination compound on a metal surface. By forming mixed base monolayer it may be possible to overcome this problem. The formation of mixed base monolayer using thiophenol and 4'(4-mercaptophenyl)-2,2': 6',2'' -terpyridine in a 1:1 molar ratio. The terpyridine (tpy) moiety pointing out from the moiety pointing out from the modified gold surface served to coordinate Ru(tpy)^{2+} to the self assembled mixed base monolayers [26]. Ruthenium coordination compounds have been mainly built on electrodes but the preparation of compound on the flat Au surface was also reported earlier. A mixed multilayer system based on two ruthenium complexes $[\text{Ru}(\text{NH}_3)\text{Cl}]^{2+}$ and $[\text{Ru}(\text{CN})_6]^{4-}$ was prepared on gold surface. Both complex are linked together through cyno bridges, $[(\text{CN})_5\text{Ru-CN-Ru}(\text{NH}_3)_5]$. This mixed valance dimeric anionic complex was electrostatically immobilized on a gold surface, previously modified with a disulphide derivative monolayer containing quaternary ammonium terminal groups [27].

3. Multilayered nanomaterial based on metal Coordination

Bottom up approach for multilayer formation using LBL procedure provides the integration of molecular units into solid surfaces with a controlled manner and having nanometer sizes. Electrostatic assembly based on sequential adsorption of polyanions and polycations, is a simple but also powerful approach which relies on electrostatic interaction between oppositely charged layers [19,28,29]. Hydrogen bonding interaction, [30,31] covalent assembly [32,33] and host guest interaction [34,35] have also been evolved for the formation of multilayer films. Alkylsilanol, thiol and disulphide are used as anchored group to a solid surface such as quartz or Au, where as bipyridine, terpyridine or isocyanide are applied for metal coordination groups.

Multilayer formation between phosphonate and metal ion and such as Zr^{4+} , Hf^{4+} , Zn^{2+} was originally developed by Mallouk and Coworkers [36,37] on a variety of surface via sequential adsorption of metal ions and bis(phosphonic acids) from aqueous solution [38]. SAM of porphyrin, porphyrin-fullerene diads or ferrocene triads on Gold and ITO electrodes [39,40,41] which leads to current photocurrent generation with high efficiency. Inorganic LBL multilayer materials based on metal coordination are attractive materials for application in many fields such as optics, biotechnology, photo and electrochemistry, nonlinear optical materials, electroluminescent devices, enzyme sensors, solar energy storage devices and molecular rectifiers [3,42,43]

4. Metal electrodes modified with coordination compounds

Modification of metal such as Au, Pt, Ag and Cu electrodes can be carried out by same approach by self assembly of metal complex as a whole on the metal electrode and LBL procedure. Experimental condition which are important for the preparation of SAM on metal electrodes (electrode pretreatment, immobilization techniques, surface coverage, surfactants, electrolytes, solvents and temperature [44-47]). Rate and mechanisms of electron transfer between the coordinated metal ions and the metal surface have to be considered because they can affect the sensibility of the modified electrode [48,49,15]. Electron impedance spectroscopy is used to characterize the modified metal electrodes with coordination compounds [50,51] and also to determine the SAM stability, surface coverage, defects formation in the structure, stability of SAM bonding, orientation of terminal groups. It is also very convenient to characterize the modifying surface with a Quartz crystal microbalance (QCM) [47]. Metal electrodes modified with coordination compounds have been found applications as sensors and as supports for building biosensors such as Cu(II) complex built on Gold electrode was used as a NO sensors. Ribose bis(thiosemicabazoneato) Copper (II) built by LBL method on a gold electrode was able to detect NO concentration down to 6 μM [52]. Electrodes modified with SAM containing ferrocenyl moieties and photoactive compounds have received special attention. Gold, platinum and Indium tin oxide films modified with 4-(4-mercaptobutyl)4'-ferrocenylazobenzene [53,54] was also reported earlier. SAM of ferrocenylundecanthiol on Au electrodes was used to catalyze the chemiluminescence of luminol. This system was used for detection of glucose in the presence of glucose oxidase [55].

5. Ruthenium and Osmium coordination compounds

Osmium and ruthenium are the only element from the second and third row transition metals which are used to form the coordination compound modifying metal electrodes. Bypyridine, tripyridine and ammonia are the ligands which are mostly used to form the immobilized ruthenium and osmium complex. Electron transfer kinetics of modified electrodes with Ru and Os have been studied earlier by Finklea and Abrunia groups and many authors [48,15,46,56-63]. It was found that electron transfer was totally different in both the cases. The electrolyte used may affect the electrochemical behaviour of the metal electrodes modified with Ru and Os complexes.

The importance of electrodes modified with redox active metalloporphyrins is described in the various research articles. The synthesis of metalloporphyrin disulphide derivatives and self assembled them to modify gold electrodes using a method that permitted stable and compact monolayers. The preparation of mixed multilayers of metalloporphyrin has also been reported therefore the mixed monolayers of bis(dinitrozen)-meso-tetramesitylporphyrinato ruthenium (II) were studied on the top of the other with a high order using bidentate pyrazine-terminated ligands. Several metalloporphyrins such as (Hb) and its analogous are known to coordinate Nitric oxide have a biological importance, so due to that reason several researchers have worked on modifying electrodes with metalloporphyrins and metallophthalocyanines in order to develop NO sensors.

CONCLUSION

Self assembly provides a very simple route to organise suitable organic molecules on noble metal and by using long chain organic molecules with various functionalities like -SH,-COOH,-NH₂, silane etc. This surface can be effectively used to build up interesting nano level architectures. Nanomaterials based on metal complexes can be prepared on a variety of surfaces via sequential metal coordination in a rational way. These nanomaterials have potential application in a variety

of functional systems or devices such as artificial photosynthesis and light harvesting. Till date synthesis of metal inorganic framework system on the surface has not been explored and it is a future challenge. Surface nanostructure with porosity or nanospace will be of great advantage in many practical applications such as gas storage, catalysis or molecular recognition of chiral catalysis or sensors. Design of a functional nanostructure on surface will play an important role in the development of future material science.

REFERENCES

- [1] J.M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, (1995).
- [2] Jr.Cao. Roberto, Garcia. Diaz .M. Alicia, Cao. Roberto, Coordination compounds built on metal surface, *Coordination Chemistry reviews* **253**, 1262-1275(2009).
- [3]. T.E. Mallouk, H.N. Kim, P.J. Olliver, S.W. Keller, *Comprehensive Supramolecular Chemistry*, **7**,189 (1996).
- [4]. G. Decher, in: G. Decher, J.B. Schlenoff (Eds), *Polyelectrolyte Multilayers in Overview, Multilayer Thin films, Wilay-VCH*, **1** (2003).
- [5]. L. Isaacs, D. N. Chin, N. Bowden, Y. Xia and G. M. Whitesides, *Perspectives in Supramolecular Chemistry*, 1999, *Wiley & Sons,Chichester*, **4**, 1 (1999).
- [6]. B.-H. Huisman, R. P. H. Kooyman, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, **8**, 561 (1996).
- [7]. K. D. Schierbaum, T. Weiss, E. U. Thoden van Velzen,J. F. J. Engbersen, D. N. Reinhoudt and W. Gopel, *Science*, **265**, 1413 (1994).
- [8]. Y. S. Shon, S. Lee, R. Colorado, Jr., S. S. Perry and T. R. Lee, *J. Am. Chem. Soc.*, **122**, 7556 (2000).
- [9]. D. J. Dı́az, J. E. Hudson, G. D. Storrier, H. D. Abruña, N. Saudararajan and C. K. Ober, *Langmuir*, **2001**, 17, 5932.
- [10]. C. Alain, M. Geissler, H. Schmid, B. Michel and E. Delamarche, *Langmuir*, **18**, 2406(2002).
- [11]. G. P. Lopez, H. A. Biebuyck, C. D. Frisbie and G. M. Whitesides,*Science*, **260**, 647 (1993).
- [12]. S. Xu, S. Miller, P. E. Laibinis and G. Y. Liu, *Langmuir*, **15**, 7244 (1999).
- [13]. G.-Y. Liu, S. Xu and Y. Qian, *Acc. Chem. Res.*, **33**, 457 (2000).
- [14]. A. Ulman, *Chem. Rev.* **96**, 1533 (1996).
- [15]. H.O. Finklea, *Electroanal. Chem.* **19**, 109 (1996).
- [16]. J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M.Whitesides, *Chem. Rev.* **105**, 1103 (2005).
- [17]. G.M.Whitesides, J.A.Williams, C.B. Gorman, *J. Phys. Chem. C* **111**, 12804 (2007).
- [18]. J.J. Hickman, P.E. Laibinis, D.I. Auerbach, C. Zou, T.J. Gardner, G.M.Whitesides, M.S.Wrighton, *Langmuir*, **8**, 357 (1992).
- [19]. J.J. Hickman, C. Zau, D. Ofer, P.D. Harvey, M.S. Wrighton, P.E. Laibinis, C.D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* **111**, 4478 (1989).
- [20]. A. Hatzor, T. Maov, H.Cohen, S. Matlis, J. Libman, A. Vasevich, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* **120**, 13469 (1998).
- [21]. G. Cao, H.-G. Hong, T. E. Mallouk, *Acc. Chem.Res.* **25**,420 (1992).
- [22]. S.D. Evans, A. Ulman, K.E. Goppert-Berarducci, L.J. Gerenser, *J. Am. Chem. Soc.* **113**, 5866 (1991).
- [23]. R. Cao Jr., A. Dı́az, R. Cao, A. Otero, R. Cea, M.C. Rodrı́guez-Arguēlles, C. Serra, *J. Am. Chem. Soc.* **129**, 6927(2007).
- [24]. T.M. Putvisnski, M.L. Schilling, H.E. Katz, C.E.D. Chidsey, A.M. Mujsce, A.B. Emerson, *Langmuir*, **6**, 1567 (1990).

- [25]. H. Lee, L.J. Kepley, H.-G. Hong, T.E. Mallouk, *J. Am. Chem. Soc.* **110**, 618 (1988).
- [26]. N. Tuccitto, V. Torrisi, M. Cavazzini, T. Morotti, F. Puntoriero, S. Quici, S. Campagna, A. Licciardello, *Chem Phys Chem.*, **8**, 227 (2007).
- [27]. T. Wei, K. Tamada, S. Yokokawa, E. Ito, K. Yase, M. Hara, *Chem. Lett.* **33**, 164 (2004).
- [28]. S. Steinberg, I. Rubinstein, *Langmuir*, **8**, 1183 (1992).
- [29]. T.T.-T. Li, M.J. Weaver, *J. Am. Chem. Soc.* **106**, 6107 (1984).
- [30]. T. Ngarivhume, A. Díaz, R. Cao, M. Ortiz, I. Sánchez, *Syn. React. Inorg. Met. Org. Nanomet. Chem.* **35**, 795 (2005).
- [31]. L. Müller-Meskamp, S. Karthäuser, R. Waser, M. Homberger, U. Simon, *Langmuir*, **24**, 4577 (2008).
- [32]. A.S. Viana, L.M. Abrantes, G. Jin, S. Floate, R.J. Nichols, M. Kalaji, *Phys. Chem.*, **3**, 3411 (2001).
- [33]. C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Majsce, *J. Am. Chem. Soc.* **112**, 4301 (1990).
- [34]. C.E.D. Chidsey, *Science*, **251**, 919 (1991).
- [35]. L.S. Curtin, S.P. Peck, L.M. Tender, R.W. Murray, *Anal. Chem.* **65**, 386 (1993).
- [36]. J. C. Yang, K. Aoki, H. J. Hong, D. D. Sackett, M. F. Arendt, S.-L. Yau, C.M. Bell, T.E. Mallouk, *J. Am. Chem. Soc.* **115**, 11855 (1993).
- [37]. H.-G. Hong, T.E. Mallouk, *Langmuir*, **7**, 2362 (1991).
- [38]. H.E. Katz, M.L. Schilling, S. Ungashe, T.M. Putvinski, C.E. Chidsey, *ACS Symp. Ser.* **499**, 24 (1992).
- [39]. H. Imahori, M. Arimura, T. Hanada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **123**, 335 (2001).
- [40]. H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **123**, 100 (2001).
- [41]. H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, *J. Phys. Chem. B* **104**, 2099 (2000).
- [42]. I. Doron-Mor, H. Cohen, S.R. Cohen, R. Popovitz-Biro, A. Shanzer, A. Vaskevich, J. Rubinstein, *Langmuir*, **20**, 10727 (2004).
- [43]. D.B. Mitzi, *Chem. Mater.* **13**, 3283 (2001).
- [44]. D. Chen, J. Li, *Surf. Sci. Rep.* **61**, 445 (2006).
- [45]. H.O. Finklea, M.S. Ravenscroft, D.A. Zinder, *Langmuir*, **9**, 223 (1993).
- [46]. M.S. Ravenscroft, H.O. Finklea, *J. Phys. Chem.*, **98**, 3843 (1994).
- [47]. Th. Wink, S.J. van Zuilen, A. Bult, W.P. van Bennekom, *Analyst*, **43R** (1997).
- [48]. R. Brito, R. Tremont, C.R. Cabrera, *J. Electroanal. Chem.* **574**, 15 (2004).
- [49]. J.F. Smalley, H.O. Finklea, C.E.D. Chidsey, M.R. Linford, S.E. Creager, J.P. Ferraris, K. Chalfant, T. Zawodzinski, S.W. Feldberg, M.D. Newton, *J. Am. Chem. Soc.*, **125**, 2004 (2003).
- [50]. Y. Gafni, H. Weizman, J. Libman, A. Shanzer, I. Rubinstein, *Chem. Eur. J.* **2** (1996), 759.
- [51]. Z. Gao, J. Bobacka, A. Ivaska, *Electrochim. Acta*, **38**, 379 (1993).
- [52]. T. Ngarivhume, A. Díaz, R. Cao, M. Ortiz, I. Sánchez, *Syn. React. Inorg. Met. Org. Nanomet. Chem.* **35**, 795 (2005).
- [53]. B.R. Herr, C.A. Mirkin, *J. Am. Chem. Soc.* **116**, 1157 (1994).
- [54]. W.B. Caldwell, K. Chen, B.R. Herr, C.A. Mirkin, J.C. Hulthen, R.P. Van Duyne, *Langmuir* **10**, 4109 (1994).
- [55]. Y. Sato, D. Kato, F. Mizutani, *Chem. Sensors*, **20**, 340 (2004).
- [56]. H.O. Finklea, D.D. Hanshew, *J. Am. Chem. Soc.* **114**, 3173 (1992).
- [57]. H.O. Finklea, M.S. Ravenscroft, D.A. Snider, *Langmuir*, **9**, 223 (1993).
- [58]. J.D. Tirado, D. Acevedo, R.L. Bretz, H.B. Abruña, *Langmuir*, **10**, 1971 (1994).
- [59]. H.O. Finklea, L. Liu, M.S. Ravenscroft, S. Punturi, *J. Phys. Chem.* **100**, 885, (1996).
- [60]. H.O. Finklea, M.S. Ravenscroft, *Isr. J. Chem.* **37**, 179 (1997).

- [61]. D.I. Brevnov, H.O. Finklea, *J. Electrochem. Soc.* **147**, 3461 (2000).
[62]. D.A. Brevnov, H.O. Finklea, H.V. Ryswyk, *J. Electroanal. Chem.* **500**, 100 (2001).
[63]. R.M. Haddox, H.O. Finklea, *J. Phys. Chem. B*, **108**, 1694 (2004).