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Review

Colorimetric sensors for rapid detection of various analytes

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ABSTRACT

Sensor technology for the rapid detection of the analytes with high sensitivity and selectivity has several challenges. Despite the challenges, colorimetric sensors have been widely accepted for its high sensitive and selective response towards various analytes. In this review, colorimetric sensors for the detection of biomolecules like protein, DNA, pathogen and chemical compounds like heavy metal ions, toxic gases and organic compounds have been elaborately discussed. The visible sensing mechanism based on Surface Plasmon Resonance (SPR) using metal nanoparticles like Au, Ag, thin film interference using SiO_2 and colorimetric array-based technique have been highlighted. The optical property of metal nanoparticles enables a visual color change during its interaction with the analytes owing to the dispersion and aggregation of nanoparticles. Recently, colorimetric changes using silica substrate for detection of protein and small molecules by thin film interference as a visible sensing mechanism has been developed without the usage of fluorescent or radioisotopes labels. Multilayer of biomaterials were used as a platform where reflection and interference of scattering light occur due to which color change happens leading to rapid sensing. Colorimetric array-based technique for the detection of organic compounds using chemoresponsive dyes has also been focused wherein the interaction of the analytes with the substrate coated with chemoresponsive dyes gives colorimetric change.

Contents

1. Introduction

Future of sensing is based on the key factors of simplicity, cost-effectiveness and rapid response. Sensors based on colorimetric approach are significant while analyzing its ideal characteristics. Earlier sensors

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are mean to be a bulk and complex one, requiring different functional blocks such as transducer, processing unit, a detection unit etc. leading to a delayed sensor response. Current technology based on colorimetry is all about the miniaturization of size, cost, in-situ and without any additional instruments. A calorimetric sensor is used for instantaneous detection of analyte and shows a color change, which can be detected visually. Nanotechnology plays an important role in current sensor technology. For example, nanoparticles like Au, Ag, Cu are extensively used in visual detection owing to its optical property known as Surface Plasmon Resonance (SPR). SPR is the phenomenon where collective oscillation of free electrons occurs due to resonance with incident light in visible region [1]. Plasmon resonance scattering (PRS) of Au and Ag nanoparticles have been utilized for bio-affinity sensing [2]. Generally, the detection mechanism is based on molecular interaction on the surface of the substrate which is modified or functionalized with certain functional groups or nanoparticles [1,2,3]. The role of nanoparticles in colorimetric sensing is reported and their results have shown that label-free assay is also possible with nanoparticles [4].

There are many challenges involved in developing an effective sensor, an ideal sensor should satisfy certain characteristics like selectivity, sensitivity, robustness, accuracy, precision, minimal error, reproducibility, linearity etc. Selectivity of a sensor is mean to be the characteristics to recognize the analyte of interest from many other interfering compounds/samples. The characteristic of a sensor to detect the analyte even at very low concentration is termed as sensitivity. It is a fact that cost may not tally with sensor characteristics. But the current technology satisfies the above-mentioned challenges. Lab-on-chip (LOC) is one among the prominent platforms on which the sensor technology is implied with high level of success [5]. It involves simple and portable devices made of polydimethylsiloxane (PDMS) being used for analyte detection by flowing liquid samples within a microchannel [5]. Microfluidics has gained wide acceptance in sensor technologies due to its low footprint and lesser user of analyte-containing reagents. Lab-on-chip technology using paper, i.e. lab-on-paper (LOP) became prominence for its low cost, rapid detection and self-sustainability. Sensor platform based on LOP for the detection of different biomolecules has already been reported by Whitesides [6]. LOP is simple, cheap and easily disposable. LOP uses cellulose paper for entrapping the molecules in a targeted site and the detection is based on the colorimetric approach. Microarray using LOP can detect different samples simultaneously.

Basically, colorimetric sensors can be classified according to the type of interaction of molecules, either chemical or biomolecules and are classified as chemical sensors and biosensors respectively. Table 1 shows a list of sensor analytes and their respective probes. In the following sections, detailed studies of different sensor systems were discussed.

Table 1
A list of sensor analytes and their respective probes.

Analyte	Probe	Reference
Chemical sensors		
Volatile organic compound	Dyes	Kenneth S. Suslick et al. [31]
Volatile organic compound	Dyes	Michael C. Janzen et al. [33]
Volatile primary amine	Inkjet printing	Tamaki Soga et al. [36]
Volatile organic compound	Colloidal crystal	Tatsaro Endo et al. [34]
Organic compound	Dye	Chen Zhang et al. [35]
Odour visualization	Dye	Neal A. Rakow et al. [32]
Trinitrotoluene(TNT)	Quantum dot	Kui Zhang et al. [64]
Hg^{2+} & Ag^{+}	AuNPs	Cheng-Yan Lin et al. [49]
Thiocyanate	AuNPs	Zhang Z et al. [66]
Cu^{2+}	Ag nanoparticles	Nalin Ratnararthorn et al. [55]
Cu^{2+}	Ag nanoparticles	Yu-rong Ma et al. [53]
Cu^{2+}	Ag coated Au nanoparticles	Tingting Lou et al. [54]
Cu^{2+}	Au nanoparticles	Ruili Liu et al. [52]
Cu^{2+}	Au nanoparticles	Xiaorong He et al. [51]
HCL gas	Nanofibrous membrane(polyimide)	Yuan–Yuan Lv et al. [60]
H_2S gas	Dye	Avijit sen et al. [61]
H_2O_2		Miao Xu t al [63]
Humidity	Copper nanoparticles	A. Luechinger et al. [58]
n-butyl phenol	Peptide coated SiO_2	T. Kinoshita et al. [8]
NH_3	Polymeric material	J. Courbat et al. [62]
Vapour sensing	Metalloporphyrin	Neal A. Rakow [32]
Biosensors		
Natural amino acid	Dyes	Huo Dan-Qun et al. [16]
Protein conformational change	AuNPs	Soon woo Chah et al. [10]
Avidin	Sio_2 thin film	R. Tominaga et al. [23]
Carcinoembryonic antigen	$ZnFe_2O_4$-MWCNT	Weiyan Liu et al. [24]
Antibody	Ag NP	Jian Ling et al. [25]
Heparin	TFP-Graphene oxide	Liping Cai et al. [43]
Heparin	Graphene oxide-Gold nanorods	Xiuli Fu et al. [40]
Protein		P-Phenyleneethynlylene
Oscar R. Miranda et al. [9]		
Bacteria(Sphingobium yanokuyai)	RNA probe	Sivakumar et al. [27]
Histidine	Ag Nps	Haibing Lai et al. [12]
Dopamine	AuNPs	Yuanfu Zhang et al. [41]
Dopamine	Au-Ag NPs	Sivakumar et al. [42]
Bacteria	Polymer	Liron Silbert et al. [26]
DNAse I	AuNps	Weian zhao et al. [28]
Enzymatic reaction	AgNPs	Hui Wei et al. [11]
Nucleic acids	Silicon substrate	Robert Jenison et al. [29]
Biomolecules	Aptamer & Au NPs	Wei Wang et al. [13]
Antibiotic protein(kanamycin)	Aptamer&AuNPs	Kyung Mi Song et al. [14]
DNA	Aptamer & AuNps	Min sik Eom et al. [30]
Protein	Aptamer &AuNps	Jwa-Min Nam et al. [15]
L-cystein& L-Homocystein	Flourescein	Oleksander et al. [17]

2. Biosensor

Nanotechnology has its own wide range of application in the medical diagnostics field, due to its specific property of Surface Plasmon Resonance possessed by metals like Au, Ag, Cu and Pt nanoparticles [1]. For sensitive sensing of biomolecules, SPR property of nanoparticles plays a crucial role. Biosensor utilizes SPR technology for many applications like an early diagnosis of diseases such as cancer, neural disorders like Alzheimer's, Parkinson diseases etc. [3,4]. Biosensor as the term implies that it senses biomolecules such as antigen or antibody, protein, DNA and also deals with interactions, enzyme detection, identification of microorganisms i.e., pathogen and DNA detection. The detection of analyte using colorimetric sensing is possible using surface modified nanoparticles, chemoresponsive dyes etc.

Biosensors focusing on biomimetics i.e., mimicking the nature and Pete Vukusic also studied iridescent color of butterfly wings [7]. Sensors based on biomimetics are fabricated due to the wide range acceptance of colorimetry interference. First of its kind has already been reported by Kinoshita et al. [8] using self-assembled monolayer (SAM) of polypeptides which is explained in detail in the following passages. Biosensors can be classified on the basis of detection phenomena as protein sensor, immuno sensor, pathogen sensor and DNA sensor.

2.1. Protein and amino acid sensors

Proteins are large biomolecules which are made up of amino acids. Sensing of protein molecules includes detection of amino acids, antigen-antibody interaction (immuno sensor) and also enzyme detection since all enzymes are proteins. Various amino acids or protein molecules like L-histidine, cysteine, lysozyme and methylases are detected using colorimetric approach. Few prominent examples of protein and amino acid sensors are explained below.

Vincent et al. [9] have been reported that the rapid and sensitive colorimetry sensing of bacteria using a supramolecular enzyme-nanoparticle assemblies. Protein conformational change is important in

understanding the biomolecular interactions. Protein conformational changes using colorimetric sensor was reported by Richard et al. [10]. The sensor uses Au nanoparticles for visual detection. According to pH variation, folding and unfolding of protein iso 1-cytochrome (cyte) makes a clear change in the color of Au nanoparticle solution, which happens due to Surface Plasmon Resonance. In order to confirm the visible color change, UV–Visible absorption/reflectance spectroscopy was done by the authors. The protein (cyte) which is covalently bound to the gold nanoparticle upon exposure to solutions of low pH unfolds and refolds for solution having high pH value, which can be distinguished easily by the naked eye. The colorimetric sensor array for the detection of enzymatic reaction using gold nanoparticles was reported by Wang et al. [11]. The colorimetric sensor array is sensitive, selective and simple. Here enzymatic reaction such as ATP phosphorylation by calf intestine alkaline phosphatase and peptide phosphorylation by protein kinase was discussed. The enzymatic activity induces color change in gold nanoparticles. It finds applications in the screening of enzymatic inhibitors. The selective colorimetric sensing of L-histidine was developed using silver nanoparticles and Hg^{2+} ions reported by Li and Bian [12]. The optical property of silver nanoparticles enables the colorimetric sensing of analyte molecules. The L-cysteine modified silver nanoparticles, which are initially monodispersed in the solution, showed yellow color. Addition of Hg^{2+} ions helps in the binding of L-cysteine modified silver nanoparticles with amino acid. When different amino acids are added to the solution containing Hg^{2+}, L-cysteine modified silver nanoparticles causes the aggregation of silver nanoparticles, which shows pink color. The exception is L-histidine which shows no color change. A novel way of detecting protein molecules such as lysozyme and small molecule like ATP (Adenosine Tri Phosphate) for cell viability was performed using an aptamer-based PDMS (Polydimethylsiloxane) – Au NPs composite film [13]. The highlighting property of this biosensor is not only the detection of bio molecules, but also the catalytic efficiency of Au NPs for silver reduction. Colorimetric analysis for quantitative measurement has been done by observing the darkness density of silver enhancement.

Polydimethylsiloxane (PDMS)-Au NPs composite film with anti-target aptamer was immobilized which inhibits the reduction of silver. When the targeted aptamer get attached the catalytic property of Au NPs causes the reduction of silver with the addition of silver enhancement solution which gives a quantitative method of determination of analyte molecules as shown in Fig. 1. Here the quantitative analysis of lysozyme and ATP molecules has been done in the range of 1×10^{-2}–1 μg/mL and 1×10^{-4} – $1x10^{3}$μg/mL respectively.

Mechanism of silver enhancement is based on charge effect and spatial effect. The electrostatic repulsion between anti-target aptamer and silver lactate solution inhibits the reduction of silver where the aptamer acts as a barrier. The attachment of target molecules causes the surface charge of the aptamer to get decreased facilitating the reduction of silver. In view of spatial effect, the absence of target causes disordered immobilization of aptamer on PDMS-Au composite film. The presence of target causes the bending of the aptamer so that barrier for silver reduction gets reduced [13].

The colorimetric method of biomolecules detection using DNA and AuNPs is simple and sensitive. The distance dependent optical property and high extinction coefficient of AuNPs enable the colorimetric detection of biomolecules. Detection of antibiotic protein kanamycin using aptamer based AuNPs was reported in [14]. The presence of kanamycin causes hearing loss and toxicity to the kidneys and its detection is essential. The surface of the AuNPs is functionalized with ky2 aptamer. When NaCl is added to the solution containing kanamycin and Au NP functionalized with ky2 aptamer the color of the solution changes from red to purple. The color change occurs because of the aggregation of Au NPs by kanamycin. Further the color change was confirmed by UV–Visible absorption spectrum which shows increase in intensity at 620 nm and the intensity at 520 nm starts decreasing. This method could detect up to 25 nM. Detection of interleukin-2, a cytokine protein using colorimetric AuNPs based bio barcode DNA was reported [15]. Three types of particles namely silica micro particles, iron oxide magnetic nanoparticles and AuNPs are used where the color of the solution turns from red to blue. The detection of protein in attomolar concentration was done using this method. Colorimetric sensors using dyes can detect approximately 20 amino acids, which are present in human body. Visible sensing using chemo responsive dyes for 10 different amino acids have been studied. The platform for the detection is an array of dye having 6×6 sites, which will produce colorimetric response according to the amino acid to be detected, by using 36 dyes. Digital imaging of this dye before and after immersion provides the colorimetric profile, which is specific for analysis of amino acids or so called analyte. Analysis

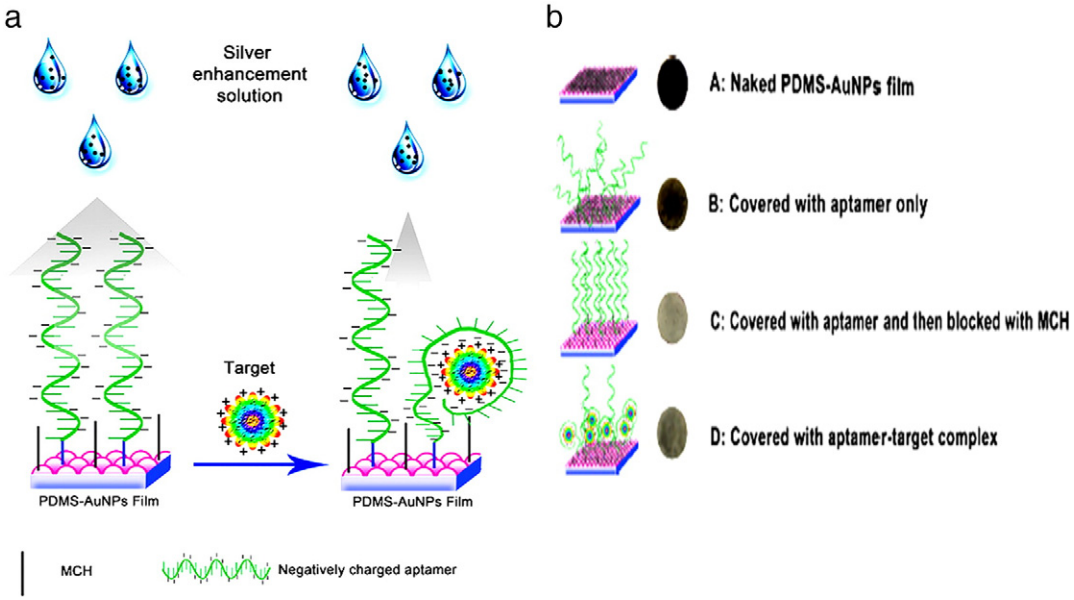

Fig. 1. a) Schematic illustration of charge effect and spatial effect b) Procedure for the fabrication of colorimetric chip (Ref [13], reproduced with the permission from Elsevier).

of the digital data is done by Principle Compound Analysis (PCA) and Linear Discriminant Analysis (LDA), which analyses the data statistically, and chemometricaly. The natural amino acid can be also identified from the obtained data from above analysis [16]. The colorimetric sensor for the simultaneous detection of both L-cysteine and L-homocysteine is also possible as reported previously [17]. The reaction of amino acid with fluorescence in produces thiazolidines, which induces color change for cysteine and homocysteine.

2.2. Immuno sensors

The term immuno is defined as the interaction of antibody with an antigen. Immune system of biological objects protects from pathogens and harmful diseases. Early detection of cancerous cells is possible by colorimetric immunosensors [18]. Specific antibodies functionalized to metal nanoparticles are used for binding to biomarkers like antigens for cancer detection. After binding color change can be noted in the sensor. Similarly, different analytes like bacteria, viral particles, disease markers and even specific peptide fragment can be detected colorimetrically using nanoparticle-based immunosensors [19–22].

Colorimetric detection of biomolecules could also be carried out based on thin film interference. Kinoshita et al. reported [8] that polypeptides are immobilized on the silica surface using Langmuir Blodgett Method where multilayer deposition could be achieved by this method. Interestingly, it is found that by depositing different layers of biomolecules on the silica substrate shows different colors. As thin film interference depends on the thickness of the layer and refractive index, color change can be observed [8] for different thickness as shown in Fig. 2.

Utilizing the principle of reflection and interference of scattered light is a unique technique of visual detection which is useful for molecular recognition. Biomolecules especially, proteins and small molecules can be easily detected through this method using silica substrate and the detection mechanism is thin film interference, where conventional labeling of biomolecules is not required. Multilayer made of avidin and dethiobiotin labeled BSA on silica substrate causes thin film interference [23]. Multilayers are helpful in studying the color change in thin film interference of scattering light. Color change of the thin film is proportional to the thickness and refractive index of the constructed multilayer.

The amplification of color change for detection of small molecule, i.e. by making protein multilayer that can be disassembled via molecular recognition is described by Kinoshita et al. [23]. It is also called as visible molecular affinity sensor, in which layer-by-layer multilayer of avidin and BSA modified dethiobiotin on a silica thin film disassembles while biotin is added. It is due to the fact that binding constant for biotin and avidin ($1.0 \times 10^{15}\ M^{-1}$) is greater than that of dethiobiotin and avidin ($5 \times 10^{13}\ M^{-1}$) thus layer thickness decreases drastically and color change is given by the interference of visible light as shown in Fig. 3.

The silica thin film is prepared by thermal oxidation method which is annealed at 960-1120 °C as shown in Fig. 4 and is modified with glycidoxyl group. This shows purple color above which multilayers of protein are constructed.

The protein layers include alternate layers of avidin and BSA modified with dethiobiotin (BSA-DSB). The increase in the layers of protein causes a color change to blue. After the construction of 8 layers a red shift occurs. When the biotin molecules are added to the multilayers, biotin avidin interaction causes the dissociation of multilayers. The change in thickness of the protein layer causes a gradual change in color causing blue shift depending on the concentration of the biotin molecule. It can be observed by Reflective VIS spectrum measurements. The spectrum of silica film with different layers was measured and red shift is observed. The possible explanation of this mechanism can be explained by using Bragg's law and Snells law and shown in Fig. 5a-b.

$$\lambda = \frac{4h_1}{m}\sqrt{n_1^2 - \sin^2\alpha} + \frac{4h_2}{m}\sqrt{n_2^2 - \sin^2\alpha} \quad (1)$$

[maximum wavelenght] $m = 2k$

[minimum wavelenght] $m = 2k-1 (k = 1, 2, 3\ldots)$

Reflective VIS spectra of silica thin-films with various numbers of avidin-BSA-DSB layer on their surface is shown in Fig. 6a. The dethiobiotin disassembled during different concentration of biotin added to the silica wafer. Exactly after the addition of 4.1×10^{-3} M biotin for 36 h, the color change occurs from blue to purple. The reflective VIS spectrum shows a shift of 56.5 nm in the Fig. 6b due to the blue shift corresponds to the decrease in thickness of 7 layers.

From the data given above it is conformed, the visual detection of biotin molecule by observing the color change in the silica substrate. This method in future is expected to apply for the detection of hormones, vitamins, agrochemicals etc. An immune sensor for the detection of carcinoembryonic antigen (CEA) has been reported recently [24]. Detection is achieved based on intrinsic peroxidise activity of $ZnFe_2O_4$-Multiwall Carbon Nano Tube ($ZnFe_2O_4$MWNTs). Chitosan and porous gold deposited on filter paper paved the way for entrapping primary antibody (Ab1) which plays the role of immune sensor platform. Secondary antibodies (Ab2) were assembled on the MWNT functional group. Colorimetric sensing occurs in the presence of H_2O_2 oxidizing agent, where immune sensor response was quantified due to oxidization of 3,3′,5,5′-tetramethyl benzindin catalyzed by $ZnFeO_4$-MWNT. Detection of CEA can be quantified not only by naked eye but also by digital

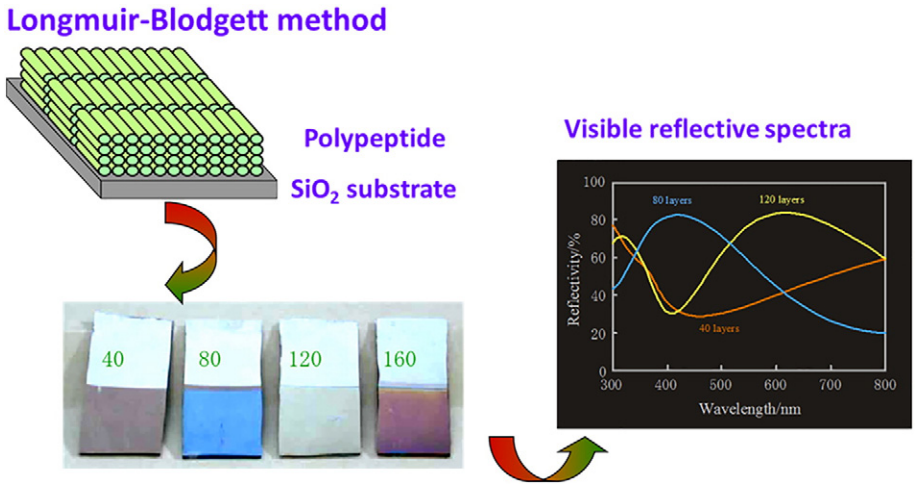

Fig. 2. Different multilayered color chip and its reflective spectra (From Ref [8], reproduced with the permission from Elsevier).

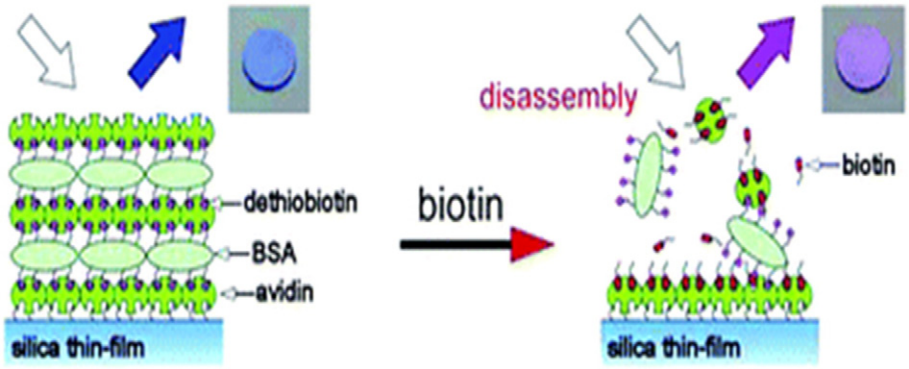

Fig. 3. Schematic illustration of the avidin–BSA–DSB multilayer, which is stabilized via the specific interaction between avidin and dethiobiotin, and disassembling of the layers by biotin addition (From Ref [23], reproduced with the permission from Royal society of chemistry).

scheme for different concentration of CEA. The label free immunoassay for antibody antigen interaction is occurred and detected using silver nanoparticles. The glass substrate immobilized with antigen, antibody is treated with the solution containing silver nanoparticles, and the AgNps are adsorbed on to the glass substrate. The visual detection is obtained by illuminating the glass slide with LED light [25].

2.3. Pathogen sensor

Most of the diseases are caused by pathogens from food contamination, unclean surroundings and insects. Adverse effects of pathogens are contagious diseases. Therefore, it is necessary to detect the pathogens as quickly as possible. Visible sensors can detect pathogens rapidly and shows the colorimetric change to identify which microorganism is detected [26].

The colorimetric sensor for the detection of bacteria has been done using self-assembled monolayer of polypeptides immobilized RNA aptamer. Conventionally, detection methods for the pathogens involve the attachment of fluorescent dyes, radioisotopes and enzymes were traditional and complex. The development of simple silica substrate along with self-assembled monolayer oligonucleotides for the attachment of bacteria was reported in [27]. Pre-colored silica chip is used as the substrate here and it is bio conjugated with poly(*E*-benzyloxycarbony-L-lysine) peptide (PBCL) monolayer using Langmuir Blodgett (LB) method as shown in Fig. 7.

Chip fabrication has done stage by stage, at the first stage the silane terminated polypeptide monolayer has attached to the pre-colored silicon substrate using the upward drawing LB method. Silicon wafer is pre-colored by high temperature (approximately 1060 °C for 3 h) sintering mechanism. Followed by making the PBCL monolayer coated silica surface from non-ionic to cationic by treating with HBr/$CH_3COOH$and benzene in which the benzyloxycarbonyl group has removed and Poly L-Lysine (PLL) formed on the surface. Silicon wafer is chosen as a perfect candidate for biosensor because of its biocompatibility and ease of availability. RNA aptamer is attached to the PLL monolayer using chemical bonds where the PLL chip is dipped on RNA aptamer solution. Oligonucleotides like RNA aptamer is best suited for sensor application due to its selectivity of specific microorganism and structural stability and most of all superior and inexpensive substitutes for other ligands like antibodies. *Sphingobium yanoikuyae* was the specific bacteria chosen for detection. By immersing the biochip coated with RNA aptamer to the bacterial solution, binding mechanism between bacteria and the chip was studied. After air drying the chip was subjected for detailed analysis using AFM for topography and UV spectrophotometer for reflective analysis. Formation of monolayer has been understood by observing the π-A isotherm of silane terminated PBCL as shown in the Fig. 8.

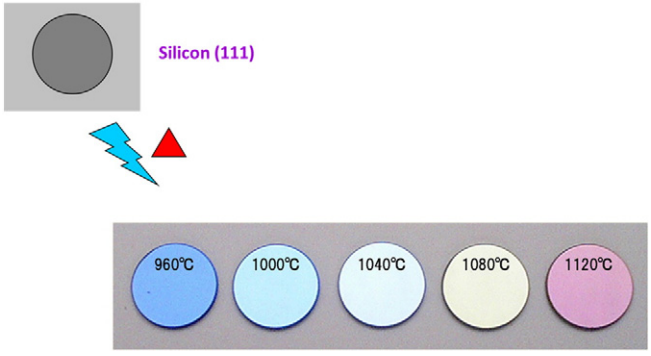

Fig. 4. Temperature influence on thin film interference (Lab image).

From the isotherm we can see two transitions are observed, the monolayer shows a gradual rise which may be owing to flexibility shown by silane junction with the peptide terminal. It is clear from the AFM image (Fig. 9) which shows the cationic surface formed with PLL is different from the silane terminated PBCL helical rod and RNA aptamer. In addition, it is noted that the PLL monolayer does not strip off during scratching with AFM probe showing that it is attached to the silane surface not by physical adsorption but by chemical bonding.

Real-time detection of bacteria is possible when the yellow colored probe modified using RNA aptamer changes to orange due to binding of bacteria. The color change was achieved for the optimum level of bacteria, *Sphingobium* concentration. Not only by real-time monitoring but also by UV reflectance spectroscopy the detection is confirmed. As shown in Fig. 10, spectral shift is observed which indicates the presence of bacteria. Also from the reflectance spectroscopy, the shift of λ_{min} from 463 nm to 481 nm is observed indicating the binding of bacteria. The colorimetric detection of both gram positive and gram negative bacteria has also been done using specific polymer. The bacteria secrete the enzyme, which interacts with agar-embedded nanoparticles comprising of phospholipid and polydiacetylene polymer. The interaction causes the color of the polymer to turn from blue to red. This sensor can be used for applications like sensing in food package and for screening antibiotic resistance [26].

2.4. Nucleic acid detection

Nucleic acids such as DNA, RNA can be detected easily by using colorimetric mode of sensing. Hybridization of DNA sequences are visually detected and hence termed as colorimetric based DNA sensors. Detection of nucleic acid is essential for the early diagnosis of cancer. DNA functionalized AuNPs colorimetric sensor system has been developed for the detection of metal ions, oligonucleotides and proteins. The

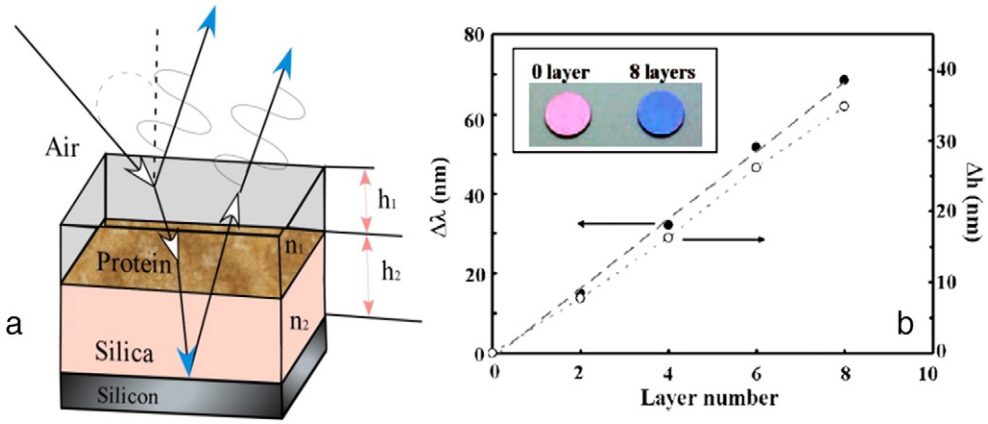

Fig. 5. a).Thin film interference and its equation brought by Bragg's law and Snell's law. b) shows the color change from purple to vivid blue as the no. of layers increases where change in thickness and wavelength were calculated using the Eq. (1) (From Ref [23], reproduced with the permission from Royal Society of Chemistry).

thermally stable, inexpensive, portable and disposable colorimetric sensor was reported in [28]. This colorimetric sensor is a paper-based sensor for the detection of DNase I and adenosine using AuNP as the probe which is either hydrophobic or hydrophilic. The paper substrate is attached with DNA-cross linked Au NP aggregates resulting in black or blue in color. When exposed to DNase I, it causes the dissociation of AuNP aggregates and shows red color within one minute. This sensor finds application in disease diagnostics, pathogen detection, quality monitoring of food and water.

Colorimetric detection of nucleic acids based on interference on optically coated silicon was reported in [29]. The polynucleotide sequence interaction can be identified to detect the specific gene (mecA gene) responsible for antibiotic resistance in *S.aureus*. The detection is based on interference that occurs between the substrate-thin film and the thin film-air interface. Based on the thickness of the film deposited on the substrate the wavelength of the reflected light gets varies which causes a change in the color. The silicon surface is optically coated which appears gold in white light. The capture probe is immobilized on the substrate, which is 20 nucleotide sequences. The target probe is 38 nucleotide sequence and 18 nucleotide biotin labeled oligonucleotide as the detector probe as shown in Fig. 11.

The complex was treated with HRP, which forms a thin film on the optically coated silicon substrate. The additional thickness on the substrate changes the wavelength of the reflected light and causes destructive interference where the color of the chip changes to blue. The reflectance spectra of the unreacted surface show higher reflectance in the orange red region so that the color of the substrate appears to be gold. The higher reflectance of the reacted surface in the shorter wavelength region due to the longer path length of the reflected light caused by the deposition of thin layer as shown in Fig. 12.

The polynucleotide sequence can be detected in the sub attomolar range using this detection method. This method is also sensitive that it shows color change only to methicillin resistant strain of *S.aureus* comparing to methicillin sensitive strain of *S.aureus* [29] as shown in Fig. 13.

AuNp based colorimetric sensor array for determining the binding strength of DNA has been reported in [30]. The single strand DNA functionalized with Au NPs is combined with complementary single strand DNA that causes aggregation of AuNPs resulting in the formation of duplex DNA. The dispersion of Au NPs, due to increase in temperature causes color change from blue to red. The weak binding DNA molecule changes to red color while the strong DNA binding molecule remains blue.

3. Chemical sensors

Chemical sensor is a device for detecting or sensing different chemical compounds such as volatile organic compounds, sensing gas molecules, toxic molecules and heavy metals. These chemical compounds are

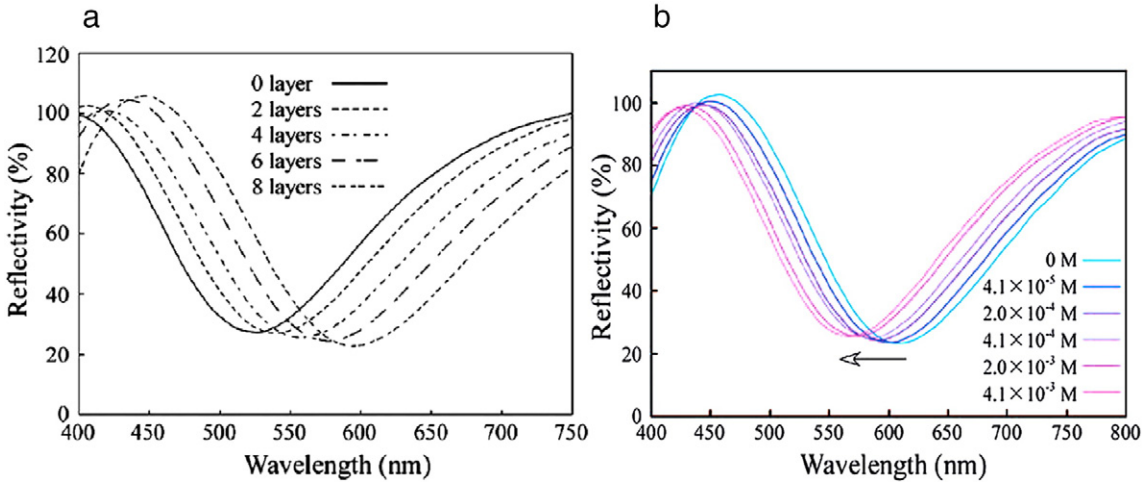

Fig. 6. a). Reflective VIS spectra of silica thin-films with various numbers of avidin-BSA-DSB layer on their surface. b) Illustrates the spectra when biotin is added at different concentration, i.e., blue shift occurs, change of color (From Ref [23], reproduced with the permission from Royal Society of Chemistry).

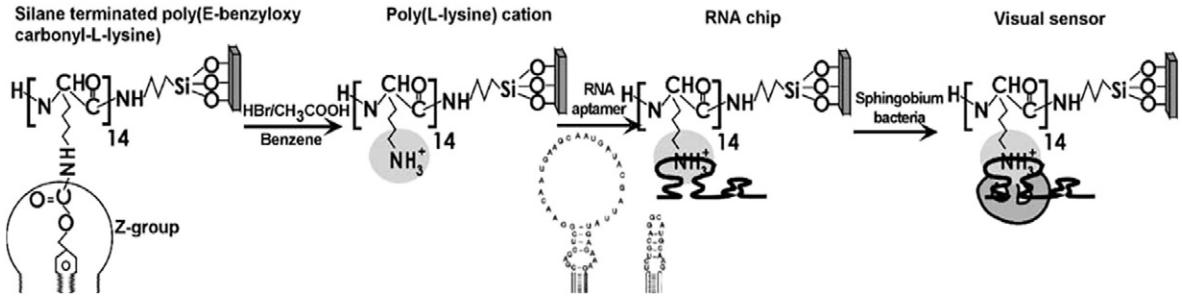

Fig. 7. Schematic for the visual detection of bacteria using self-assembled polypeptides (From Ref [27], reproduced with the permission from IOP).

the effluents from the industries, which pollute the environment and causes health hazards to all living creatures. So the detection of these chemical compounds becomes necessary. Colorimetric detection techniques include array based technique, aptamer based detection, disposable paper based techniques and so on. The detection is based on intermolecular interaction of the compound present in the environment. Based on the type of the analyte detection, chemical sensor can be classified as organic compound detection, heavy metal ion detection, explosive detection and also poisonous gas detection alias gas sensing. Chemical sensors based on colorimetric detection of various analytes were discussed under different sections.

3.1. Organic compound detection

A colorimetric array based technique has been employed for the detection of a volatile organic compound. Previously electronic nose based technology has been used for the detection of volatile organic compound. But it is less sensitive for the detection of compounds at low concentration, causes interference due to moisture and the interaction between the analyte and substrate depends only on the weak forces like Vander Waals force and physical adsorption. The colorimetric array-based technique overcomes the above drawbacks as the substrate is hydrophobic so that it is non-responsive to humidity, strong interaction exists between analyte and the substrate. The sensor array can discriminate the compounds of same functional group so that its selectivity

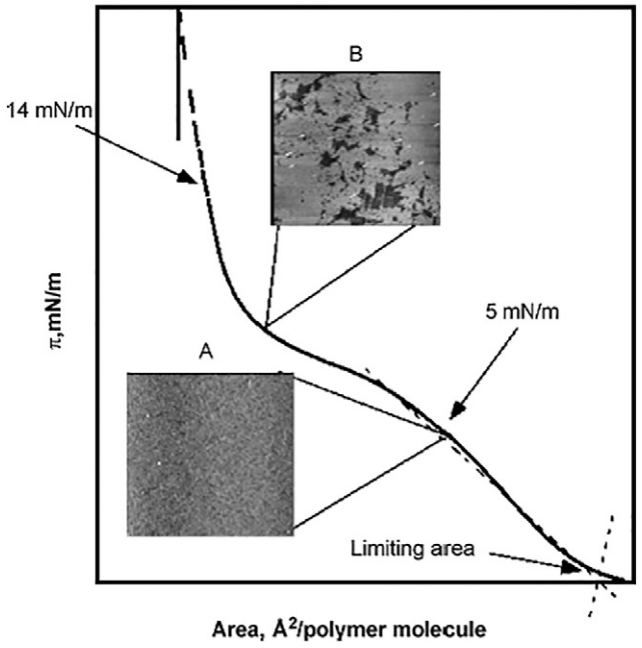

Fig. 8. π –A isotherm of silane terminated PBCL monolayer at air water interface (From Ref [27], reproduced with the permission from IOP).

is high. The detection principle used in chemo responsive array is the strong interaction of analyte with the chemoresponsive dye. The chemoresponsive dye used may be Lewis acid/basic dyes, Bronsted acid /basic dyes, solvatochromic dyes and metalloporhyrin which shows difference in color for different analytes. The colorimetric sensor array for the detection of volatile organic compound developed [31] and involves Zn substituted bis-pocketed metalloporphyrins based on ortho-substitution of the tetraphenylporphyrin core which is used to differentiate analyte based on size and shape. The sensor array has been reported to have shown responses to various functional groups like amines, arenes, alcohols, aldehydes, carboxylic acid, ester, halocarbon, ketones, phosphene, sulfides and thiols even at very low vapour pressure. The analyte response is represented as 72 dimensional vectors in principal compound analysis (PCA). The analysis from PCA shows very high dispersion range hence a wide range of analyte detection is made possible. The sensitivity of the sensor can also be improved by enhancing the imaging technology. The colorimetric sensor array with metalloporphyrin as the chromophore for the qualitative and quantitative detection of vapour phase organic compounds was developed in [32]. The sensor array is fabricated on silica gel plates where methylene chloride or chlorobenzene is immobilized on it. Interference from humidity is avoided due to the presence of hydrophobic silica gel as the substrate. Metalloporphyrin has the property of showing color change upon interaction with ligand due to the presence of open coordination sites. The color change profile can be obtained by subtracting the new image from the original scan.

Colorimetric sensor array can be miniaturized by coating Teflon with thin film metalloporphyrin to provide rapid response. Another colorimetric sensor array for the detection of 100 volatile organic compounds, which has the advantage of low cost, sensitive and non-responsive to humidity, was also reported [33]. The response of the array to the analyte is based on the interaction of the molecules of analyte and the substrate coated with chemoresponsive dye. This array also shows response to alcohols, aldehyde, aliphatic amines, aromatic amines, carboxylic acid, ester, hydrocarbon, ketones, phosphine and thiols. This sensor array is represented as 108 dimensional vectors. Principal compound analysis (PCA) is also done to determine the number of independent dimensions being probed by the array. The increased dimension enables the identification of much closely related compounds.

A colorimetric sensor for the detection of volatile organic compound using colloidal crystal was reported [34]. The colorimetric sensor gives change in color depending on the polarity of the organic compound. This method of detection is reversibly simple, cost effective technique compared to conventional methods. The colloidal crystal is a three dimensional structure made of polystyrene nanoparticles and PDMS elastomer. Based on the Bragg's refraction, the refracted wavelength of light depends on the swelling and shrinking property of the PDMS which in turn depends on the property of the organic compound. Both polar and non-polar organic compounds can be detected by this technique. Thus variation in color occurs due to different organic compounds.

The detection of an organic compound using colorimetric sensor array in water was reported [35]. This sensor array has the sensitivity

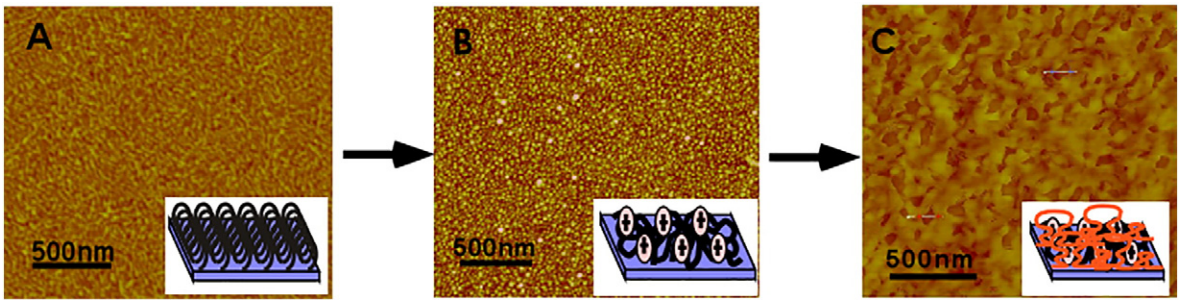

Fig. 9. AFM images of the monolayer of silane terminated PBCL helical rod (A), PLL random coil (B) and RNA aptamer (C) on silica substrate, respectively (From Ref [27], reproduced with the permission from IOP).

of 1 μM and the array substrate is hydrophobic with 36 sensor dyes being printed on it. The array can be represented as 108 dimensional vectors. Hierarchical cluster analysis (HCA) is also done which provides quantitative data of the family of chemical compounds in the form of Dendogram. The colorimetric sensor array for the detection of a specific class of chemical compounds was reported [36]. This sensor array involves dye along with polymer nanoparticles with different polarities for the detection of volatile primary amine. The substrate used is standard copy paper on to which dye encapsulated with polymer nanoparticles are printed using inkjet printing making the sensor flexible. Based on the polarity of the analyte the sensor is able to distinguish the different compounds and it does not show any changes when exposed to humidity. The sensor finds application in the food industry for the detection of bacteria. Detection of formaldehyde is essential as it is an active ingredient of air pollution. Early methods for detection of formaldehyde are expensive and time consuming. Colorimetric sensor strips for the detection of formaldehyde using polyacrylonitrile nanofibrous membranereported in [37] exhibit high selectivity. Similarly N-butyl phenol one of the toxic organic chemical compounds found in wastewater has been detected in a colorimetric way. Rapid, cost-effective detection of the compound without the use of any additional devices is done by using the colorimetric method. Colorimetric sensor based on iridescence colors was reported by Kinoshita [38]. The silica substrate is coated with multilayers of peptides layer by layer deposition technique or Langmuir Blodgett technique as shown in Fig. 14.

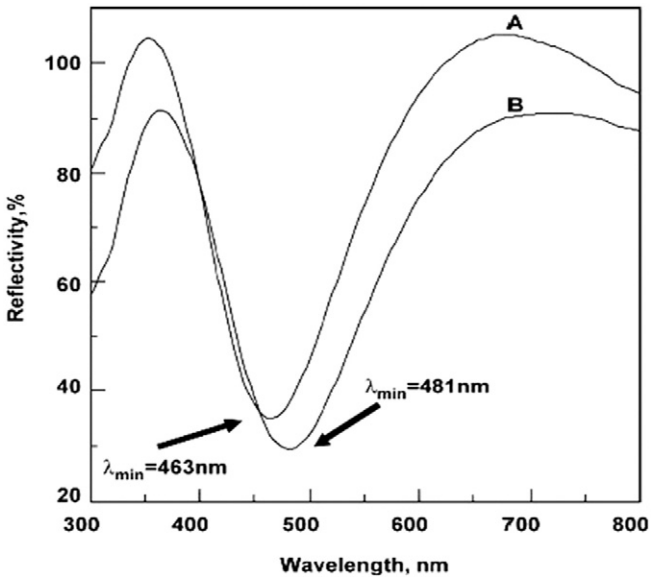

Fig. 10. UV reflective spectra of RNA chip with (B) and without (A) S.yanoikuyae bacteria at an incident angle of $10^{0.}$ (From Ref [27], reproduced with the permission from IOP).

The peptide coated chip is immersed into the solution containing n-butyl phenol. Depending on the concentration of the n-butyl phenol, swelling of the peptide layer causes reflection and interference to occur. As the concentration of the n-butyl phenol is increased from 50 ppm to 400 ppm the chip shows a change in color from light yellow to blue as shown in Fig. 15.

Vapour sensing of various analytes has been done using photonic structures. The photonic structures have the limitation of low sensitivity. The nanoscale structures present in Morpho sulkowskyi butterfly scales having high reflectance, higher ridge density and regular lamellar structure lead to selective detection of vapour molecules due to its iridescence property. The iridescence color arises from laminar structure acting as nanoreflectors and ridges acting as diffraction grating [39]. The butterfly wing is exposed to water, methanol and ethanol. The spectral response was obtained at different wavelength for different vapours. The detectable concentration was 1-2 ppm for water, methanol and ethanol vapours. The different periodicity of the butterfly wings contributes to the response at a different wavelength. The spectral response is due to the combination of two mechanisms, physical adsorption and capillary condensation. These phenomena occur in the nanostructured scales present in the butterfly wings. High selectivity towards the mixture of vapours will enable the development of highly ordered photonic structures [39]. Colorimetric sensor which is highly simple, selective and sensitive for the detection of heparin using graphene oxide and gold nanoparticles was reported in [40]. The interaction of gold nanoparticle on graphene oxide is prevented by protamine which has a stronger interaction with graphene oxide. This helps gold nanoparticles to exhibit the color. The addition of heparin allows gold nanoparticles to interact with graphene oxide resulting in the disappearance of color of gold nanoparticles. The concentration of heparin is detected based on the amount of gold nanoparticles get self-assembled to graphene oxide. It has a detection limit of 5 ng/mL.

The detection of dopamine by colorimetric detection was reported using Au and Ag—Au nanoparticles in [41,42]. The optical property of Au and Ag—Au nanoparticles causes the color change to occur due to the aggregation and dispersion of nanoparticles. The previous method for the detection of dopamine was spectrophotometry, which is simple, but it is less sensitive and selective to analytes. The colorimetric detection overcomes the above limitations. In this sensor amine group of dopamine is attached to the Ascorbic acid based Au nanoparticles or L-Histidine based Ag and Au Nps and the H-bonding between the neighboring dopamine causes the aggregation of Au and Ag nanoparticles so that the color of the solution changes from red to blue/purple or orange to red. The colorimetric detection of heparin using graphene oxide and oligonucleotide was reported in [43]. Fluorescent quenching occurs between graphene oxide and oligonucleotide. In the presence of heparin, the fluorescent quenching is minimized which gives yellow color indicating the presence of heparin. Melamine a milk adulterant has been detected colorimetrically by both using silver and gold nanoparticles [44–46]. Very recently interference/interruption in the synthesis of silver nanoparticles by the analyte melamine leading to its

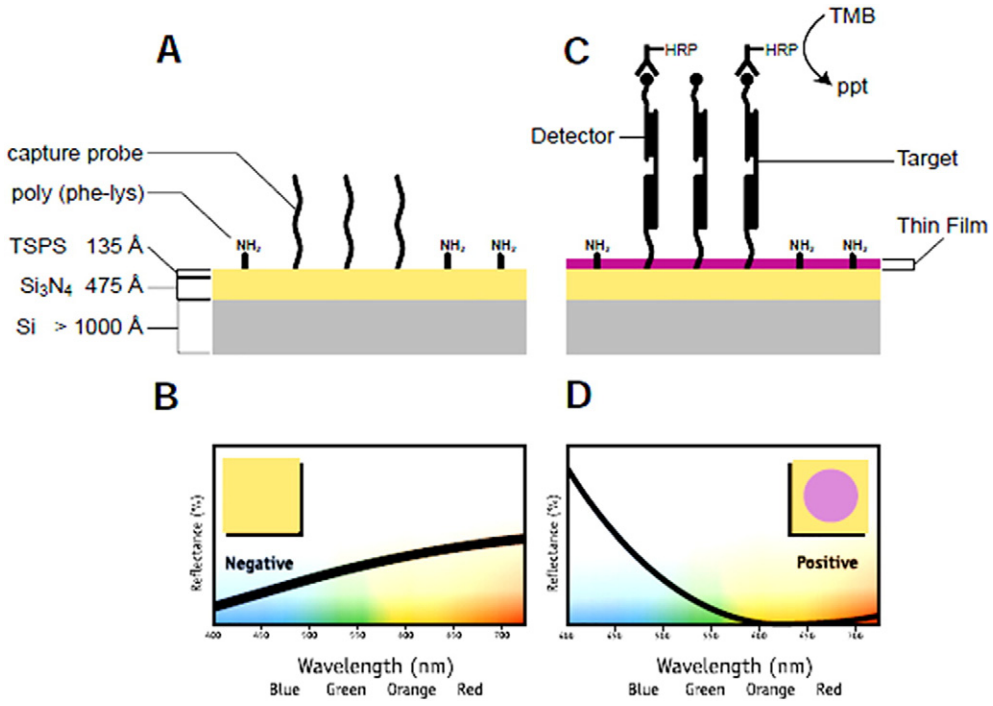

Fig. 11. (A) & (C) Schematic representation of the coated silicon hybridization based biosensor respectively. (B) & (D) Reflectance spectra of detected and undetected surface respectively. (From Ref [29], reproduced with permission from Nature publishing group).

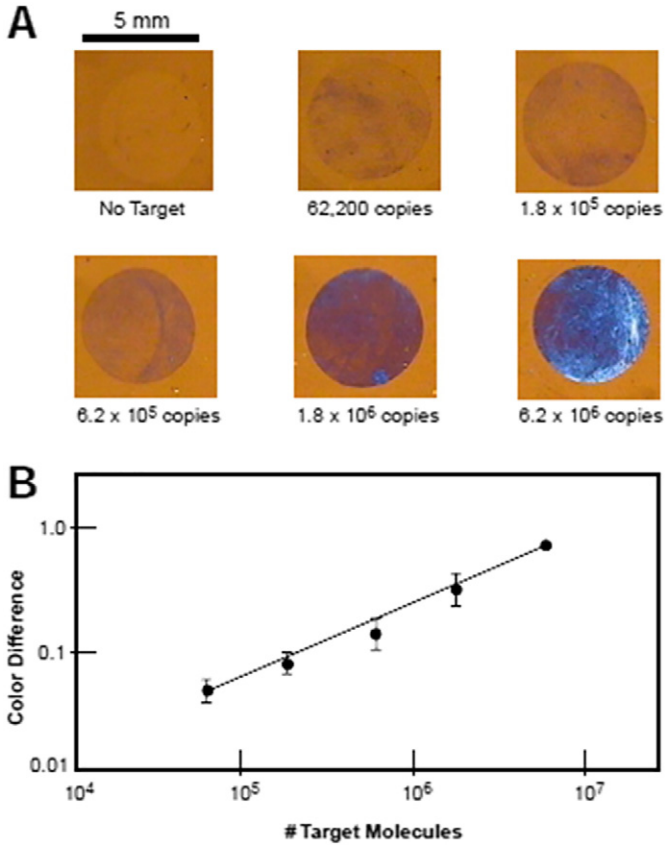

Fig. 12. Sensitivity of TSPS/PPL substrate for the detection of target DNA (From Ref [29], reproduced with the permission from Nature Publishing group).

colorimetric detection by using *Parthenium histerophorus* leaf extract as well as ascorbic acid as a reducing agent has been reported [47,48].

3.2. Heavy metal detection

Heavy metals include transition metals such as mercury, lead, cobalt, copper, silver, chromium, nickel, cobalt, Arsenic. These heavy metals are highly toxic and are one of the main causes of environmental pollution. These heavy metals are emitted from household products, industrial effluents, oceanic and volcanic eruption, mining, solid waste incineration and more. In order to monitor the amount of the heavy metal in the environment heavy metal detection is important. The prior techniques for heavy metal detection such as electrochemical technique, fluorescent

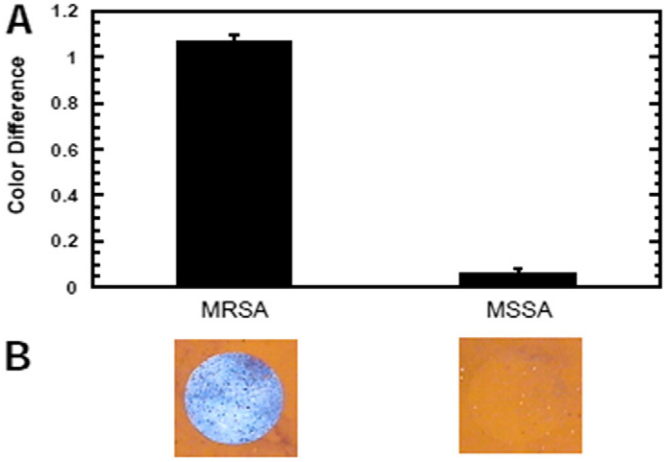

Fig. 13. Graphical representation of color difference as a function of target concentration (From Ref [29], reproduced with permission from Nature Publishing group).

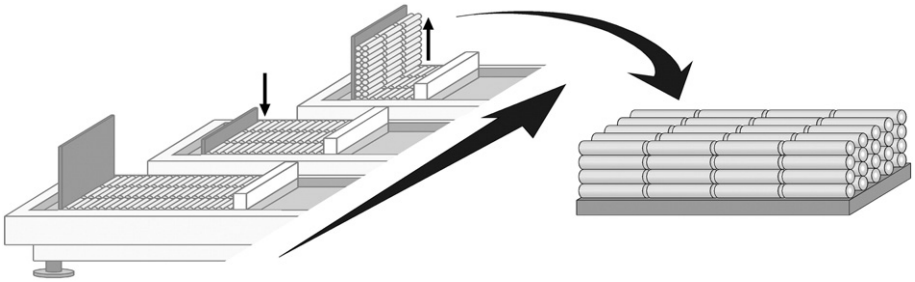

Fig. 14. Layer by layer deposition of peptides on the silica substrate using Langmuir Blodgett technique.

method, photonic crystal, absorption and emission spectra, quartz crystal microbalance are expensive, time-consuming and involve complicated devices. The limitation can be overcome by a simple, cost effective colorimetric technique which provides real time analysis due to its simple configuration. For the detection of the heavy metals, noble metal nanoparticles like Ag, Au and Cu are used due to its unique property of SPR. The detection mechanism is based on either the aggregation or disassembly of nanoparticles. The colorimetric sensor for the detection of Ag^{+} and Hg^{2+} ions using gold nanoparticles was reported [49]. The Au NPs are surface modified with Tween 80 molecules, which stabilizes the gold nanoparticles. After the formation of Hg—Ag alloy complex and Ag on the surface of gold nanoparticle by citrate ions, tween-20 is removed so that gold nanoparticle gets destabilized and causes the aggregation of gold nanoparticles which gives color change. It could sense up to 0.1 μM. Another colorimetric sensor using gold nanoparticles for the detection of Co^{2+} ions in aqueous solution was reported in [50]. Gold nanoparticles were stabilized by thiosulfate in the presence of ethylenediamine to form a complex, which is then oxidized, and react with thiosulfate and reduce the surface charge of gold nanoparticles so that aggregation of gold nanoparticles occurs. The color changes from wine red to blue. Detection of Cu^{2+} ions in organic solvent using gold nanoparticles was reported [51] where the detection mechanism is based on the quenching property of the Au NPs. The Au NPs together with the chromophore causes the quenching of the fluorescent color emitted from thee chromophore. In the presence of Cu^{2+} ions the interaction between the Au NPs and Cu^{2+} ions increases causing an increase in intensity of the emission. The visual detection is possible with the change of color from purple to orange. The change in absorption spectrum was observed in the presence of metal ions. This type of detection is sensitive up to 1 μM range. Another colorimetric label-free detection

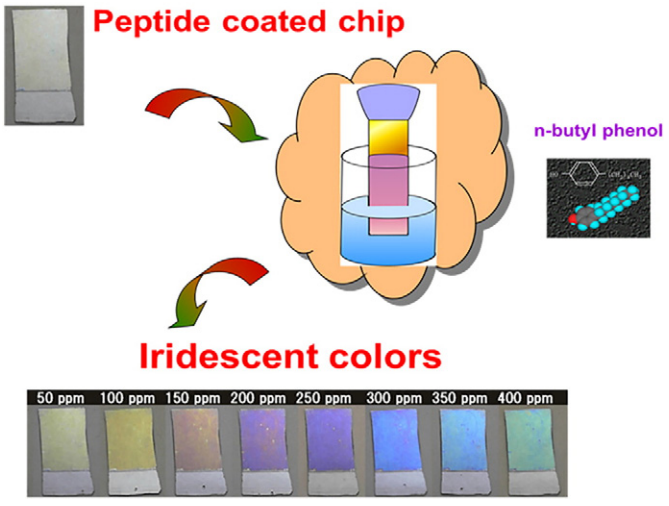

Fig. 15. Colorimetric chemical sensor based on iridescent color (From Ref [38], reproduced with the permission from Trans.Mater.Res. Soc. Japan).

of Cu^{2+} ions using gold nanoparticles as reported [52]. The sensing mechanism is based on the dissolution of Au NPs by the dissolved oxygen in the presence of $S_2O_3^{2-}$. The presence of Cu^{2+} ions increases the dissolution of Au NPs which act as the catalyst. The dissolution of Au NPs causes the red color of the solution to fade away thus enabling the visual detection of Cu^{2+} ions. Colorimetric detection of $Cu2^{+}$ ions using dopamine stabilized Ag NPs is based on the aggregation of dopamine functionalized Ag NPs due to the interaction of Cu^{2+} ions with nitrogen and oxygen atoms of dopamine. The color of the solution turns from light yellow to dark brown. The method of detection is rapid that the color change occurs within 10 min. It is sensitive in the range of 3.2-512 ppb [53].

Catalytic leaching of silver-capped Au NPs in thiosulfate solution enables the sensing of Cu^{2+} ions which act as the catalyst [54]. Cu^{2+} accelerates the leaching of the metal nanoparticles in the presence of thiosulfate. The increase in the concentration of Cu^{2+} ions causes a decrease in the size of the nanoparticles so that the SPR property gets reduced and the color of the solution changes from yellow to pink as shown in Fig. 16.

The change in the absorbance spectrum was also observed as the reaction time was increased. As the reaction proceeds for long duration the solution becomes colorless which indicates the dissolution of Au NPs which was also confirmed using TEM. This colorimetric detection is highly sensitive which could detect up to the level of 1 nM and selective towards Cu^{2+} ion with a wide range linear detection range of 5-800 nM [54]. The color of the solution changes from yellow to purple due to the dissolution of silver nanoparticles by Cu^{2+} ions and gold nanoparticles are left in the solution. If the concentration of Cu^{2+} ions is increased dissolution of gold nanoparticles occurs which turns the purple color of the solution to colorless as shown in Fig. 17a.

The SPR absorption monitored using UV visible absorption spectroscopy was shown in Fig. 17b, c. Initially, a strong absorption was found to be at 405 nm. With the addition of $Na_2S_2O_3$ the absorption at 405 nm gets reduced. With the increase in the concentration of Cu^{2+} ions the peak gets shifted to 520 nm and the intensity is also reduced due to the dissolution of Ag nanoparticles.

Colorimetric sensing of Cu^{2+} ions using Ag NPs by paper-based analytical devices was first reported in [55]. The colorimetric sensing of Pb^{2+} ions using DNAzyme and Au nanoparticle was reported in [11]. The substrate cleavage by DNAzyme in the presence of Pb^{2+} ions causes color change by the aggregation of Au nanoparticles. This color change indicates the presence of Pb^{2+}. The detection limit is 500nM. Colorimetric detection of Cu^{2+} ions present in tap water and human serum using gold nanorods was reported [56]. The presence of Cu^{2+} causes the etching of Au nanorod and thereby the aspect ratio of the nanorod gets changed, which causes color change. Other heavy metals can also be sensed visually using metal nanoparticles as reported [57]. Heavy metal detection using gold nanoparticles capped with chitosan. This sensor is used for the detection of heavy metal ion detection like Zn^{2+}, Cu^{2+} in water. The optical property of the gold nanoparticles gives the color change.

The development of low cost rapid detection of humidity is necessary for food packaging. The sensing mechanism is based on Plasmon

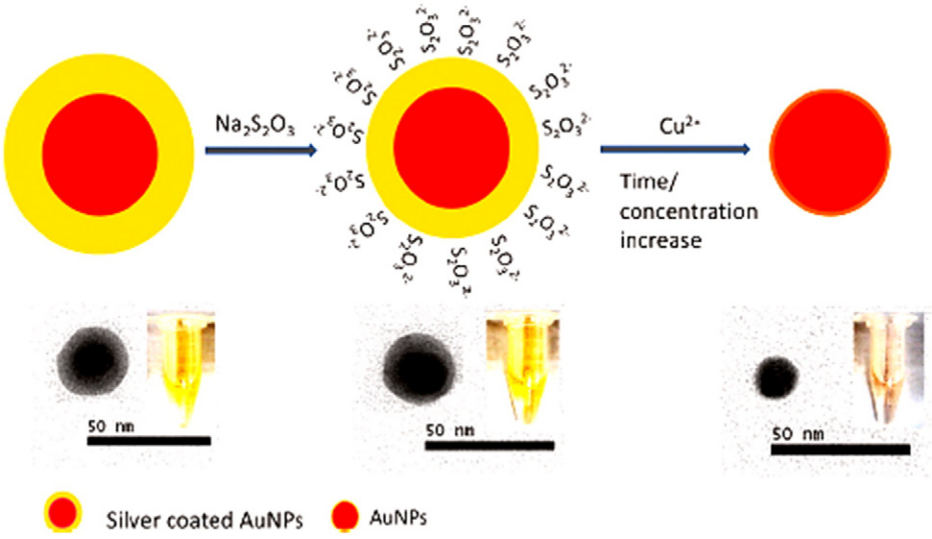

Fig. 16. Schematic representation of sensing mechanism of the $S_2O_3^{2-}$Ag/Au NPs for the colorimetric detection of Cu^{2+} based on catalytic leaching of Ag coated Au NPs (From Ref [54], reproduced with the permission from American chemical Society).

resonance and interference phenomena. Depending on the thickness of the film and the angle of incidence the color gets varied. The humidity sensor is also based on the above two techniques. Humidity sensor based on metal/polymer hybrid film which shows color change based on Plasmon resonance and interference at low relative humidity and high relative humidity respectively [58] shown in Fig. 18. The copper nanoparticles are coated with a layer of carbon in a polymeric film (polyether modified polydimethylsiloxane). At 50% RH no change in coloration and UV absorption peak is found at 560 nm attributed to the Surface Plasmon Resonance. At about 65% RH the color of the film

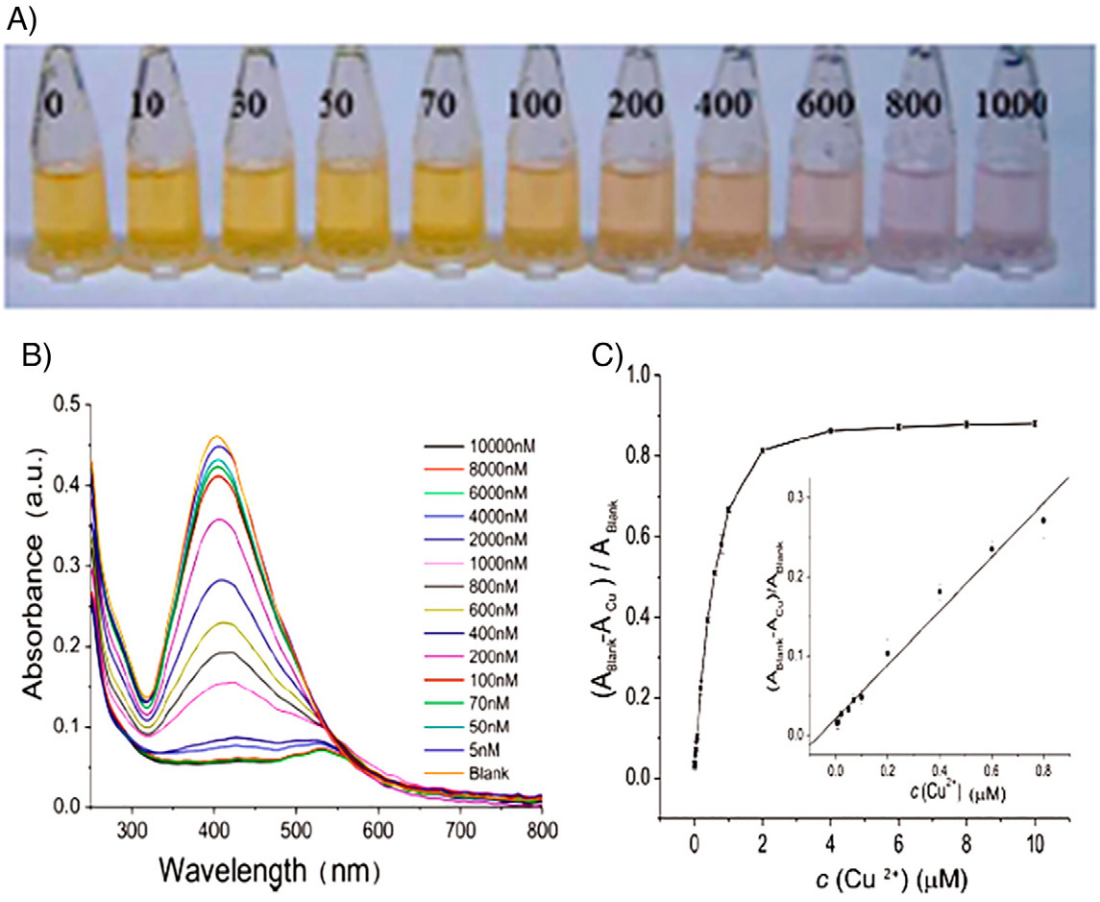

Fig. 17. a) Photographs and b) absorption responses of $S_2O_3^{2-}$-Ag/AuNP solution on addition of Cu^{2+} and c) plot of $(A_{blank}-A_{Cu})/A_{blank}$ (at 405 nm) values versus Cu^{2+} concentration (From Ref [54], reproduced with the permission from American Chemical Society).

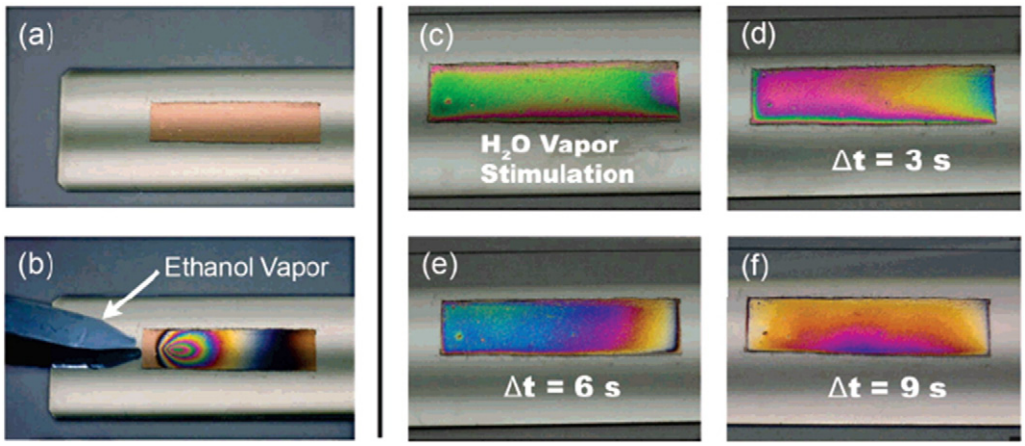

Fig. 18. a) Deposition of C/Cu dispersions on a glass substrate results in metallic copper films. b) Exposure to a stream of ethanol vapour resulted in rapid and reversible intense iridescent coloration. c) Exposed to saturated water vapour at room temperature gives green color that gradually shift back to (d) pink (e) blue (f) orange (From Ref [58], reproduced with the permission from Langmuir).

shifts to green and the absorption peak also shifts. Further, increase in RH to 70% the color of the film shifts to blue. The absorption shifts to 50 nm per 1% increase in RH.

In the hybrid, dry film there is no change in color and the broad absorption peak is found to be at 560 nm which corresponds to the Surface Plasmon Resonance of the copper nanoparticles. At relatively low humidity, water molecules adsorb on the surface of the film which causes the swelling of the polymer causing shift in the absorption band. At relatively high humidity the excess water molecules forms a thin film. The interference occurs at the interface between the surface of the film and water molecules adsorb on the surface. The mechanism behind the color change was shown in Fig. 19. Depending on the angle of incidence, thickness of the film and the refractive index the color changes with increase in humidity. The shift in the absorption spectrum is also observed as shown in Fig. 20.

3.3. Toxic gas detection

Toxic gases emitted from industries are highly poisonous and they cause several effects. The most toxic gases emitted from the industries include NH_3, NO_2, H_2S, HCl. These gases can be detected by array based colorimetric detection, Micro Electro Mechanical Systems (MEMS) technology, chemoresponsive dyes which are simple and highly sensitive. The use of microarrays contains chemoresponsive dye was developed which provides rapid and sensitive detection of 20 toxic industrial chemicals (TIC) at their permissible exposure limit (PEL) [59]. It shows advantage over numerous conventional methods such as GC/MS, IMS, and electronic nose technology. Microarray based colorimetric sensor are based on optoelectronic technique using chemoresponsive dye compared to electronic nose technology which use weaker or less specific intermolecular interaction like Vander Waals and physical adsorption. Microarray for gas sensing consists of chemoresponsive dye such as metalloporphyrin, vapochromic/solvochromic dye that respond to local polarity, pH indicators and metal salt redox indicators. These dyes are immobilized in the array using organically modified silosane. Toxic Industrial chemical such as harmful gases like amine, NO_2, H_2S, SO_2, F, Cl etc. shows color change dependent upon concentration of each analyte. Colorimetric detection is based on chemochromic reagent in a porous matrix. Mostly this sensor is used for fire detection i.e. by detection of CO and NO_2 gases. Comparing to other technologies in market this technology works on colorimetric films and is low power technology which is MEMS compatible for the detection of CO, NO_2 gases. The colorimetric sensor for the detection of Hydrogen Chloride gas using porphyrinated polymers was developed in [60]. This colorimetric sensor was fabricated from the nanofibrous membrane made of porphyrinated polyimide (PPI) using electrospun technique on a glass slide. The sensor shows high sensitivity and has fast response time. The combined colorimetric and fluorescent detection provides an additional advantage for sensing.

Polyimide polymer has high thermal chemical stability and mechanical strength with large surface area to volume ratio was used as the effective material for the sensing of analytes even at trace level. The

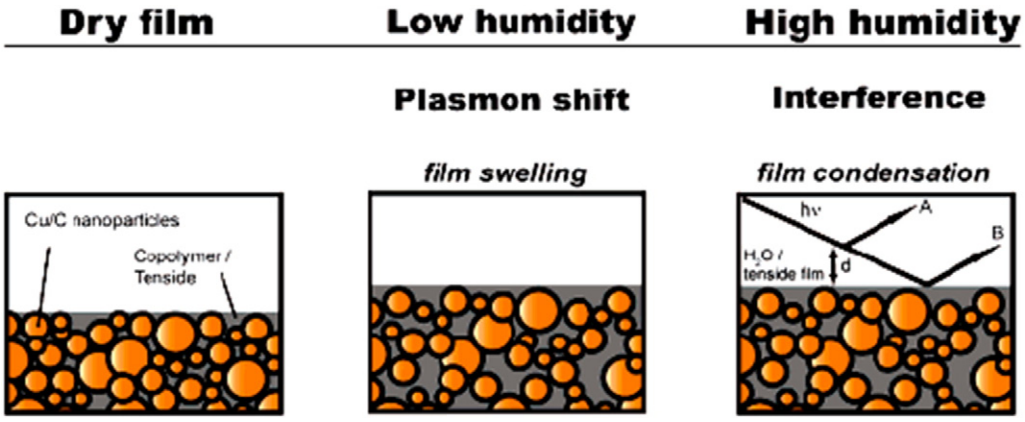

Fig. 19. a) Schematic representation of a) Polymer/Tenside Matrix of Dry Hybrid film b) At low humidity swelling of polymer occurs and causes shift in Plasmon resonance peak c) At high humidity interference occurs due to the excess humidity deposited on the surface of the film (From Ref [58], reproduced with the permission from Langmuir).

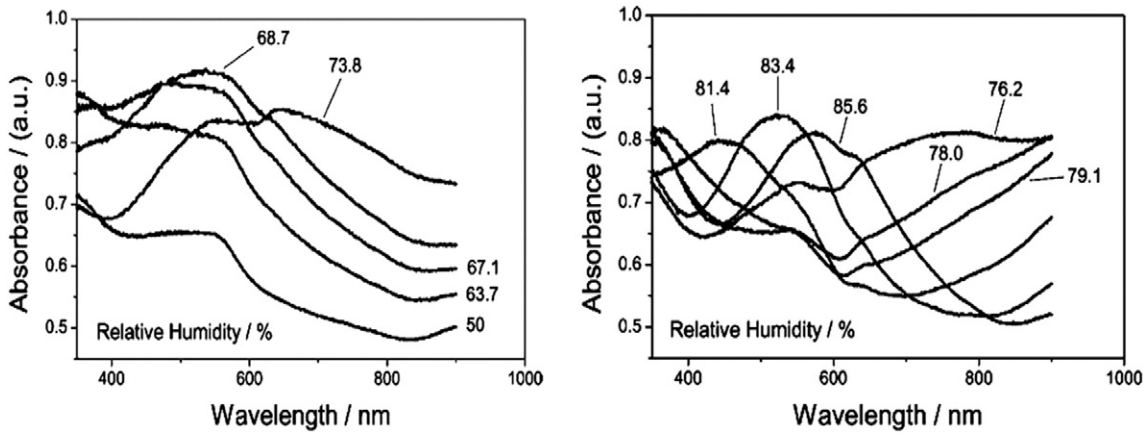

Fig. 20. UV visible absorption spectra of Cu/C film exposed to different relative humidity from 50% to 85.6% (From Ref [58], reproduced with the permission from Langmuir).

nanofibers produced by electrospun technique has average diameter of 350 ± 54 nm. The PPI nanofiber is exposed to HCl gas and the color changes from pink to green. The response time is high where color change occurs within 10s as shown in Fig. 21a. The increase in the concentration of HCl gas increases the intensity of color which is due to the protonation of neutral porphyrin. Moreover, structural change also occurs from planar to saddle conformation. SPR response of PPI nanofiber to different concentration of HCl was further investigated which shows an increase in SPR response with the increase in the HCl concentration as shown in Fig. 21b. This sensor has an additional advantage of reusability upon exposing to nitrogen for certain time.

Hydrogen sulphide is highly toxic, flammable and corrosive gas. Detection of these toxic gas was done using chemoresponsive dyes which react with the analyte and shows a change in color. It is also able to detect the different concentration of H_2S gas [61]. Another colorimetric detection using optical waveguide using polymeric material for the detection of ammonia was developed by where the light propagating through the optical waveguide experience the phenomena called total internal reflection and produces an evanescent wave. A colorimetric film is deposited over this waveguide so that the change in light intensity produced by evanescent wave shows color change. The optical waveguide enhances the sensor sensitivity [62]. The development of colorimetric paper based sensor for hydrogen peroxide vapour detection which is a simple, disposable and one-time used sensor. H_2O_2 vapour detection can be carried out at parts per billion levels. Ti (IV) oxo complex is surface modified on the paper towel for the detection of H_2O_2 vapour. The vapour on reaction with the complex form Ti (IV) – peroxide bond, which turns the complex from colorless to bright yellow, showing an absorption maximum of 400 nm. Such binding is exclusively for H_2O_2 detection and no color change can be observed with the presence of other materials like oxygen, water, organic reagent or other chelating reagent [63]. The colorimetric sensor for vapour sensing using metalloporphyrin, which shows change in color upon ligand or metal ion binding and provides a simple technique compared to the signal transduction. The analyte is recognized by taking the difference of the image before and after exposure to target analyte. This sensor is able to provide both qualitative and quantitative analysis [32].

3.4. Detection of explosives

Detection of explosives is a major problem in the society as it causes several hundreds of people to loss their lives. There are several techniques for the detection of low, medium, high vapour pressure explosives. Some of the techniques used are electronic nose technology, x-rays detection method, neutron detection method. The colorimetric detection of explosives enables simple and easy detection of analytes. The colorimetric sensor for the detection of trinitrotoluene using dual emission quantum dot was reported in [64]. The selectivity of the sensor is

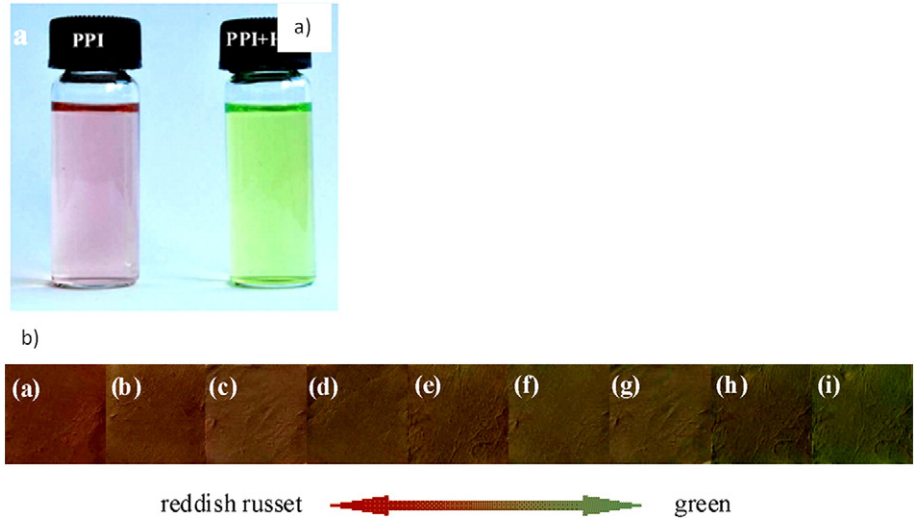

Fig. 21. a) Colorimetric change in the presence and absence of HCl b) Photographs of PPI nanofibrous membrane when exposed to different concentration of HCl vapour for 10s (a) 0 ppm (b) 5 ppm (c) 10 ppm (d) 20 ppm (e) 30 ppm (f) 40 ppm(g) 50 ppm (h)70 ppm (i)100 ppm (From Ref [60], reproduced with the permission from Elsevier).

high. The previous technique used is costly and are not applicable for onsite identification of TNT. The ratiometric fluorescent probe consists of two quantum dot of different size. The larger quantum dot giving red fluorescence is embedded in silica nanoparticles and the surface of the silica nanoparticle is attached smaller quantum dot emitting green fluorescence. The attachment of trinitrotoluene to smaller quantum dot quenches its fluorescence and causes the color change. Label free colorimetric sensor for the detection of nitrite is based on the etching of gold nanorods by nitrite and color change occurs from bluish green to red and then to colorless. It could sense up to 4 μM [65]. Detection of thiocyanate in aqueous solution was done using gold nanoparticles capped by citrate ions and stabilized by the addition of Tween-20. Upon the addition of thiocyanate ions citrate ions were removed and Tween-20 molecules get separated resulting in the aggregation of gold nanoparticles, further the color changes occurred from red to blue [66].

4. Conclusion

Of the various sensing technologies, available colorimetric sensing is simple, rapid, highly sensitive and selective. The detection is done in a single step with no complex instrumentation. The colorimetric approach can detect various kinds of molecules in a short time. Colorimetric detection of the pathogen has been done using silicon by the interference phenomenon exhibited by it when subjected to different layers. The challenges such as usage of harmful chemicals in sensor platform, cost of the instruments, label free detection, real time analysis, single step detection and portability will be a hurdle for existing conventional sensors available in the market. Colorimetric sensors can gain wide range acceptance in these challenging fields. The future scope of sensing technology depends on the implementation of nanotechnology in the sensor field for rapid sensing. Various colorimetric sensors for the detection of chemical compounds as well as biological molecules using metal nanoparticles have been discussed. This will pave the way for the detection of various disease causing pathogens, chemicals, explosives and could help in the early diagnosis of diseases as well as detection of harmful heavy metals present in the environment.

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