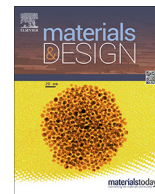




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# Reversible self-assembly of gold nanoparticles in response to external stimuli



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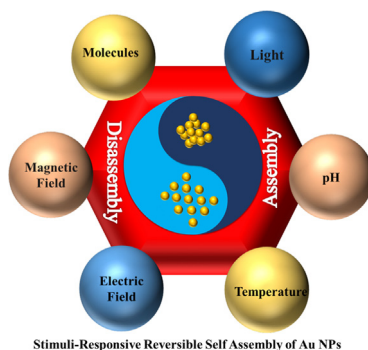
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## HIGHLIGHTS

- Discussion of recent progress in reversible assembly of Au NPs, to include challenges and solutions.
- Importance of assembly/dissassembly of different materials especially noble nanoparticles.
- Reversible assembly of Au NPs induced by light, pH, temperature, electrical and magnetic field.
- Stimuli responsive ligands and polymers covering the surface of Au NPs for reversible assembly.
- Factors influencing the possible attractive and repulsive forces between the nanoparticles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Noble metal nanoparticles are highly attractive, owing to their optical, physical, electrical and chemical properties. Specifically, ease of surface modification, exceptional plasmonic and optical properties of gold nanoparticles (Au NPs) have created increasing interest in the assembly process. Once assembly is achieved successfully, the disassembly of the Au NPs is considered to be an exciting challenge. There are different kinds of forces involved in the assembly and disassembly process of Au NPs with a great deal involving the chemistry of surfactants. These forces can be externally triggered to achieve reversible assembly and disassembly. Less effort has been devoted to collate the study and mechanism involved behind environmentally or chemically triggered reversible assembly of Au NPs. Hence, the emphasis of this review is to highlight a number of promising stimuli such as light, pH, temperature and magnetic fields that can cause the reversible assembly of Au NPs. In addition, the surfactants utilized for assembly and disassembly of Au NPs under external stimuli response are examined. Furthermore, this review gives an account of the mechanism and chemistry of reversible assembly of Au NPs, taking into account the latest published literature. Indeed, it covers many ligands, biomolecules and thiol-mediated surfactants that can be linked to the surface of Au NPs and can also respond to external stimuli, realizing reversible assembly. The emerging challenges and an outlook on future developments in this research area are also discussed. The ultimate goal of this review is to encourage synthetic chemists to use ligand functionalized

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Au NPs (building blocks) for complex chemical systems as it will revolutionize the organic ligand synthetic processes that are responsive to different stimuli.

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## 1. Introduction

Nature continuously impresses scientists with great enigmatic wonders such as the self-assembly concept. For example, in marine life sea salmon and magnetotactic bacteria contain assembled magnetic nanoparticles similar to that of migratory birds [1–3]. Inspired by nature, self-assembled patterns and their functions, scientists have observed similar concepts of assembly in nanomaterials and have indeed utilized them in numerous advanced applications [4–6]. Self-assembly is the spontaneous formation of well-arranged and homogeneous structures of nanomaterials, polymers, colloids and molecules from disordered patterns. The principle of assembly is based on inter and intermolecular weak interactions, with or without guidance from an external source [7]. Self-assembled synthetic routes are similar at macro/micro and nano levels but significant changes in physio-chemical properties have been observed at the nanoscale and researchers continue to be interested in the self-assembled mechanism in nanoparticles and assembled nanofilms [8–10].

The promising behavior of ligands including biomolecules, polymers, monomers, and functionalization of these molecules and polymer on the surface of nanoparticles offered various advantages and contributed toward an interesting field of research. Surface modification of Au NPs is well established to realize assembly behavior with or without external stimuli. Such self-assembled Au based hybrid nanocomposites show enhanced electrical, magnetic, plasmonic, optical, catalytic properties over individual nanoparticles [11–14]. Therefore, these functionalized Au NPs have promising uses in technological applications, including biomedical sensors, devices, catalysts, surface-enhanced Raman spectroscopy (SERS) and cancer therapy [15–19]. Consequently, the self-assembly presents a significant process for the preparation of multifunctional NPs. Another interesting phenomena in the field of nanotechnology is to design fully programmable nanoparticles with reorganizable properties (reversible self-assembly, i.e. the spontaneously or stimulated transitions between primary NPs and aggregated NPs). However, the novel design mechanism and complete control over reversible self-assembly at nanoscale is a challenging objective.

Covering the theory behind the reversible assembly of Au NPs in response to the external stimuli is the scope of this review. We have also attempted to provide a range of ligands, biomolecules and thiol-mediated surfactants that can be functionalized on the surface of Au NPs for versatile applications and can simultaneously respond to external stimuli for reversible assembly phenomena. Stimuli responsiveness of Au NPs can originate either from the ligand covering the surface or from the inorganic core of Au NPs. External stimuli, to direct reversible assembly of Au NPs, such as light, pH, temperature and the magnetic field are discussed here in detail. This review also highlights extensive studies based on the light responsive reversible assembly of Au NPs and covers recent promising work related to pH, temperature, magnetic and electric fields along with dual stimuli mediated reversible assembly of Au NPs. The ultimate goal of this review is to encourage synthetic chemists to use ligand functionalized NPs as the building blocks of increasingly more complex chemical systems. Many new applications would be anticipated with successful control over reversible assembly of Au NPs.

## 2. Self-assembly of gold nanoparticles

The importance of 0D, 1D, and 3D nanomaterials cannot be neglected but preferences of 2D organized NPs provide properties like quantum size effect, electric and electronic features, high surface to volume ratio, ease of synthesis, high thermal conductivity and the formation of lower thickness films at interfaces [20,21].

Over the past few decades, graphene, carbide, and nitrides 2D materials have obtained fame and studied extensively for various applications (Fig. 1). However, researchers also understand the reputation of noble metal based 2D nanomaterials films, 2D organic and metal organic frameworks (MOF), 2D organic polymers and inorganic oxides films. The self-assembly process plays an important role in the synthesis of above mentioned 2D materials, proceeding by directed methods such as self-organization by polymers, template mediated self-assembly or assembly by using external stimuli such as light, magnetic/electric fields and pH control [22–24]. Grzelczak, et al. have recently explained the possible tools for chemical interactions and proposed mechanisms for the directed self-assembly of nanomaterials [25]. Furthermore, they have discussed the externally driven self-assembly processes. Well-arranged structures based on magnetic materials such as Fe, Co, and Ni may be designed [26–28], but noble metal based nanoparticles have attained tremendous attention due to their optical and chemical properties [29,30].

2D monolayer films in the nanometer (nm) range and specifically, 2D monolayer films of noble metal materials Au and Ag have coined new usage in biomedical treatment, sensors, electronic devices, biomolecules detection, catalysis, and SERS [31–34]. Hence, the potential optical properties of Au and Ag nanoparticles, their monolayer structures and advanced applications, has emerged as an exciting research field. In this regard, a nanoporous structure based on noble metal materials offered self-assembly behavior with different applications in electrochemical fuel cells, catalysis, and sensors [35]. Au NPs have different shapes such as rods, stars, triangles, quasi-spheres and branches and have promising impact on advanced applications such as drug delivery, cancer detection, nanomotors, biosensors, and heavy metal ion detection [36,37]. Considering the importance of structure and property relationship, Murphy et al. demonstrated a synthetic procedure along with assembly and optical properties of non-spherical Au NPs specifically gold nanorods (Au NRs) [38]. Authors have explained the effect of length of nanorods on the optical properties and the assembly of nanorods by an evaporation method. Different assembly techniques are involved in this regard such as Langmuir Blodgett method, directed self-assembly, evaporation induced assembly, laser-induced assembly and nanoparticle adsorption [39–41].

Similarly, Au NPs self-assembly can be used for the Surface-Enhanced Raman Spectroscopy (SERS) enhancement. The basic concept is to localize surface plasmon resonance (LSPR) i.e. collective oscillation of the nanoparticle conduction electrons. LSPR excitation in silver and gold nanoparticles produces strong extinction and scattering spectra [42]. Self-assembly of Au NPs can also be acquired by using host-guest interaction, by hydrogen bonding and complex formation [43]. Mix particle assemblies are also possible and Fan et al. deliberated a polymeric glue supportive assembly of Au NPs around Au NRs. In this system, Poly-N-isopropylacrylamide acted as a glue and formation of satellite-

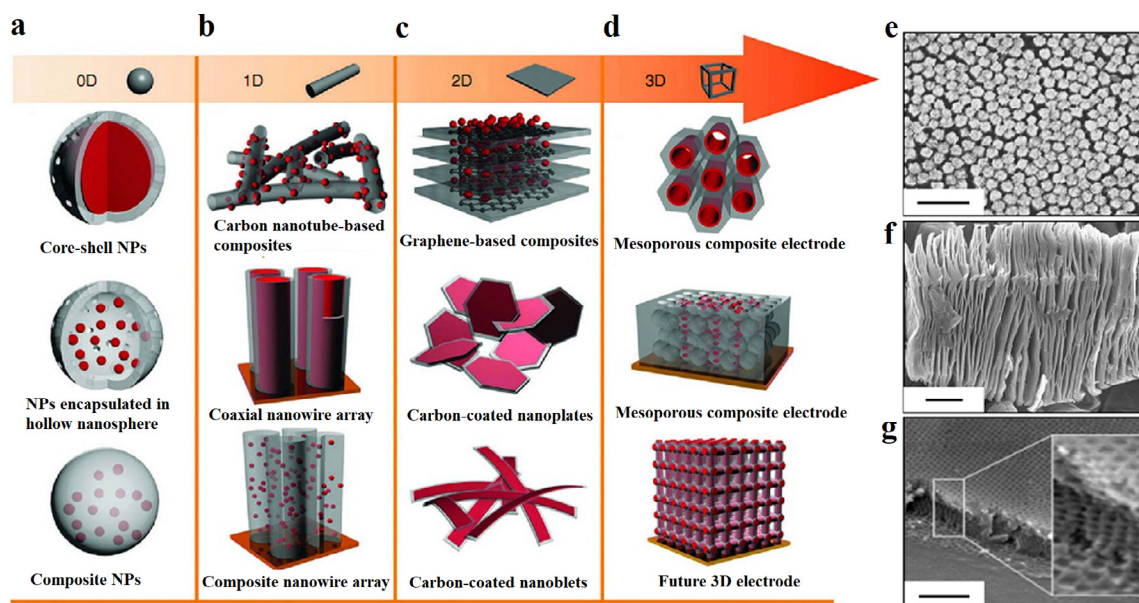


Fig. 1. Different dimensionality based assembled heterogeneous nanomaterials. Reproduced with permission from Ref. [21]. Copyright (2016) Springer Nature.

like structure developed by the assembly of Au NPs around the Au NRs[44]. The importance of synthesized Au NPs, their self-assembled 0D, 1D, 2D, and 3D structures cannot be neglected, but to disassemble these structures is another charming endeavor. Hence, NPs can be reused with the help of reversible assembly which is itself beneficial, however complete control of this is challenging [45].

### 3. Reversible self-assembly of gold nanoparticles

Reversible self-assembly of nanoparticles is an exciting phenomenon for fundamental and applied purposes. In the current era of nanotechnology, scientists are passionately looking for easy, low cost and feasible methods to develop reversible assembly of nanoparticles. Van der Waal's attractive forces are important in the assembly of nanoparticles. Whereas, according to the Derjaguin–Landau–Verwey–Overbeek (DLVO), the disassembly process of NPs can be carried out by electrostatic repulsive potential [46,47]. DLVO theory principally explains the potential of interactions that cause the stability of colloids and their aggregation behavior. The total potential  $V_{\text{Total}}$  is defined as the combination of the charge–dipole interaction potential, the van der Waals attraction potential, the dipolar interaction potential and the electrostatic repulsion potential in case of assembly and disassembly of Au NPs, – see Eq. (1) [48].

$$V_{\text{Total}} = V_{\text{elec}} + V_{\text{vdW}} + V_{\text{dipole}} + V_{\text{charge-dipole}} \quad (1)$$

where elec = Electrostatic, and vdW = van der Waals

Stability of nanoparticles is significant for many applications and depends on different factors such as type of solvent, the forces between the nanoparticles, particle size, shape and density. Mainly, stability can be increased with the increase of particle size. Manipulation of different forces between the nanoparticles can cause assembly behavior and smaller nanoparticles offer reversible assembly more conveniently as compared to those of larger size [49,50]. The synthesis and assembly of different metal nanoparticle such as Au, Pd, Ag, Pb, Ti, Ni, Fe, Co, and Cu has been well studied [51,52].

Self-assembly involves controlling spatiotemporal structures for the design and fabrication of functional supramolecular assem-

blies and reversible assembly behavior using amphiphilic properties has been reported by Wang et al. [53]. Tuneability of the amphiphilic behavior of supramolecules using reversible chemical reactions and supramolecular approaches, and different external stimuli (Fig. 2) can be used to trigger reversible changes. The reversible assembly of nanoparticles, mostly noble metal nanoparticles (Au and Ag), is capable of inducing enhanced properties and usage in advanced applications like catalysis, imaging, writing without ink, heavy metal detection and switchable sensing [54–56].

The reversible assembly concept is not limited to nanomaterials as mentioned above. The behavior of 2D and 3D metallo-supramolecular architectures can be considered because they had shown an efficient response to different stimuli [57]. To explore this concept, Lusby et al. explained the assembly and disassembly behavior of carbo-platinum complex by just changing pH of the solution [58]. The versatility and advancement in the field of different external stimuli is shown in Table 1. Not only light, temperature and pH-responsive materials are developed but also electric and magnetic field along with molecular mediated reversible assembly behavior has been observed. The following sections will focus on the reversible assembly of Au NPs under external stimuli such as light, pH, temperature and electric and magnetic field in more detail.

#### 3.1. Light-responsive reversible assembly of Au NPs

In light responsive assembly and disassembly processes, the surface of Au NPs must be modified with photo-responsive materials which can be activated/deactivated when subjected to radiation of a specific wavelength. Au NPs reversible assembly work has been carried out using methods like host–guest interaction and mostly azobenzene and spiropyran were used as light reactive materials after modification with thiol groups, which have affinity for Au. To induce assembly/ disassembly behavior of different shapes and sizes of Au NPs under light is remarkable [84]. Dennis et al. used the radical reversible addition fragmentation chain transfer (RAFT) polymerization to use a methacrylate type monomer with azobenzene which was then grafted on the surface of Au NPs to induce light responsive materials [3].

Shiraishi et al. modified Au NPs with thiol containing spiropyran (SP) under UV light irradiation and successfully achieved

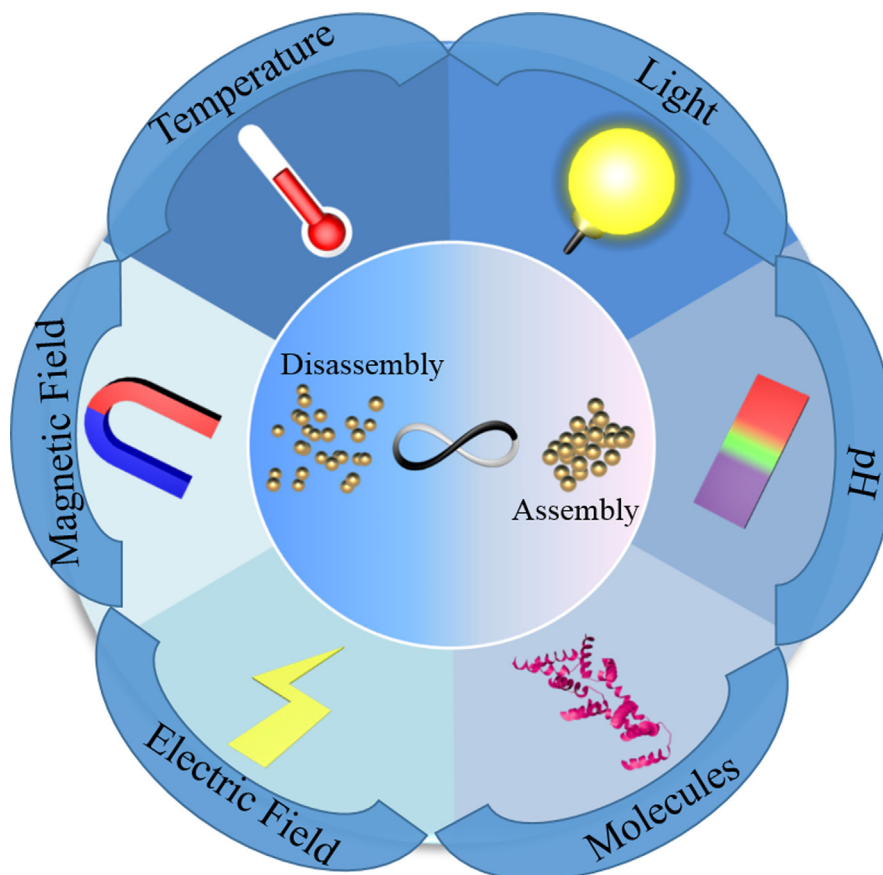


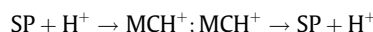
Fig. 2. Stimuli-responsive gold nanoparticles (Au NPs) in response to different stimuli.

aggregation of NPs using the concept of ring opening of the SP molecule [85]. Visible light was then used to obtain monodisperse nanoparticles by taking advantage of the ring-closing function of SP (Fig. 3A). The TEM image shows the well-dispersed particles under dark and light conditions at 0 sec. Aggregation was observed after UV irradiation of sample at about 10, 15 and 20 min (Fig. 3B1–B3). The as-synthesized thiol-SP modified Au NPs revealed good stability in the dark as compared to other Au NPs light-induced reversible assembly (LIRA) systems. The aggregation and monodispersing phenomena also observed from change in diameter of the NPs measured by dynamic laser scattering after the exposure of UV and visible light respectively as shown in Fig. 3(C, D).

An alternative strategy was reported to achieve light-induced assembly of Au NPs by modifying SP dye with a thiol group. This chemically different approach does not rely on the attachment of Au NPs with SP-S. After exposure to UV light, the SP-S converted into the merocyanin (MC) form with negatively charged S atom, followed by attachment to Au NPs and subsequent aggregation [86]. They also found very interesting process related to assembly and disassembly behavior of Au NPs in the dark. The Au NPs have shown repulsive interactions in the dark which causes a stable suspension of Au NPs. In the UV/vis spectra, there was a visible change in wavelength from 450 nm to 531 nm as the isomerization of SP occurred under UV light. However, without using UV light even for 12 h the SP could not isomerize and the peak shift was not observed. Consecutive UV light irradiation of the solution resulted in repeated spectral change. This data suggested that SP undergoes reversible merocyanin isomerization by UV irradiation. The considerable factor regarding LIRA is the amount of SP-S, an increase of which caused intensive aggregation. Furthermore, UV light intensity and also the different forces those act between Au NPs cause

assembly and disassembly behavior. Hence, it is always required to modify SP with thiol containing groups. These groups could possibly be long chain but mostly short chain thiol groups have been used to achieve reversible assembly behavior of Au NPs. Short chain thiol containing SP groups have shown faster response as compared to long chain. Another interesting factor related to SP-S modified Au NPs is the involvement of attractive and repulsive forces in response to isomerization of SP-S under different wavelength of light.

Azobenzene ( $C_{12}H_{10}N_2$ ) is also a light-responsive molecule. But in case of spiropyran, the ring opening protonated merocyanin form ( $MCH^+$ ) and ring closing again transformation to spiropyran could be achieved by using light, while in the case of azobenzene the polarity difference can be induced by light. UV light can cause the formation of a highly polar form of azobenzene, and the non-polar form of azobenzene can be obtained using visible light. Manna et al. modified azobenzene with a thiol group and made possible the attachment of Au NPs with this thiolate modified azobenzene [87]. UV irradiation produced the polar form of azobenzene in solution and developed the assembly of Au NPs due to attractive forces while visible light created the disassembly of Au NPs because of conversion to the non-polar form.



Another study showed that azobenzene polarity could impact on the reversible assembly behavior of Au NPs. This was achieved by modifying the surface of Au NPs with thiol containing azobenzene molecule (4,4'-bis(11-mercaptopundecanoic) azobenzene (ADT)). Azobenzene must have two thiol groups on both ends to obtain the regular assembly of Au NPs. In this case, the Au NPs reversible assembly depends on the dipole-dipole interaction, light

**Table 1**  
Summary of external stimuli controlled assembly and reversible assembly of Au NPs.

Stimulus	Chemicals	Interaction and Assembly and Reversible assembly (NMTs and SPM)	Reference
<b>Light response</b>			
Assembly	Azobenzene	Chemical/Au NPs, Spherical Keplerate-type polyoxometalate, sugar (galactose/mannose)	[59–61]
Assembly	Arylazopyrazoles	Chemical/ cyclodextrin-functionalized Au NPs	[62]
Assembly	Spiropyran	Chemical/Au NPs, Au NRs,	[63,64]
Reversible assembly	Pillar[5]arenes	Chemical/Au NPs and anthracenes	[65]
Assembly	O-nitrobenzyl ester	Chemical/nanomaterials, the photocleavable block copolymer	[66]
Reversible assembly	Laser light induced assembly	Physical/Au triangle	[67]
Assembly	Dithienylethene (DTE) ligands	Chemical/ Pd3L6,	[68]
<b>pH response</b>			
Reversible assembly	PH, 4-mercaptobenzoic acid (4-MBA) and oleylamine (OL)	Covalent interactions/ AuNano vesicles	[69]
Reversible assembly	Poly (acrylic acid), (PAA) and (poly(N-isopropyl acrylamide), PNIPAM)	Chemical/magnetic nanoparticles	[70]
Reversible assembly	Polystyrene-block-poly(acrylic acid) and Rhodamine 123	Electrostatic attraction/ Au NPs	[71]
Assembly	Doxorubicins	Covalent/Au NPs	[72]
Reversible Assembly	Casein proteins	Chemical/ Ag NPs	[73]
Reversible assembly	DL-penicillamine and N-acetyl-DL-penicillamine	Covalent/Au and Ag nanoparticles	[74]
<b>Temperature response</b>			
Assembly	Poly poly[1-methyl-3-(2-methacryloyloxy propylimidazolium bromine)]-block-(N-isopropylacrylamide)	Covalent/Au NPs	[75]
Assembly	PNIPAM- <i>b</i> -PEG- <i>b</i> -PNIPAM	Physical/PNIPAM- <i>b</i> -PEG- <i>b</i> -PNIPAM nanoparticles	[76]
Reversible assembly	Oligo (ethylene Glycol)	Covalent interaction/Au NPs	[77]
Reversible assembly	poly (N-isopropylacrylamide-co-acrylic acid) with a pyridyl disulfide	Covalent/Vault nanoparticles (Protein)	[78]
Reversible assembly	Poly(N-isopropylacrylamide)	Covalent/Au NPs	[79]
<b>Molecular and voltage mediated response</b>			
Assembly	TiO <sub>2</sub> nanoparticles and Hamilton receptor	Hydrogen bonding/ Porphyrins	[80]
Reversible assembly	1-dodecanethiol and oleylamine	Ligand exchange/Cu, Ag nanocrystals	[81]
Reversible assembly	[2.2.2]cryptand, potassium picrate (K+(pic <sup>-</sup> )) and trifluoromethanesulfonic acid	Chemical/octadecyl guanine (G)	[82]
Reversible assembly	Voltage	Host-guest interaction/ poly(styrene)-beta-cyclodextrin and poly(ethylene oxide)-ferrocene	[83]

irradiation time and covalent binding between Au NPs. Theoretically, it is also explained that the main interaction between Au NPs was due to dipole-dipole interaction of isomerized form of ADT. Based on this evidence, adhesion energy  $E_{ad}$  when two particles of radii  $R$  come into proximity can be expressed as (Eq. (2)).

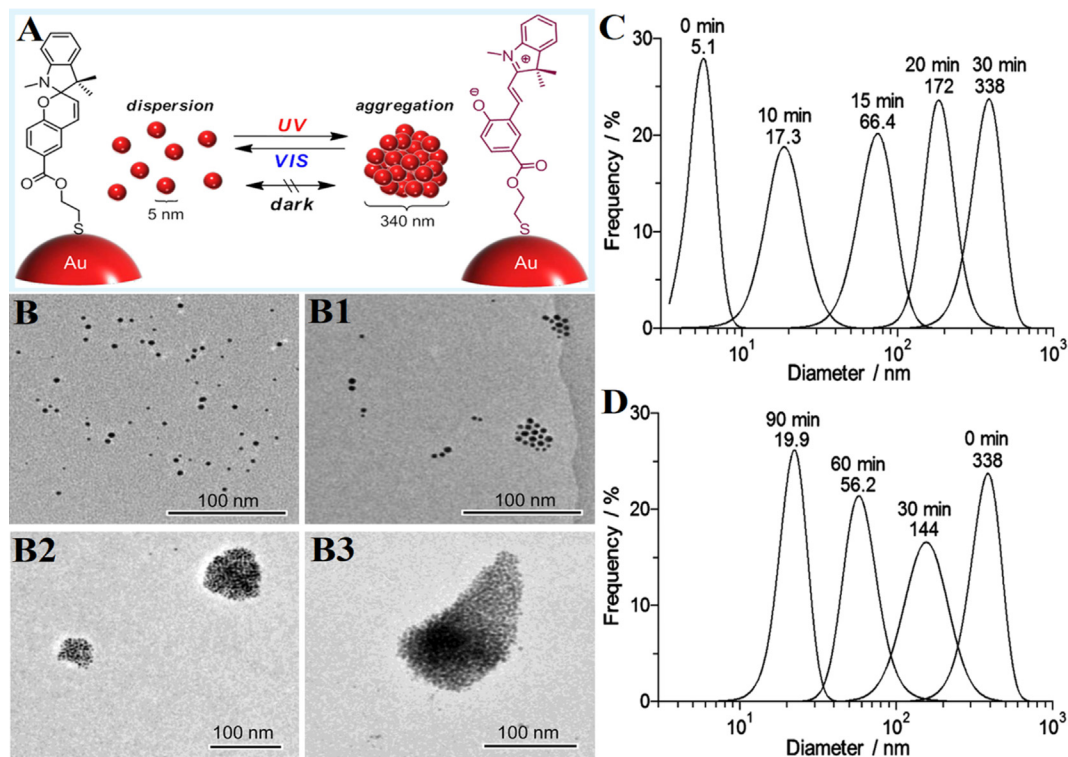
$$E_{ad} = A_{eff} (\sigma_{11} - 2\sigma_{12}) \quad (2)$$

where,  $A_{eff}$  is the contact area between two Au NPs,  $\sigma_{11}$  is the surface energy of two NPs, and  $\sigma_{12}$  is the surface energy between NPs and solvent interface. The effect of concentration of *cis*-ADT has played a key role in assembly/disassembly behavior. For example, if the concentration is high, reversible behavior will be diminished (Fig. 4A). TEM pictures correspond to a separate experiment and labeled as NP: unaggregated NPs, RC: light-reversible crystals, AP: amorphous precipitate, IC: irreversible crystals, and SS: supraspheres with the scale bar 100 nm. In fact, the reversible assembly of Au NPs is achieved under irradiation (365 nm) for this system (Fig. 4B). The problem related to azobenzene can be the difficulty in synthesizing thiol-modified light responsive molecules, as thiol modified SP or azobenzene are not available commercially, so researchers have to rely on different approaches to avoid these difficulties.

In this regard, He et al. synthesized coumarin modified Au NPs and the reversible assembly behavior was achieved by using photodimerization and photocleavage of the coumarin group in the

presence of 365 nm UV light as shown in Fig. 5A [88]. Not only light, but the assistance of tetrahydrofuran (THF) was also significant in this case as THF played two important roles. First, it assisted the dispersion of coumarin modified Au NPs and secondly it caused the electron donation in the coumarin modified Au NPs system to assure the photocleavage and rapid disassembly of Au NPs. In solution based chemistry, solvent has played a crucial characteristic along with the light responsive ligands.

In other light responsive molecules, aliphatic thiol containing groups have been used extensively. In order to examine whether there is any difference in assembly behavior by modifying aromatic Sulphur containing groups with a light responsive ligand, Oleksii et al. demonstrated a different approach which involved modification of Au NPs with UV and NIR responsive material (6-nitro BIPS spiropyran (SP) modified with a disulfide-terminated aliphatic chain) as illustrated in Fig. 5B [89]. Basically, the SP modified systems present the same concept for reversible assembly as that of spiropyran/merocyanine forms under blue light or UV irradiation, but here NIR (785 nm) also induced the ring opening mechanism which is an important factor for drug delivery approaches. Hence, by modifying the surface of Au NPs with different wavelength absorbers, it is possible to cover a wide range of light wavelength and such systems could possibly be used in advanced applications including capture and release of different molecules/drugs under light.



**Fig. 3.** (A) Mechanism of UV/vis light-induced reversible assembly of Au NPs modified with spiropyran, (B) TEM images of well dispersed Au NPs, (B1–B3) 10, 15 and 20 min UV irradiation of particles, (C) time dependent change in diameter of the particles under the UV, and (D) visible light irradiation. Reproduced with permission from Ref. [85]. Copyright (2014) American Chemical Society.

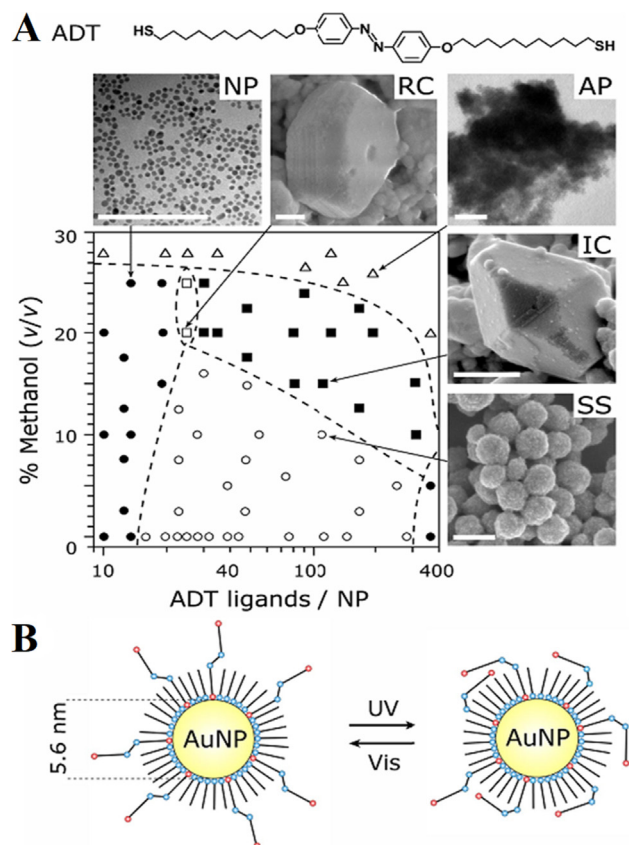
Light controlled reversible assembly of photoresponsive ligands attached to Au NPs has also been utilized in catalytic activity. In this context, Wei et al. reported the catalytic control of azobenzene modified Au NPs (Fig. 5C) [90]. In the presence of UV light, aggregation commenced due to the conversion of molecules from trans to cis form with dipole moment valued 5 debye, hence total solvent exposed area for the nanoparticles reduced which caused the switch off phenomenon. Kundu et al. utilized the SP light responsive molecule which can be converted to another colored form using blue UV light (365 nm) (Fig. 5D) [91]. The surface of Au NPs was modified with 11-mercaptoundecanoic acid (MUA), and after the addition of SP, assembly of nanoparticles was achieved in solution due to spontaneous formation of MCH<sup>+</sup>. Then, the disassembly behavior of Au NPs was obtained by using blue light which transforms the aggregation of Au NPs into a mono-dispersion with the formation of SP via proton donation. Whereas, the reverse behavior was obtained spontaneously, as SP is acting as a base. The assembly and disassembly behavior is triggered by protons and it is not surprising to get the reversible assembly behavior by using the acid-base system. Although all the above-mentioned groups have done extensive work with different applications like catalysis, self-erasing inks and making images by using nanoparticle assembly/disassembly by light, but the processes have been carried out in either polar or non-polar solvents.

Few reports have focused on the controlled assembly/disassembly behavior of Au NPs using light, which can lead to changes in plasmonic, optical and electrical properties. Based on this concept, Zhang et al. presented oligomer formation of amphiphilic Au NPs by using UV light. They designed a new approach for the light-induced formation of oligomers, Au NPs modified with hydrophilic polyethylene glycol and hydrophobic polymethacrylate containing SP by Atom Transfer Radical Polymerization (ATRP) [92]. Firstly, the hydrophilicity of polyethylene modified Au NPs causes con-

trolled aggregation and then UV light induced oligomer formation which showed reversible behavior under visible light.

Mostly, researchers have studied light induced reversible assembly (LIRA) by modification of Au NPs with light responsive molecules or polymers. However, a feasible approach without the light responsive moiety on Au NPs has been explained by Ding et al. [93]. They utilized the concept of laser-induced heating capability to control reversible aggregation of Au NPs in solution as shown in Fig. 6(A–F). A ligand exchange method was used to replace citrate with Poly-N-isopropyl acrylamide (PNIPAm). Amine groups of Poly-N-isopropyl acrylamide bind with Au NPs, as PNIPAm has the lower critical temperature about 32 °C. Therefore, Au NPs generated heat about 33 °C after the laser irradiation. At lower critical temperature, PNIPAm converts from chain to coil form and induced the aggregation of nanoparticles. The change in UV spectra from 535 nm to 631 nm is evidence for aggregation of nanoparticles upon laser heating (Fig. 6B). An advantage of this innovative work is not just related to non-photoresponsive reversible assembly of PNIPAm modified Au NPs, but also the advancement in nanoactuators due to chain opening and closing of PNIPAm. After the laser irradiation, the opening of PNIPAm is fast enough to provide an elastic force that can cause disassembly of nanoparticles and this produces an actuating phenomenon. The mechanically simple approach by using low-intensity laser light for heating of Au NPs due to plasmonic photothermal effect causes the reversible switch between individual and aggregated Au NPs to be successfully observed.

In another study, Lin et al. described the laser-induced assembly and disassembly of Au nanotriangles (Au NTs) by exploiting the plasmonic thermal behavior of Au NPs [67]. The interesting feature of this work related to Au NTs assembly can only be observed on the plasmonic substrate utilizing the plasmonic and heating properties of Au NPs Fig. 6(G–H). Non-photoresponsive surfactant



**Fig. 4.** Phase illustration and mechanism related to light induced self-assembly (LISA). (A Top) photoswitchable dithiol azobenzene ligand (ADT) facilitated LISA of gold nanoparticles. By using a different concentration of methanol in biphasic methanol/toluene mixture the (lower A) phase diagram shows different suprastructures obtained for a different number of ADT adsorbed on the nanoparticles. (B) The azobenzene groups of ADT ligands can be switched between trans and cis with the help of UV and visible light. Reproduced with permission from Ref. [23]. Copyright (2007) National Academy of Sciences of United States of America (NAS).

(cetyltrimethylammonium chloride) modified Au NPs were directed towards the laser spot at the interface between a plasmonic substrate and the nanoparticle dispersion. Further simulation and experimental results revealed that the plasmon-enhanced temperature-gradient field and the thermally persuaded local electric field induced delivery and assembly of gold nanoparticles. According to above mentioned strategies, it is obvious that stimuli responsive ligands and polymers are required to attach on the surface of Au NPs. Furthermore, a specific wavelength of light and specific temperature increase induced by laser is compulsory for reversible assembly of Au NPs.

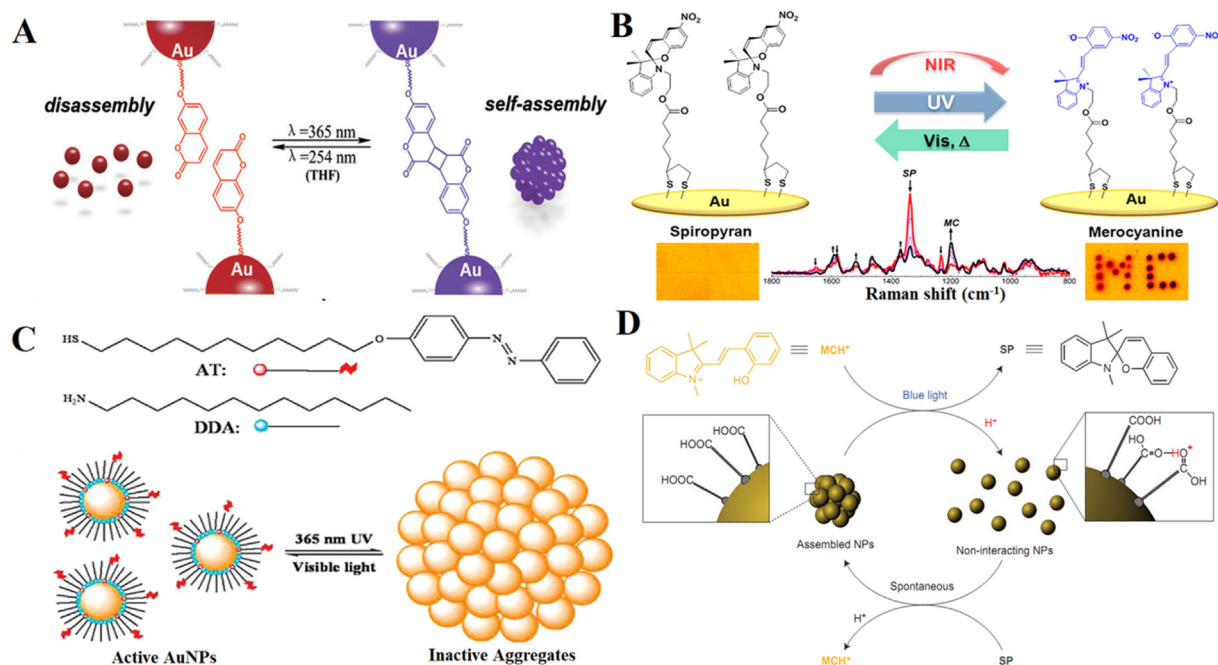
Recently, the concept of surface modification of Au NPs with ligands and polymers changed to block co-polymers as comparatively more complex systems are introduced, being useful for tuning the properties of Au NPs by using light. The mechanism behind the distribution of Au NPs in block co-polymers considered changes in amphiphilicity of the material. In this perspective, Song et al. demonstrated a diverse approach by utilizing poly(styrene)-*b*-poly(*o* nitrobenzene acrylate) (PS-*b*-PNBA) modified Au NPs [94]. By exposure to UV light, the deprotonation of the poly(*o*-nitrobenzene acrylate) leads to the formation of the hydrophilic block containing poly(acrylic acid) (PAA) which further interacted with poly(2-vinylpyridine) (P2VP) of the PS-*b*-P2VP matrix by hydrogen bonding and developed the assembly of Au NPs in block co-polymer system. Although it is not reversible but it is interesting to see the patterned assembly for block copolymers.

Light is always considered to be the safer stimulus and can be used as activation source for Au NPs to study biocompatible systems like in vivo studies, drug delivery and molecular imaging. Therefore, by utilizing the interaction between thiol containing DNA modified with Au NPs- azobenzene molecules, a light responsive reversible assembly behavior was successfully achieved and well explained by Yan et al. [95]. When light of specific wavelength (365 nm) irradiated the sample, the trans to cis conversion of azobenzene destabilized the DNA duplex which further resulted in the disassembly of Au NPs. The reverse isomerization using blue light causes the assembly of Au NPs (Fig. 7A). Likewise, Cheng et al. studied the similar mechanism of reversible assembly of non-photoresponsive nanoparticles by utilizing the proton release mechanism of a photoacid named as diphenyl iodonium nitrate (DPN) [96]. Firstly, Au NPs were modified with spiropyran bases and then the introduction of DPN produced the assembly and disassembly of Au NPs upon generation of the proton by DPN under light irradiation. The particles had a red color in the presence of DPN, while upon irradiation with UV light the assembly behavior can be seen clearly. 4-[1-(lipoic acid ester-polyethylene glycol (11–13)-ester)]-phenylboronic acid (SPB) also shows pH-responsive behavior and the presence of DPN (5 mM) cause 3.5 units decrease in pH of the solution which induces possible interactions with the assembly of Au NPs. Furthermore, the decrease in pH from 6.7 to 4.7 resulted in the aggregation of Au NPs, and by reversing the pH the reversible assembly of Au NPs was observed (Fig. 7B). To further demonstrate the concept of the reversible assembly of Au NPs functionalized with a polymer, Chen et al. reported a new class of Au NPs modified with star-like amphiphilic diblock co-polymer named poly(acrylic acid)-block-poly(7-methylacryloyloxy-4-methyl coumarin) (PAA@PMMA) [97]. To control the molecular weight of polymer, atom transfer radical polymerization (ATRP) was introduced and different parameters such as pH, temperature, and concentration of polymer influenced on the size of Au NPs. The assembly behavior was achieved using 365 nm UV light causing photo cross-linking of polymer PMMA with coumarin. Furthermore, the disassembly can be processed under 254 nm light irradiation with the photocleavage of PMMA chain that is functionalized on the surface of Au NPs as illustrated in Fig. 7C.

The reversible assembly feature is not limited to spherical Au NPs but also the end to end and side by side reversible assembly of gold nanorods (Au NRs) has been successfully demonstrated [98]. Au NRs present special optical and plasmonic properties with enhanced applications like photothermal therapy, cancer imaging, SERS, and biosensing but few strategies have focused on the reversible assembly of Au NRs [99–101].

Similarly, by controlling the interactions between different surfactant modified Au NRs, reversible assembly behavior was achieved using near infrared light (NIR) as stimulus by Huang, et al. [98]. They designed a simple scheme by modifying the Au NRs surface with elastin-like polypeptide (ELP) and obtained the assemblies by NIR irradiation (Fig. 8A). The aggregation of Au NRs-ELP assemblies occurred due to the transferable heating effect of NRs to ELP which induced phase transformation and aggregation. Basically, the temperature of the NRs increased due to NIR irradiation and reached lower critical solution temperature (LCST) of a polypeptide which further caused transformation in structure and induced assembly of NRs, while in the absence of NIR light the monodispersed NRs were observed. In addition, reversible assembly of Au NRs containing dithiolane modified SP was demonstrated by Mochizuki et al [64]. The photoisomerization of SP has shown a quick response to the specific wavelength of light which leads to assembly and disassembly behavior.

Similarly, Wu et al. explained the reversible dispersion of Au NRs by utilizing the host-guest interactional study of thiol-



**Fig. 5.** (A) Light-induced reversible assembly of coumarin modified Au NPs under different wavelengths of light in the presence of tetrahydrofuran, (B) representation of a photoswitchable Au NPs system and newly synthesized SP modified on the surface of Au NPs and UV/visible, NIR induced reversible assembly for SERS and light-induced writing, (C) molecular structures of the "background" didodecylamine (DDA) surfactant and of the photoresponsive azobenzene-thiol ligand, AT, and (D) assembly of COOH group modified Au NPs in a photoswitchable medium containing MCH<sup>+</sup>. Under irradiation of blue light, the pH of the system decreased and caused disassembly of nanoparticles. While in the dark reassembly of the particles occurs spontaneously. Reproduced with permission from Refs. [88–91]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Copyright (2016, 2013, 2010, 2015) Wiley Vch Verlag GmbH & Co. KGaA, Weinheim, American Chemical Society and Springer Nature.

modified beta-cyclodextrin [102]. The host-guest interaction can occur between beta-cyclodextrin and di-azo functionalized monomer. Then, thiol-containing beta-cyclodextrin interacts with Au NRs through a covalent interaction. Irradiation of 365 nm light further produced the breakage of host-guest interaction which leads to dispersion of Au NRs in the solution. Additionally, the homogeneous dispersion of Au NRs can be obtained by the addition of acid (HCl) due to guest competition (Fig. 8B). The TEM analysis of modified Au NRs confirmed the assembly during irradiation of light (254 nm) and also disassembly of nanorods can be clearly seen in Fig. 8C(a–d) after irradiating at 365 nm.

In some cases, light response not only can create the assembly of nanoparticles but it can also modify the shape of NPs such as the conversion of nanoparticles into nanovesicles with the help of UV irradiation [103]. The main concept of conversion of different shapes of nanoparticles can be made possible by utilizing different methods like etching, light response, and laser irradiation. The conversion of nanospheres to nanorods using the above mentioned methods will have a great impact on synthesis. In the context of the light-induced shape change of nanomaterial, Bian et al. achieved the conversion of thiol-modified Pt-NPs, Au NPs, Pd-NP, and Cd-Se quantum dots into nanovesicles by applying UV light [104]. The Au NPs modified with a thiol molecule with a chromophoric end group 7-(12-mercaptododecyloxy)-2H-chromen-2-one (MDC) in oleylamine cause the formation of vesicles under UV light of (300–400 nm) wavelength. TEM images Fig. 9(A–D) of Au NPs capped with dodecanethiol and polyamine in the presence of two phasic solvent system containing toluene/butanone. It is interesting to know that without using some chromophore, a fine response of light attained in the assembly behavior but type of solvent and polarity played a great role in assembly behavior. Recently, Rival et al. modified Au<sub>25</sub> nanoclusters with thiolated azobenzene to acquire reversible assembly upon the irradiation

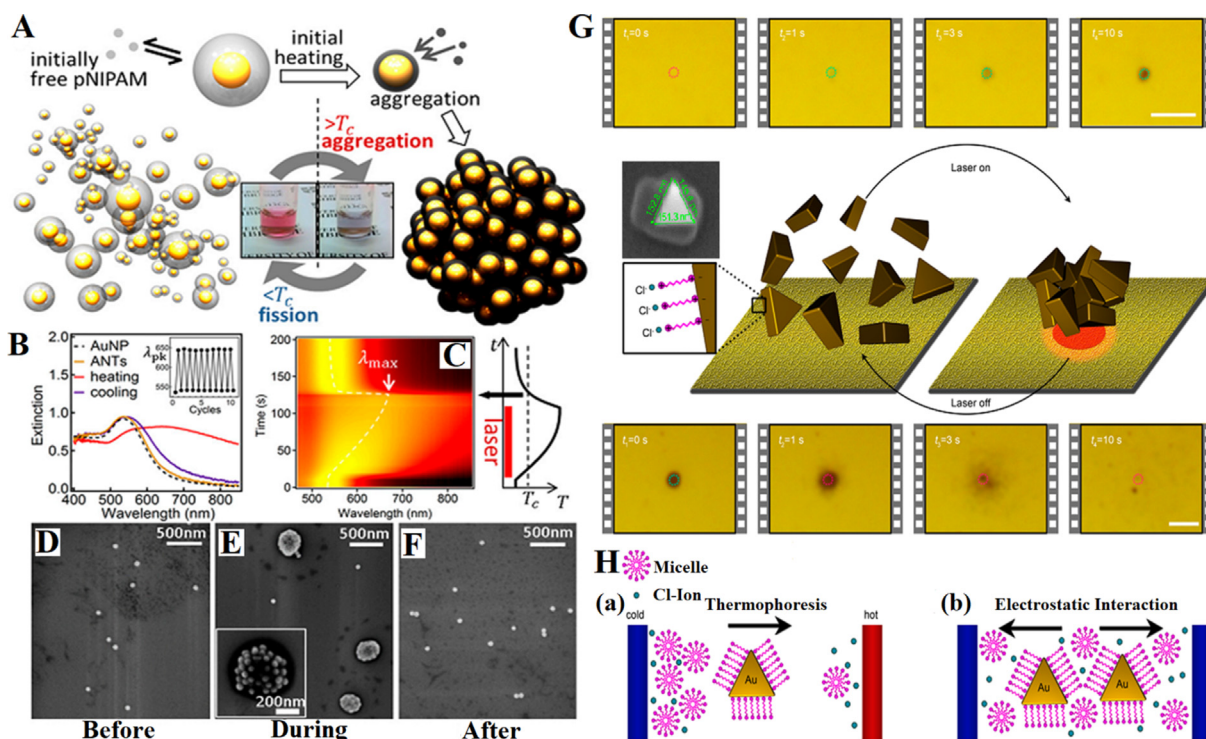
of different wavelength of light. Under the irradiation of 345 nm UV light, disc like colloidal nanoclusters were assembled with diameter ranging from 100 to 1000 nm, while these superstructures readily disassembled into individual nanocluster at 435 nm wavelength of light (Fig. 9E) [105]. The mechanism of assembly and disassembly of these nanoclusters followed similar chemistry of photoisomerization as explained earlier. Researchers proposed a unique observation based on their experimental results that induce assembly of NPs shown in Fig. 9F. After irradiation of UV light, mercapto groups on the surface of Au NPs oxidized to sulfonic groups in the presence of biphasic solvent system. The oxidized sulfonic group had a weaker interaction with the Au NPs and caused partial detachment. This further increased the attractive forces between Au NPs and induced aggregation. A similar type of assembly/disassembly phenomena was observed in some other materials such as Ag and TiO<sub>2</sub>.

Hitherto, the reversible assembly of Au NPs under irradiation of light has been reviewed, covering a wide range of light responsive ligands. Light is the cheapest source that can be utilized for such an interesting phenomenon and could possibly cause a great impact on stimuli responsive nanomaterials applications in controlled catalysis and biomedical. It is possible to continue and stop the catalytic process by irradiating light on the light responsive nanoparticles. Hence, the synthesis of new small ligands, polymers, and biocompatible molecules which respond to light will always open new path towards the stimuli responsive assembly and disassembly behavior of Au NPs.

### 3.2. pH-responsive reversible assembly of Au NPs

It is well known that the surface chemistry of Au NPs played an eminent contribution in stability and dispersion of NPs. Highly positive or negative surface charge can persuade assembly and dis-





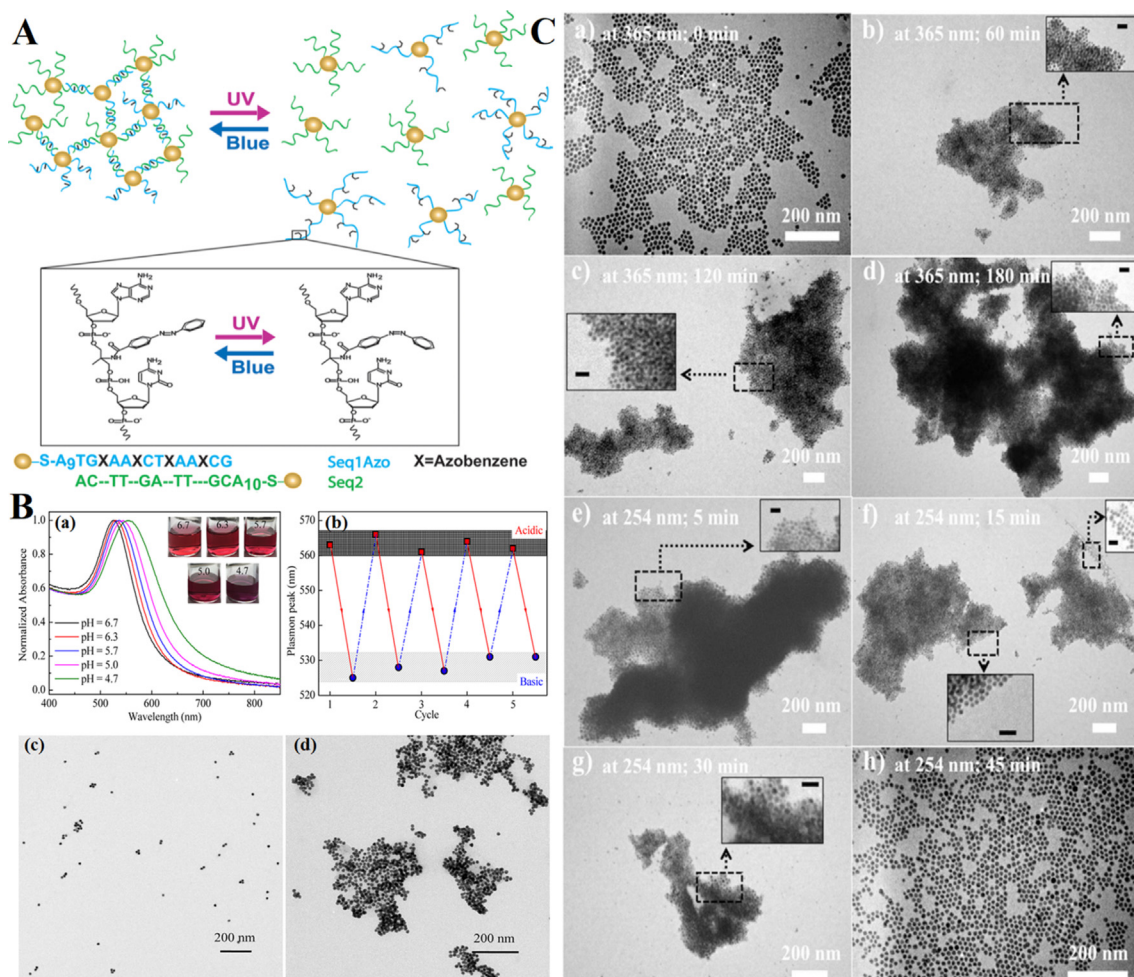
**Fig. 6.** Reversible assembly of actuating nano transducers. (A) schematic of reversible assembly of Au NPs and attachment of PNIPAM, below is the temperature-induced reversible assembly and color change from red to little black vice versa, (B) UV spectra for Au NP, actuating nano transducers, during heating and after heating peak change, (D-F) TEM images of Au NPs before, during and after laser irradiation (10 W/cm<sup>2</sup> for 5 min) respectively and (G) mechanism of assembly of Au NTs (H) Working principle of light-directed reversible assembly of plasmonic nanoparticles (using Au NTs as an illustrative example). (a) Schematic illustration of the migration of a CTA<sup>-</sup>-modified Au NTs from cold to the hot region in the light-induced temperature-gradient field, which is known as thermophoresis. (b) Schematic illustration of the release or redispersion of an Au NTs assembly due to electrostatic repulsive interaction when the laser is off and the temperature-gradient field disappears. Simulated temperature distribution at the interface between the plasmonic substrate and particle solution in a cross-sectional view. Reproduced with permission from Refs. [93,67]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Copyright (2016) National Academy of Sciences of United States of America (NAS) and American Chemical Society.

assembly behavior of Au NPs dependent on the solvent type (polar or non-polar). Hence, by modulating pH, the chemistry of terminal groups attached on the surface of Au NPs could induce reversible assembly. This section will focus on the pH responsive assembly/disassembly behavior of Au NPs [106]. pH change by drafting of acid or base has an impact on the assembly and disassembly of Au NPs and also avoids the formation of toxic residuals which can damage e.g. DNA-NPs systems [107]. For instance, Qian et al. designed a unique structure by modifying Au NPs with pH-responsive poly methacrylic acid, amphiphilic poly ethylene glycol block and a terminal lipoic acid anchoring group [108]. The polymer structure collapsed at pH > 4 and demonstrated the aggregation of nanoparticles, while at lower pH < 3 the individual particles regained their plasmonic peak. The particle size decreased from 85 nm to 65 nm with pH change from 7 to 3 respectively. Mostly, pH-responsive behavior was achieved using polymers like poly-acrylic acid (PAA), poly-(N-isopropyl acrylamide (PNIPAm), Polystyrene-block-poly(acrylic acid), polymethacrylic acid (PMAA), and an amphiphilic polyethylene glycol (PEG).

The assembly behavior of Au NPs utilizing pH responsive materials has been discussed by many researchers. The interaction mechanism involved in pH-responsive assembly/disassembly of Au NPs is based on hydrogen bonding interaction as in case of DNA modified Au NPs systems. Further, hydrophobic interactions, electrostatic interactions between the Au NPs and pH-responsive materials, van der Waals interactions manipulation, and bonding between surfactant covered different aspects of reversible assembly behavior [109,110]. In this regard, the pH-responsive reversible assembly has been successfully attained by synthesizing thiol con-

taining oligonucleotide-modified Au NPs system [111]. In this system, Oligo A and Oligo B contained different bases sequence attached with Au NPs with triplex formation under pH < 5 observed due to protonation of the oligonucleotides and lowered repulsion between the phosphate groups of Oligo A and Oligo B resulting in assembly of Au NPs – see Fig. 10A. A similar case was reported by Chen et al. such as Au NPs modified with Oligo A and Oligo B but different sequence of bases [112]. The triplex to duplex conversion at pH values from 6.5 to 8.0 respectively caused the association and dissociation of Au NPs modified with Oligo A and Oligo B as demonstrated in Fig. 10B.

Regarding DNA modified Au NPs, research directions have been moving toward simple/effective methods for surface modification of Au NPs. As previously mentioned, the indirect change in pH has been observed by utilizing light source as stimuli and protonation/deprotonation behavior was achieved. Consequently, commonly used surfactants have also been utilized for the pH-responsive reversible assembly of Au NPs. Moaseri et al. described a system of Au NPs (5 nm) modified with glutathione (GSH) to form clusters (20–100 nm) in response to pH (Fig. 10C) [113]. The pH window for GSH modified Au NPs was about pH 5.6 to 3.8. At lower pH, the GSH converted into its zwitterionic form that causes intra hydrogen bonding and resulted in the limited nanocluster formation of Au NPs. Although, citrate had inhibited the growth of clusters and it was also helpful to study the diameter of clusters that can be cycled reversibly multiple times by varying the pH. Recently, Park et al. has demonstrated that Au NPs modified with single stranded DNA and cytochrome at acidic pH (5.5) assemble due to electrostatic interactions. While at higher pH pro-



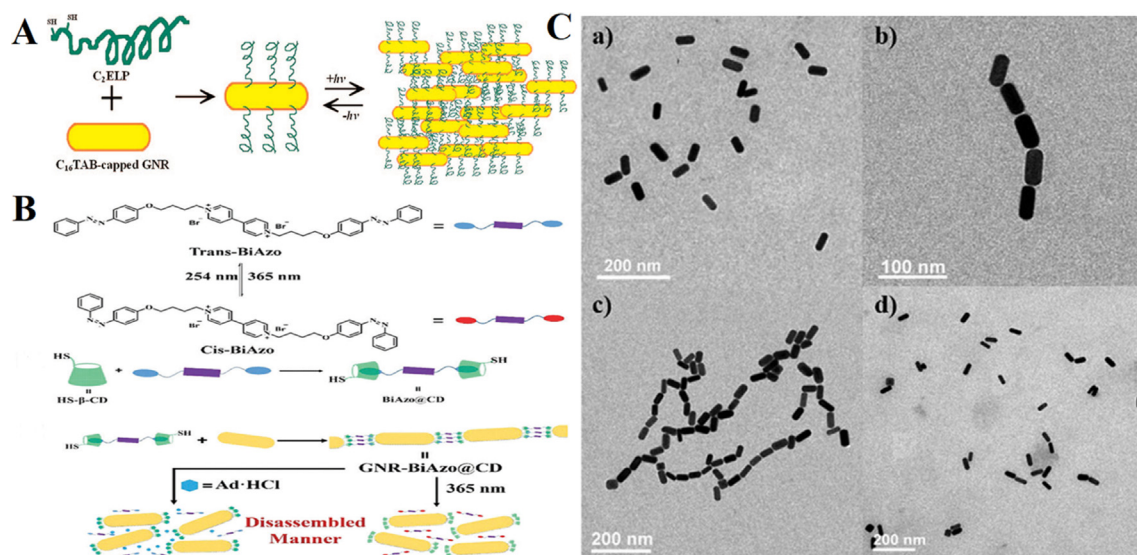
**Fig. 7.** (A) Reversible assembly of azobenzene modified DNA-functionalized Au NPs conjugates, (B) time-dependent UV – vis spectral change of SPB-functionalized Au NPs in the presence of DIN under light (a), plasmonic peaks of Au NPs at 5 mM DIN (b), and TEM images of SPB-functionalized Au NP dispersion in the presence of 5 mM DIN before (c) and after (d) UV irradiation for 16 min. (C) reversible assembly of PMAMC capped Au NPs. TEM images of PMAMC-capped Au NPs after the PMAMC-capped Au NPs solution was visible to 365-nm UV light (a-d) with time (a)  $t = 0$  min, (b)  $t = 60$  min, (c)  $t = 120$  min, and (d)  $t = 180$  min of irradiation, and (e and f) 254-nm UV light for a given time (e)  $t' = 5$  min, (f)  $t' = 15$  min, (g)  $t' = 30$  min, and (h)  $t' = 45$  min. (Scale bars: Insets, 50 nm.) 365-nm UV exposure times are. Under 365-nm UV light irradiation, the assembly behavior is visible (a-d) while after irradiating the Au NPs with 254-nm light the dispersion of Au NPs was observed (e-g). Reproduced with permission from Refs. [95–97]. Copyright (2012, 2018, 2018) American Chemical Society and National Academy of Sciences of United States of America (NAS).

ton transfer caused electrostatic repulsion between Au NPs (Fig. 10D) [114].

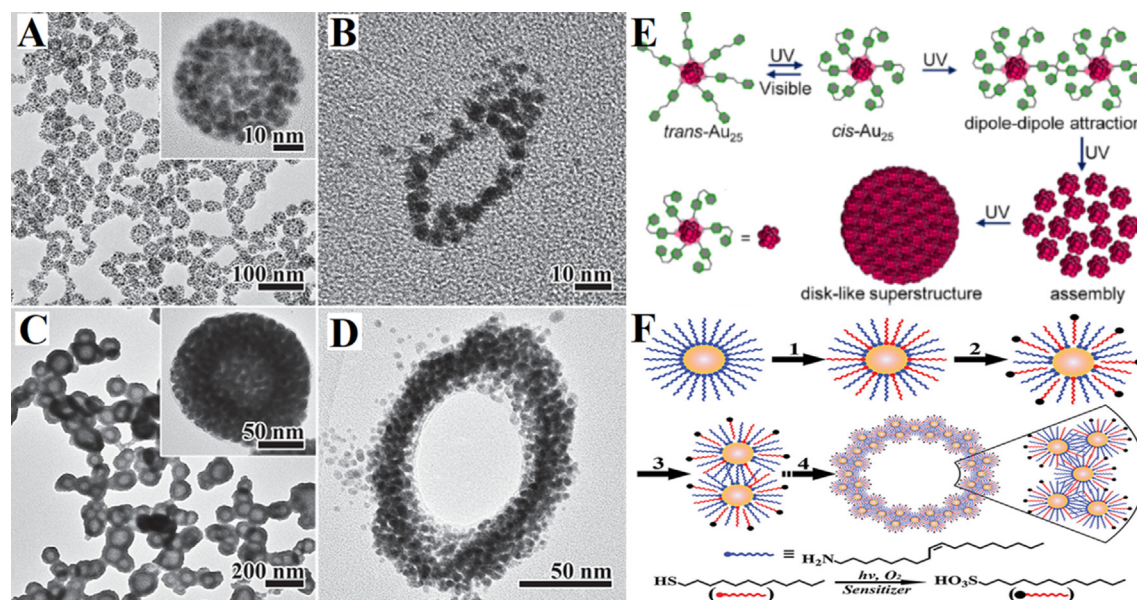
Ma et al. reported pH response of tertiary amine and PEG-modified Au NPs, where manipulation of hydrophobic and steric interactions was taken into account [115]. As the PEG ligand results in steric repulsion between Au NPs, it can cause the dissociation of Au NPs. But the assembly behavior of NPs could be achieved successfully if the hydrophobic interactions can be overcome. The assembly behavior of Au NPs due to decrease in pH, deprotonation of tertiary amines causes an increase in hydrophobic interactions which are dominant over repulsive interactions, leading toward assembly. UV visible spectroscopy, the naked eye and TEM are the best techniques regarding confirmation of the assembly and disassembly behavior of Au NPs induced by pH change. For example, Liu et al. designed Au NPs conjugated with “i-motif” DNA as a pH-responsive system to achieve assembly and disassembly behavior [116]. They prepared two samples Au NPs (15 nm) containing DNA strands at pH = 8 with different DNA strand length, one was about 30-mer and second was 27-mer in length, with 3C-T mismatches on second strand. These NPs were dispersed well in buffer solution (pH = 8.0) and both samples have shown a UV peak at about 523 nm. After fixation

of these two samples, a duplex of DNA formed which caused movement of Au NPs close to each other and induced a peak shift to about 563 nm with a color change to purple, indicating the formation of assemblies of Au NPs. Furthermore, upon addition of HCl, the pH of the solution was maintained at 5 and visible color change appeared (red) with Au NPs dispersion giving rise to a UV peak at 523 nm due to the formation of the quadruplex structure because of base intercalation. This change was reversible upon addition of NaOH (0.1 M). The UV visible spectral change according to the state of Au NPs was recorded from 523 nm to 563 nm.

In another report, Hazarika et al. designed a DNA mediated approach to induce reversible aggregation of Au NPs. By taking advantage of two complementary fueling oligonucleotides Fa and Fd as shown in Fig. 11A, the reversible aggregation of Au NPs was observed [107]. Transformation mainly started from the state where the DNA modified Au NPs has shown a plasmon resonance peak at about 526 nm. The aggregation of Au NPs occurred after the addition of 32 equivalents of oligomer Fa and peak shifted to 625 nm state II. Assembly of Au NPs dispersed in block copolymers can be achieved by using light as stimulus. In a recent perspective, the arrangement of Au NPs in polymers has been attained by different researchers, which depends on the distribu-



**Fig. 8.** (A) Schematic of light responsive Au NRs modified with polypeptides, (B) schematics representation of trans to cis isomerization of biazobenzene molecule, complex synthesis of BiAzobenzene@cyclodextrin (1:2), preparation of Au NRs-BiAzo@CD by the attachment of Au NRs with BiAzobenzene@cyclodextrin and finally end-to-end assembly by irradiation of 365 nm UV light or adding Ad-HCl. (C) TEM images of (a) Au NRs-BiAzo@CD (b, c) assemblies of modified Au NRs irradiation under 254 nm light (d) disassembly of functionalized Au NRs under 365 nm light. Reproduced with permission from Refs. [98,102]. Copyright (2008, 2017) American Chemical Society and The Royal Society of Chemistry.

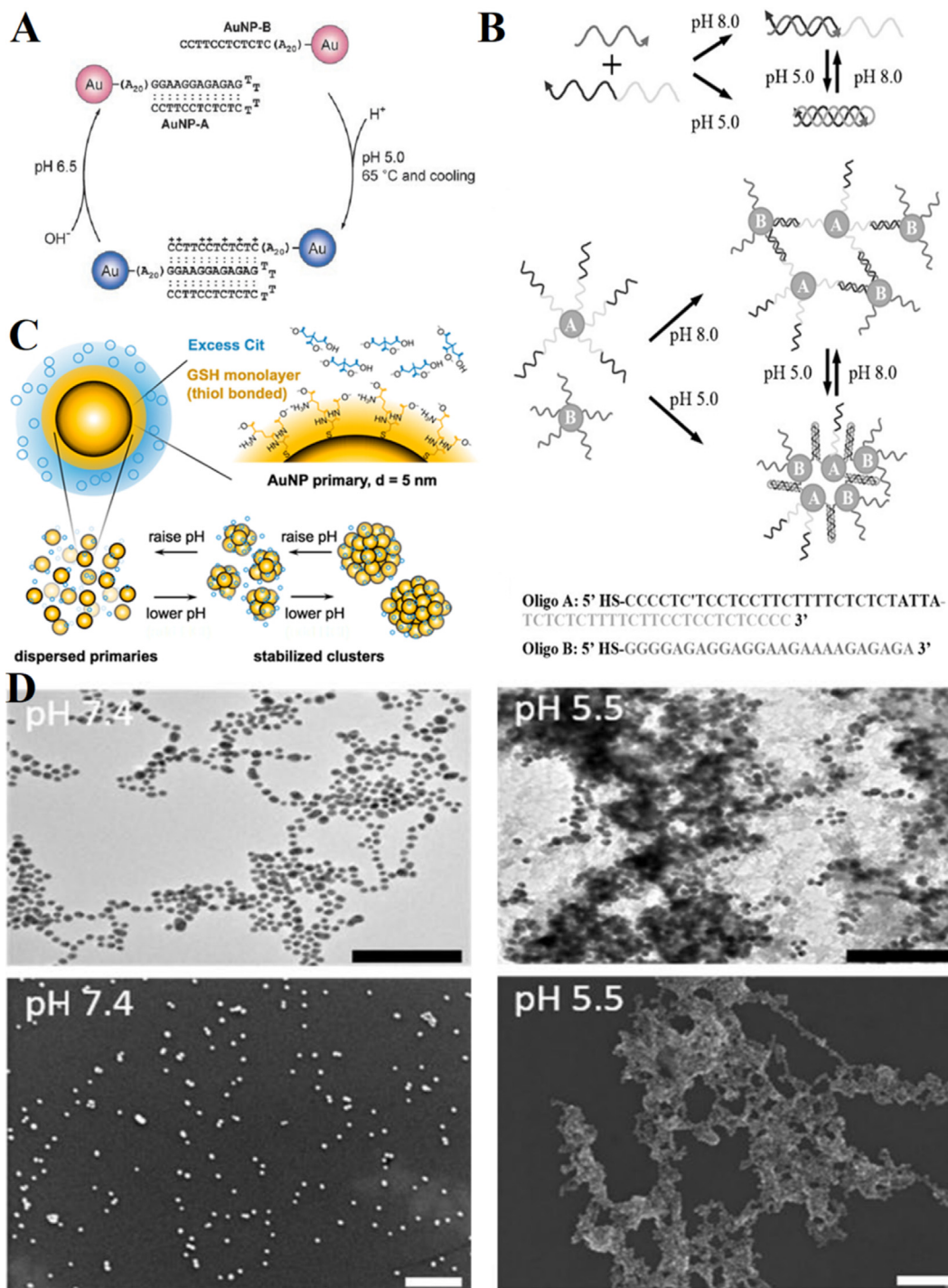


**Fig. 9.** (A, C) TEM images of overhead view and (B, D) cross-section of vesicles assembled from MDC/OL-capped Au NPs upon UV irradiation (300–400 nm) in (A, B) toluene/acetone and in (C, D), toluene/butanone solvent mixture. (E) Light mediated reversible assembly of Au nanoclusters and (F) Schematic diagram of light induced assembly of Au NPs into nanovesicles by light triggered oxidation of mercapto group to sulfonic group.: 1. ligand exchange with SH groups; 2. under UV light irradiation; 3. Rearrangement of ligand and self-assembly of Au NPs; 4. incessant assembly behavior. Reproduced with permission from Refs. [104,105]. Copyright (2014, 2020) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and American Chemical Society.

tion of Au NPs after surface modification with some polymers. In addition, by changing the concentration of surfactants, the assembly of Au NPs in polymers has been achieved successfully. Fan et al. described the pH-responsive reversible assembly of Au nanovesicles [69]. Au NPs were modified with 4-mercaptobenzoic acid (4-MBA) and oleylamine cause the protonation and deprotonation of 4-MBA which leads to self-assembly and disassembly of Au NPs (Fig. 11B). From an application point of view, rhodamine was loaded onto the surface of Au NPs to investigate the drug delivery concept and successfully carried out by varying the pH value. The most important phenomenon in the case of Au NPs was naked eye

detection, as the color of the sample changed from red to purple for monodispersed nanoparticles to aggregated nanoparticles, respectively. The color change phenomenon from red to purple in case of 11- mercaptoundecanoic acid (MUA) modified Au NPs was also observed. The addition of base causes the color change of Au NPs from red to purple while the reverse case can be seen upon addition of acid. Similarly, other researchers have explained this color change mechanism for reversible assembly of Au NPs by using the concept of external stimuli [117,118].

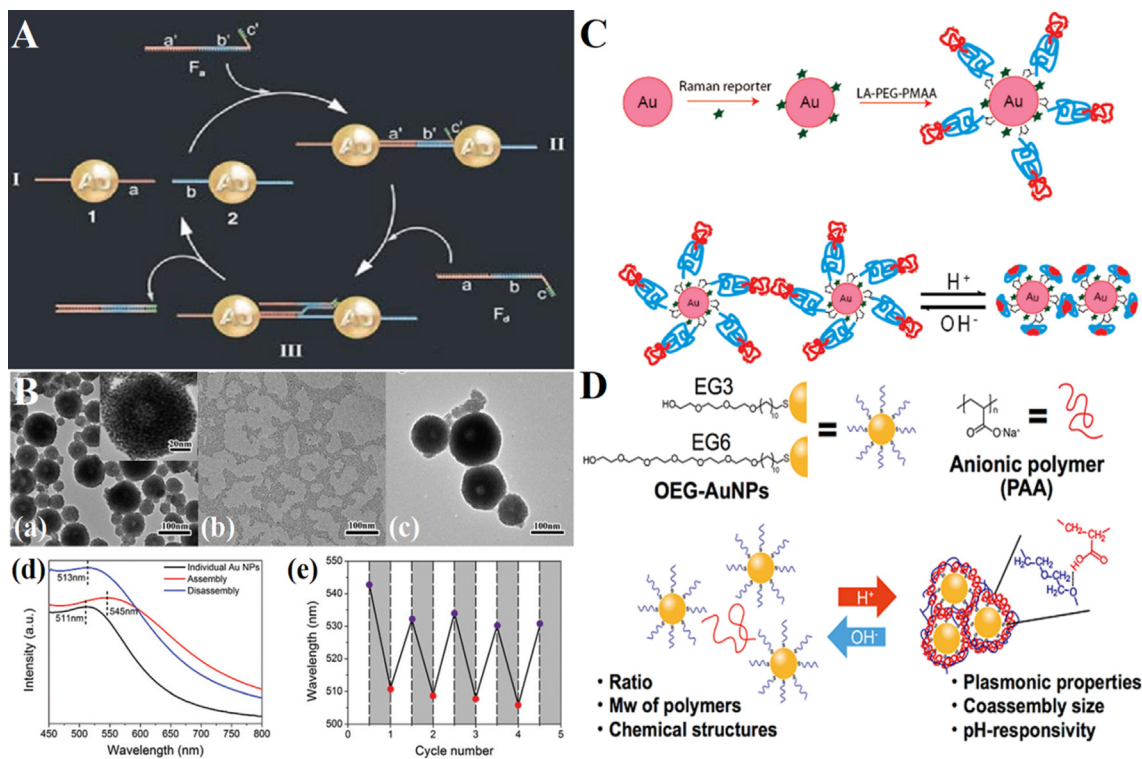
By using TEM, particle agglomeration and dispersion might be clearly observed. Simultaneously, the change in the wavelength



**Fig. 10.** (A) Assembly behavior of Au NPs conjugates at different pH value. C + is used for the protonated cytosine. Numerous duplicates of oligonucleotides presented on the single Au NP surface; only single oligonucleotide has been shown for demonstration. Three-dimensional networks of Au NPs obtained with the triplex-driven assembly of Au NPs. (B) Illustration of the control in the interparticle spacing of Au NPs aggregates based on DNA triplex formation under different pH value. The top is the schematic of the construction/separation of a cytosine-containing DNA triplex that is stable at pH = 5. In the middle, Au NPs (NP-A and NP-B) modified with oligos A and B form aggregates upon mixing. The interparticle separation in Au NPs aggregates is greater at pH 8.0 than at pH 5.0. With the change in pH of solution, the two states of assembly and disassembly can be switched as triplexes can form and dissociate. At the bottom is DNA sequences of the DNA strands used for this system. (C) Illustration of the reversible assembly of the glutathione functionalized Au NPs in the presence of citrate, on decrease in pH cluster size increased to limited extent. (D) TEM images of reversible assembly of Au NPs at different pH values. Reproduced with permission from Refs. [111–114]. Copyright (2006, 2008, 2017, 2019) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and American Chemical Society, Springer Nature.

of the plasmonic peaks further provided strong evidence regarding nanoparticle aggregation and dispersion. The reversible assembly behavior is not only limited to Au but also Ag nanoparticles have shown the same observable behavior. In the case of casein modi-

fied Ag nanoparticles, the pH-dependent reversible assembly behavior was attained [73]. At higher pH > 7 the disassembly behavior of Ag nanoparticles realized and at lower pH < 3.3 the dispersible response obtained. In this regard, Qian et al. explained



**Fig. 11.** (A) Mechanism of the reversible assembly of DNA modified Au NPs exploiting fueling oligonucleotides Fa and Fd. Fa contains three stretches (a', b', and c', that are attached with the Au NPs-bound 12-mer oligomers, a and b). Stretch c' systems a flaccid end in the aggregated particles (state II), which endorses the hybridisation of Fa and Fd (Phase III i.e. intermediate state). (B) From top to bottom (a,b,c) TEM images of self-assembly of Au nanovesicles and disassembly into Au NPs along with again reassembly into nanovesicles, (d) UV-visible spectra of assembled Au nanovesicles, disassembled Au NPs, and original Au NPs, (e) base and acid-induced reversible change in surface plasmon resonance absorption peaks of Au nanovesicles and Au NPs. (C) Synthesis of dye-coated Au NPs, aggregation of nanoparticles induced by conformational changes in polymer results in plasmonic coupling and SERS, each Au NPs (60 nm) was coated with ~1,000 organic dyes molecules and further encapsulated with PEGPMAA copolymer molecules. (D) Schematics of assembly and disassembly of Au NPs modified with OEG, and an anionic polymer. Reproduced with permission from Refs. [107,69,108,119]. Copyright (2007, 2016, 2009, 2017) The Royal Society of Chemistry and American Chemical Society.

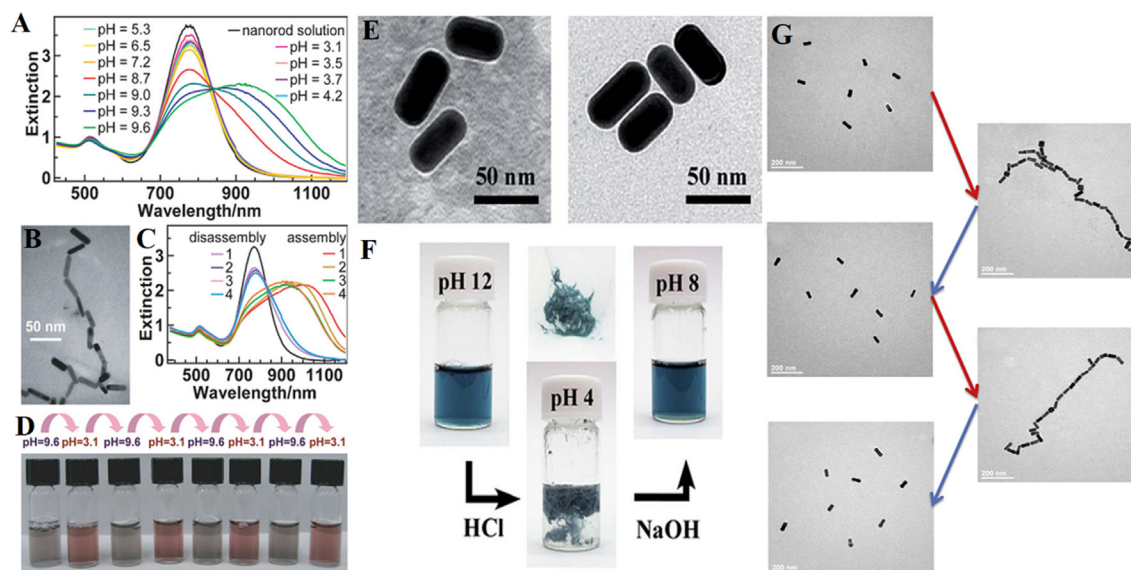
polymer PMAA functionalized pH-responsive reversible assembly of Au NPs [108]. The modulation of plasmonic and optical properties of Au NPs can be achieved by using this system but the aggregation was limited to trimers or tetramers of nanoparticles (Fig. 11C). Various polymeric systems are available that are responsive to acid and base. Modification of such stimulus responsive polymers and block co-polymers with Au NPs always resulted in some interesting phenomenon of assembly and disassembly. Torii et al. designed a face strategy by modifying the surface of Au NPs with oligo(ethylene glycol) (OEG) [119]. Simple hydrogen bonding between the OEG modified Au NPs surface and PAA was the main factor that induced the assembly and disassembly behavior of Au NPs as can be seen in Fig. 11D. Upon addition of protons, the hydrogen bonding between polymer and OEG caused the formation of assemblies that were confirmed by plasmonic peaks as well as hydrodynamic nanoparticle size measurements. Upon deprotonation, the de-anionic behavior of polymer caused disassembly of Au NPs.

Moreover, the interactional study revealed that mostly hydrophobic and steric repulsions are responsible for assembly and disassembly of NPs e.g. work presented by Ma et al. contained poly(ethylene glycol) (PEG) dibutyl amine (Bu), and pyrrolidones (Py) modified Au NPs [115]. PEG acted as a ligand, while its shielding and deshielding behavior was observed by changing pH resulting in assembly and disassembly. At relatively higher pH > 7.2 due to deprotonation of amine groups present in PEG, the hydrophobic interactions were dominant over steric repulsion. Hence, assembly behavior was obtained and at acidic pH due to protonation the

reverse mechanism was achieved. Interestingly, different dimensions (1D to 3D) of Au NPs can be acquired by extending the pH range and this interesting behavior was explained by Si et al [117]. Au NPs were modified with carboxylated peptide and obtained a wide pH range (2.5–10) assembly. At pH 2.5, Au NPs shown 3D structure formation, while moving towards basic pH from 2.5 to 4 leads to 1D and 2D nanostructured of Au NPs characterized by UV-vis. The hydrogen bonding interaction between two carboxylic acids attached to adjacent Au NPs caused the assembly of NPs.

Due to tunable optical and physical properties of Au NRs, pH-responsive reversible assembly of Au NRs has also been studied. To get stimulus responsive reversible assembly behavior, it is necessary to modify nanoparticles with a monomer or polymer which can respond to a specific stimulus. In this context, Sun et al. designed the Au NRs modified with 3-mercaptopropionic acid (MPA) which shows a steady response to pH change. The end to end assembly was obtained when the pH > 8, while pH < 8 can cause the disassembly of Au NRs. UV data and color change of the solution explained the assembly and disassembly process of Au NRs manifested in Fig. 12(A–D) [120].

Similarly, Au NRs precipitation or aggregation and re-dispersion behavior was achieved by Morita-Imura et al. by utilizing the solubility of Au NRs modified with 3-[(2-carboxy-ethyl)-hexadecyl-amino]-propionic acid (C16CA) [121]. Basically, the solubility of C16CA depends on pH change and by maintaining the pH in between 2 and 5 the precipitation of Au NRs is shown in Fig. 12E. The re-dispersion behavior of Au NRs depends on the



**Fig. 12.** Assembly and disassembly of Au nanorods induced by MPA. (A) UV visible spectra of Au NRs at variable pH with 1 mM MPA concentration, (B) TEM image end to end assembled Au NRs acquired at pH = 9.6, and (C) different cycles of assembly and disassembly of Au NRs. The assembly and disassembly behavior was achieved at pH 9.6 and 3.1 respectively. (D) Digital pictures of different cycles of assembly and disassembly of Au NRs with color change, (E) TEM images of the well dispersion of Au NRs-CTAB with C16CA, (F) color change upon the assembly and disassembly behavior of Au NRs-C16CA according to pH change, and (G) from top to down TEM images of assembly and disassembly of Au NRs at different pH system. Reproduced with permission from Refs. [120–122]. Copyright (2008, 2015, 2017) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, The Royal Society of Chemistry and Elsevier Ltd.

pH dependent solubility of C16CA, when the pH is increased to about 12 then the redissolution of C16CA happened which causes the dispersion of Au NRs (Fig. 12F).

Correspondingly, Xu et al. achieved the pH-dependent host-guest interaction based reversible assembly of Au NRs [122]. After modifying the Au NRs with 4,4'-bipyridine containing two sulfide groups (guest) and cucurbit [8]uril ( $C_{48}H_{48}N_{32}O_{16}$ ) (CB [8]) (host), the assembly and disassembly response was carried out by changing the pH value as revealed in Fig. 12G. In this case, the basic mechanism behind assembly and disassembly of Au NRs is based on the ternary complex formation between host and guest molecules. In acidic condition, 4,4'-bipyridine units have not shown any interaction with the cucurbit [8]uril (CB [8]) resulting disassembly of Au NRs. But in the case of deprotonation, an end to end assembly of Au NRs can be seen clearly observed as 1 [5-(5-[1,2]dithiolan-3-ylpentanoyloxy)-pentyl]-[4,4']bipyridinyl-1-ium;b romide (BiBpy@CB [8]). To conclude, the assembly and disassembly process of the Au NPs is purely dependent on the nature of surfactant. Various pH responsive surfactants are available to cover the surface of Au NPs and in response to get reversible assembly behavior. It is a useful aspect to control the drug delivery and cancer cell ablation by using Au NPs modified with pH responsive surfactant.

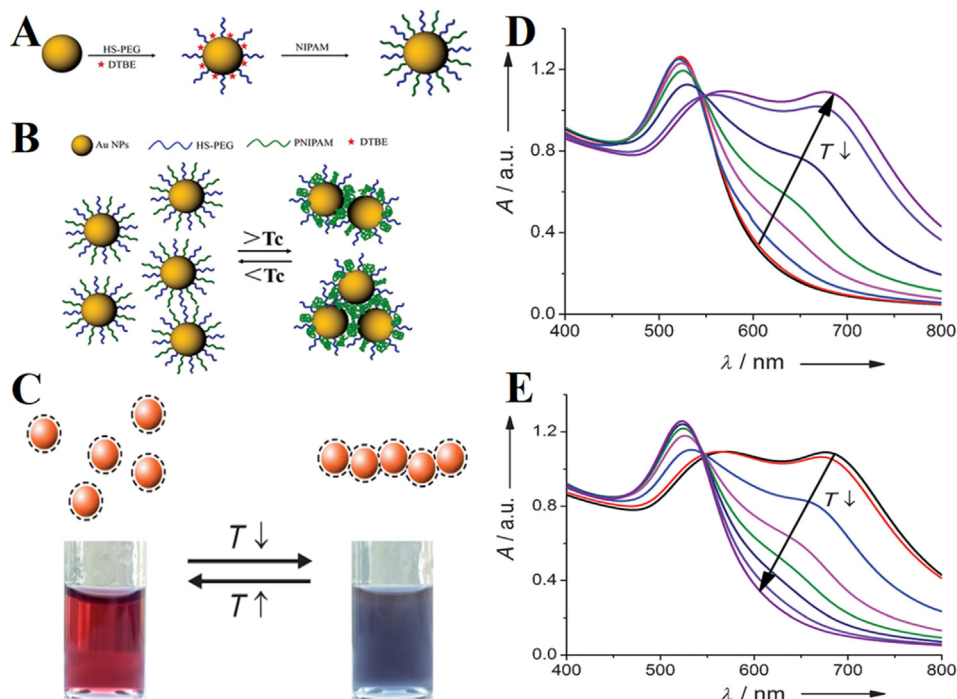
### 3.3. Thermoresponsive reversible assembly of Au NPs

Manipulation of nanoparticles in solution can also be made by using temperature responsive materials. Temperature is readily controllable stimulus that can be easily applied and removed. As described above in Table 1, different types of temperature responsive ligands can be applied on the surface of Au NPs like thermoresponsive polymer (PNIPAM), bis(p-sulfonatophenyl)-phenyl phosphine (BSPP) and several others to acquire thermoresponsive behavior. The possible outcomes in case of Au NPs reversible assembly behavior can easily be predicted by the color change of solution from red to blue or purple, with the change in optical properties (absorbed wavelength) and also by spectroscopic investigations. To achieve the controlled reversible assembly behavior, it

is necessary to control the interactions between the adjacent Au NPs. Dai et al. synthesized an amphiphilic Au NPs system contained PNIPAM and thiol-containing polyethylene glycol coated on the surface of Au NPs [123]. Due to LCST of PNIPAM, as the temperature raises to LCST > 30 °C then PNIPAM showed hydrophobic properties and PEG causes the reorganization of Au NPs into oligomers. The reversible/disassembly phenomenon was observed when the temperature was lower than LCST < 30 °C Fig. 13(A–B).

In another study, negatively charged Au NPs were modified with BSPP by a ligand exchange method [118]. Then, by manipulating electrostatic interactions between two nearly approached Au NPs and utilizing agarose addition along with NaCl, the assembling and disassembling process of Au NPs was clearly observed. Notably, agarose, NaCl, and temperature all contributed a crucial role in this process. Agarose does not cause any optical properties to change in Au NPs but it determined the assembled chain length of Au NPs. The UV visible results clearly indicated the change in wavelength at low temperature in assembled form (Fig. 13C).

Most of the methods explained the uncontrolled aggregation of nanoparticles, but for applications of nanoparticles in the field of catalysis, information storage and diagnosis, well-defined sizes and controlled aggregation of nanoparticles are required [124]. In the recent perspective, Durand-Gasselin et al. obtained a controlled aggregation of thermosensitive polymer-coated Au NPs [45]. They designed a unique approach by modifying the surface of Au NPs with thermoresponsive statistical copolymers poly(EOx-st-POy) in the presence of same compositional chemical triblock copolymers Pluronic poly (ethyleneoxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO), the nanoparticles aggregation and disaggregation behavior achieved during phase transition of polymer at lower and higher temperature. At lower temperature the hydrophilic behavior of the polymers grafted on Au NPs surface cause good dispersion in aqueous solution, while at higher temperature the dehydration behavior of polymers caused the phase change and showed hydrophobic behavior of polymers which resulted in the aggregation of Au NPs in aqueous solution. The presence of PEO-PPO-PEO caused the controlled aggregation of Au NPs because it is responsible for the interactional



**Fig. 13.** (A) Schematic representation of the synthesis of amphiphilic Au NPs (B) and their reversible self-assembly practices persuaded by temperature, (C) temperature mediated reversible assembly of Au NPs, (D) UV/vis kinetics at 16 °C, and 35 °C. Reproduced with permission from Refs. [123,118,45]. Copyright (2016, 2011, 2012) American Publisher Society, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and American Chemical Society.

competition between the nanoparticle-nanoparticle attractive interaction and nanoparticle-surfactant adsorption. Without the presence of triblock polymer, the aggregation temperature ( $T_{agg}$ ) was about 12 °C, while in the presence of triblock polymer the aggregation was not observed even at 30 °C. Hence PEO-PPO-PEO has played a critical rule in the controlled assembly and disassembly behavior of Au NPs as shown in Fig. 13(D-E).

Typically, PNIPAm has been widely used a thermoresponsive polymer with Au NPs due to its phase transition and easily attachment with Au NPs. Different parameters have to be controlled during the assembly and disassembly response of PNIPAm modified Au NPs such as temperature, PNIPAm concentration, charge on particles and other additives like NaCl. To some extent, the temperature is the primary and most important parameter for the controllable assembly and disassembly behavior of PNIPAm modified Au NPs. In the case of PNIPAm concentration, it was a matter of debate before Jones et al [125]. explained in detail about the concentration effect of PNIPAm on the surface of Au NPs. They used a grafting to and grafting from approach to explain the aggregation behavior of PNIPAm coated Au NPs. As explained by Turek et al., at higher temperature the aggregation behavior occurs and at a lower temperature or at cold state the disassembly behavior was observed [126]. They also explained clearly that the reversible assembly behavior was not dependent on the nature of functional groups that are attached with PNIPAm ( $NH_2$ , SH, COOH) but the charge on the surface of NPs and temperature are the main factors that affect the reversible assembly behavior. Zhu et al.[79] designed thiol modified PNIPAm by a reversible addition-fragmentation chain transfer (RAFT) technique to obtain Au NPs functionalized with S-PNIPAm. The same reversible behavior has been achieved by using this simple strategy of hydrophilic and hydrophobic phase transition of PNIPAm in response to temperature. Li et al. explained a new strategy that although based on a polymeric modification of Au NPs it can respond to both pH and temperature depending on the core of the system [127]. They have

designed two unique block copolymers protected Au NPs with poly (methacrylic acid)-block-poly(N-isopropylacrylamide) (SH-PMAA64-b-PNIPAM35) and poly (N-isopropylacrylamide)-block-poly(methyl acrylic acid) (SH-PNIPAM40-b-PMAA60) through thiol bonding. Furthermore, on changing the temperature from 25 to 60 °C, block co-polymeric system containing the core of PNIPAm the PNIPAm chain demonstrated hydrophobic character and led to the aggregation of nanoparticles, while the Au NPs modified with PNIPAm@PMMA even heated to high temperature has not shown any aggregation. The use of stimuli-responsive polymers is common due to well shielding of polymer and easy modification of polymers on the surface of Au NPs. Hence, researchers have tried to control the interactions between different polymers by using external physical stimulus like temperature. In another aspect, control of hydrogen bonding between the Au NPs surface modified with poly(styrene-r-2-vinyl pyridine) [P(S-r-2VP)] and the matrix containing poly(styrene-r-4-vinyl phenol) [P(S-r-4VPh)] polymer. At room temperature, the strong hydrogen bonding between surfactant polymer and matrix polymer provide mono dispersity to the Au NPs. But as the temperature increased to 200 °C, the breaking of hydrogen bonding causes the attractive interactions between the Au NPs and induced aggregation behavior that was reversible upon lowering the temperature to about 120 °C. Furthermore, they monitored the response of these nanoparticles in polystyrene polymer alone and an irreversible response was observed. Thermoresponsive assembly and disassembly of Au NPs always required surface modification with a suitable polymer that can respond to a range of temperatures and size, while the temperature range of surfactant was a significant factor.

### 3.4. Magnetic and electric field

The assembly behavior of different nanoparticles has been successfully achieved in the presence of ferromagnetic core materials such as iron, nickel, or cobalt. An advantageous aspect of the mag-

netic field is its uniform, controlled and accurate applicability to the system. Although different reports have demonstrated the clear concept of the assembly of magnetic nanoparticles e.g. Taheri et al. who synthesized magnetic nanocubes and by using three-dimensional equilibrium dipole system. They explained the assembly behavior of these magnetically active cubes into sheets, chain, and cuboids on implying external magnetic field [128]. Achievement of reversible assembly using a magnetic stimulus is not yet studied well. Furthermore, core-shell and composites of Au NPs along with magnetic nanoparticles have been studied for biomedical, catalytic or detection applications because of the magnetic response of magnetic nanoparticles and plasmonic properties of Au NPs [129–131]. Dimensionality of the magnetic nanoparticles assembly can be controlled by using an external magnetic field of different intensity. Principally, two forces are involved to obtain a one-dimensional chain of magnetic nanoparticles under the external magnetic field i.e. van der Waals force and magnetic dipole-dipole force. Monte-Carlo simulations were utilized by Xue et al. [132] to calculate the interactions between the magnetic nanoparticles containing with Au shell using interaction energy ( $U_{\text{int}}$ ) based equation under the applied magnetic field Eq. (3) [133].

$$U_{\text{int}} = U_{\text{dd}} + U_e + U_{\text{vdw}} \quad (3)$$

where  $U_{\text{dd}}$  is the magnetic dipole-dipole energy,  $U_e$  is the electrostatic repulsion energy, and  $U_{\text{vdw}}$  is the van der Waals potential energy. As already explained, the magnetic nanoparticles present with the Au NPs have shown a great response to a magnet for the reversible assembly and disassembly behavior.

Electric field is the only stimulus that has not been explored well for self-assembly of Au NPs. In the last few years, hardly one report explained the reversible assembly of Au NPs after applying an external electric field. Montelongo et al. demonstrated the first ever report on the reversible assembly of Au NPs of size 16 nm under the application of voltage window  $\pm 0.5$  at the liquid-liquid interface [134]. By applying the voltage, they realized the visible change in reflectivity and spectral position of absorption band. The assembly of Au NPs form a reflective mirror and disassembly of Au NPs cause the formation of transparent window under the applied voltage. Such kind of responses opens doors for micro and nano electrochemical cells.

### 3.5. Doubly stimuli-responsive

Extensive studies have demonstrated the reversible assembly behavior of Au NPs by irradiating light, changing pH and by applying electric and magnetic field. Controlled modification of Au NPs surface with two different kinds of polymers that could possibly response to two different stimuli was a great challenge. Different ideas are established for developing a system that can simultaneously respond to two different stimuli such as modification of magnetic nanoparticles with light responsive monomers. For this system, Das et al. synthesized the core of  $\text{Fe}_3\text{O}_4$  whose surface is covered with light-responsive azobenzene monomer [135]. The inter particle interactions were well controlled by using this dual responsive system.

UV light was used to get spherical aggregates of nanoparticles first, and then the magnetic response has shown a great impact on these spherical aggregates nanoparticles by converting it into the long chain or extended aggregates system. Similar to this system, supramolecular nanoparticles have been extensively studied due to their high stability for biomedical applications. The assembly and disassembly behavior for such kind of system has not been widely studied for noble metal nanoparticles. But, Stoffelen et al. proposed dually responsive reversibly assembled supramolecular nanoparticles composed of cucurbit[8]uril (CB[8]), a methyl violo-

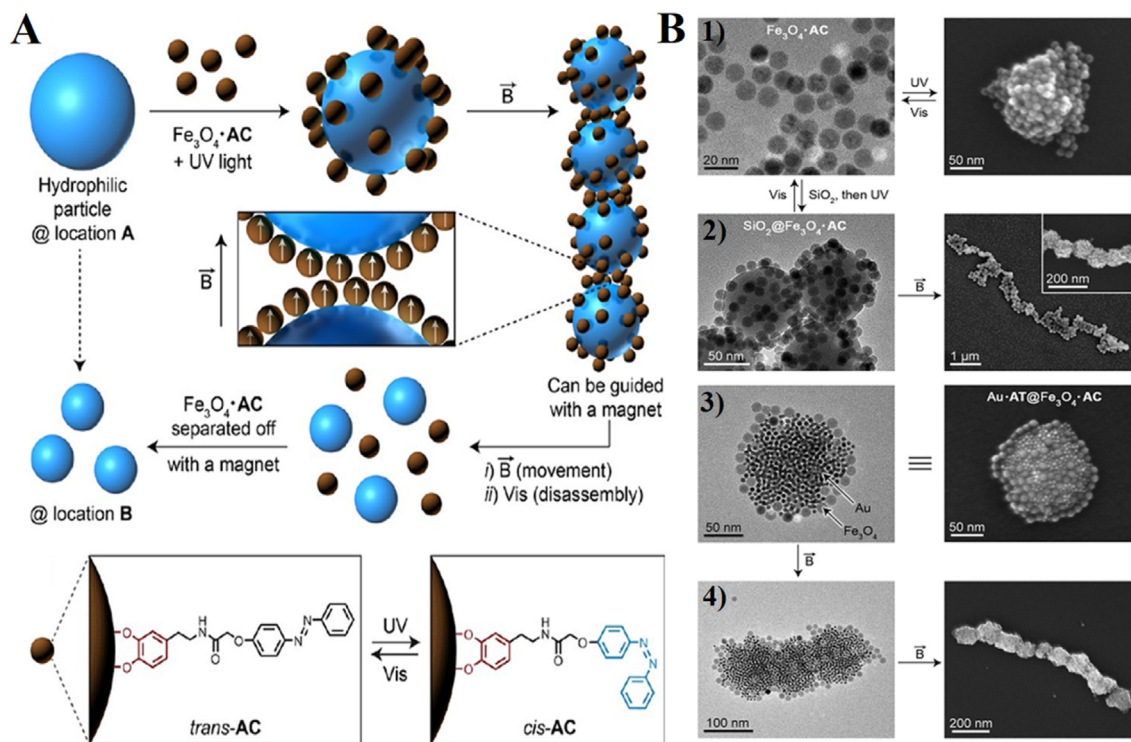
gen (MV) polymer, and mono- and multivalent azobenzene (Azo) [136]. Reversible assembly and disassembly of supramolecular nanoparticles can be achieved by using light-induced transformation of azobenzene molecule and irreversibly by chemical reduction of the methyl viologen units. To check further duality in the nanoparticles systems, Chovnik et al. synthesized dual responsive 11 nm core of superparamagnetic Fe nanoparticles with trans-azobenzene as a shell [137]. Long term stability was achieved due to the presence of hydrophobic azobenzene monolayer in the non-polar solvent like toluene. Furthermore, UV light-induced the aggregation behavior of Fe nanoparticles due to conversion from trans to cis form. The aggregates are 1 magnitude larger than the single nanoparticle size. These aggregates under the applied external magnetic field cause the linear long chain assembly of the nanoparticles Fig. 14(A). Upon utilization of visible light, the conversion of azobenzene from cis to trans occurred which further cause no magnetic effect as there will be no aggregation of Fe nanoparticles, hence, they are magnetically inactive in the well-dispersed state. To confirm the response, TEM images of Fe-azobenzene (Fig. 14B1) nanoparticles were taken that have shown good agreement of aggregation behavior under the application of UV light and further long chain assemblies formation under the applied external magnetic field. Similarly,  $\text{SiO}_2$ -Fe-azobenzene (Fig. 14B2), Au core and Fe shell with azobenzene monolayer and their aggregation behavior were examined along with linear assemblies of these aggregates upon external applying magnetic field Fig. 14B(3–4).

The ease of modification of nanoparticles and the introduction of Janus nanoparticles has broadened the way of thinking. By modifying nanoparticles with different polymers or monomers, dual response in case of temperature and pH becomes an easy task. A lot of work has explained the synthesis of Janus nanoparticles [138–141]. Further, the stimuli-responsive behavior of monomers and polymers coated on Janus nanoparticles provide new applications for drug delivery, magnetic resonance imaging (MRI) and nanodevices [142,143].

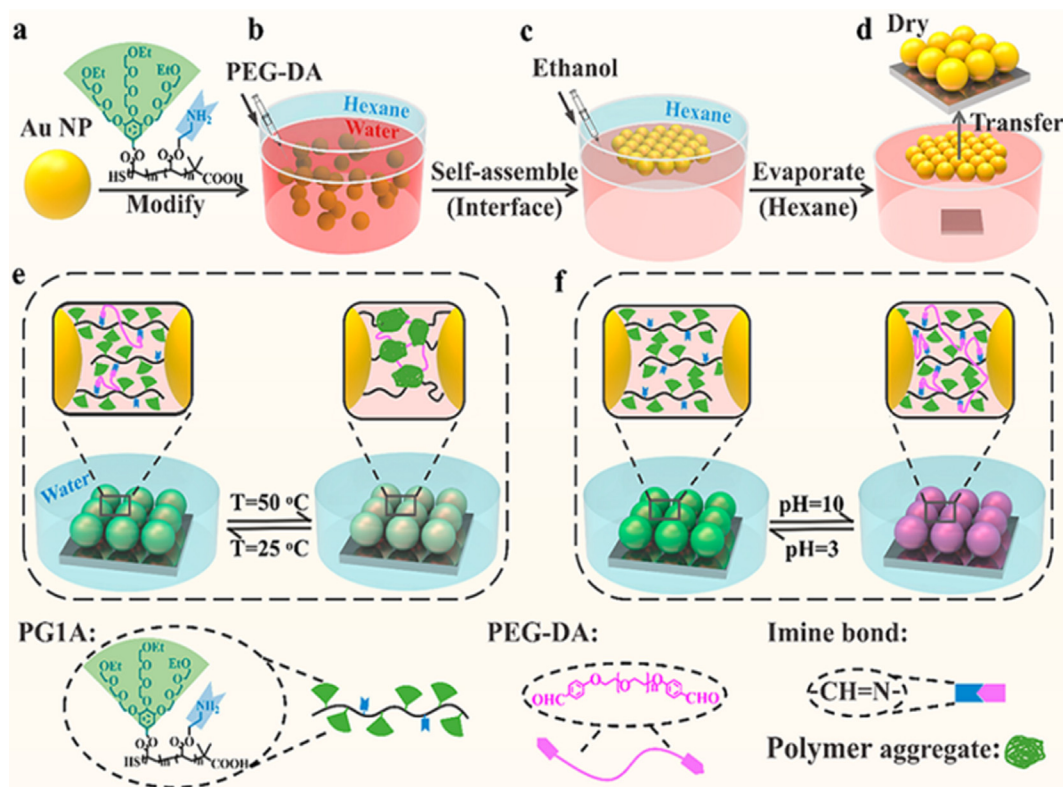
For example, Isojima et al. synthesized Janus magnetic nanoparticles (5 nm), with one side coated with pH dependent polymer [poly(acrylic acid), PAA], while the second side was functionalized with temperature-responsive polymer [poly(N-isopropyl acrylamide), PNIPAM] or with pH-independent polymer (polystyrene sodium sulfonate, PSSNa) [70]. The two different types of Janus nanoparticles have shown a response to pH and temperature. In the first case, PSSNa modified and PAA coated on magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) revealed stable dispersion due to repulsive interaction between charged nanoparticles. On the other hand, at low pH, PSSNa and PAA system demonstrated amphiphilic behavior and resulted in attraction between magnetic nanoparticles, resulting aggregation. Similarly, to get a thermal response, PNIPAM and PAA modified magnetic nanoparticles were used. PNIPAM has shown hydrophobic behavior at a relatively higher temperature from 30 °C and hence cause aggregation of magnetic nanoparticles and interesting reverse behavior was observed at a temperature lower than 30 °C. Though reversibility has been observed, the simultaneous reversible response has not been achieved by using pH and temperature for Janus magnetic nanoparticles.

In the case of dual stimuli responsive Au NPs, Liu et al. described an extraordinary approach by utilizing oligoethylene glycol (OEG)-based dendronized copolymer (named PG1A) coated Au NPs [144]. In addition, polyethylene glycol dibenzyl aldehyde (PEG-DA) was introduced to interact with the amino moieties from PG1A and achieved successful control on the gap distance between Au NPs by using pH and temperature response for 2-D monolayer film at the interface. To demonstrate the temperature and pH response, the monolayer film was transferred to Si grid and reversible plas-

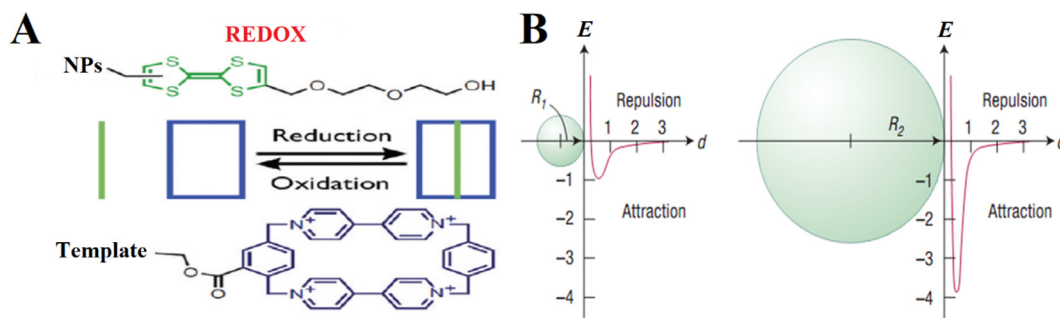




**Fig. 14.** (A) Reversible assembly of diamagnetic nanoparticles by applying external magnetic field followed by UV light irradiation. At the bottom is the reversible isomerization of azobenzene molecule upon irradiation of UV and visible light and (B) TEM images showing reversible assembly of magnetic nanoparticles and core-shell nanoparticles containing Au NPs under dual stimuli. Reproduced with permission from Ref. [137]. Copyright (2012) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim and American Chemical Society.



**Fig. 15.** Schematic diagram for the synthesis process of Au NPs monolayer film at air-liquid Interface, the modification of Au NPs with PG1A copolymer, temperature and pH change the gap distance as well as color of the Au NPs monolayer film at Si grid. Reproduced with permission from Ref. [144]. Copyright (2018) American Chemical Society.



**Fig. 16.** (A) The reversible redox reaction, (B) schematic force–distance functions for particles of different size but interacting through the same type of force, for example, the attractive van der Waals force. Reproduced with the permission from Ref. [25,151]. Copyright (2010, 2008) American Chemical Society and Macmillan Publishers Limited.

monic shift to about 70 nm was obtained upon changing the pH and temperature with a visible color change Fig. 15(a–f).

#### 4. Factors affecting the reversible assembly of nanomaterials

The most important condition to achieve the assembly and disassembly behavior of nanoparticles is the availability of surfactants that could respond to some external stimuli which shows some transformations and further trigger the reversible assembly behavior of Au NPs. Sometimes these transformation are based on the solubility of material such as the reversible conversion from hydrophilic to hydrophobic properties due to host–guest interaction upon cooling and heating mechanism [145]. In the case of materials like polyarenes, upon interaction with azobenzene molecules under UV light irradiation trans to cis confirmation change was observed, while reversible conformational change was possible with visible light [146]. As previously mentioned, such kinds of interactions are feasible in the reversible aggregation of nanoparticles. Surfactants suitability along with interactional study is the most important factor to consider for the reversible aggregation of Au NPs. In this regard, modification of azobenzene, spiropyran or some other stimuli-responsive surfactants is employed for the direct attachment onto the surface of Au NPs after modifying stimuli responsive surfactants with thiol groups. Interestingly, thiol-protected noble metal based nanomaterials also overcome uncontrolled aggregation in self-assembly process [147]. In few cases, for instant Klajn et al. described that modification of Au NPs with some stimuli-responsive materials is not a necessary condition. To get the assembly and disassembly behavior without such kind of modification involved interesting chemistry.

Assembly and disassembly of nanoparticles can be achieved by using some kind of templates either soft or hard. In the case of soft templates small molecules, polymers, and biomolecules are involved. In general, the soft templates provide less binding sites for nanoparticles. So, in some cases electrochemically active guests were utilized for the attachment with Au NPs and then this Au NPs attached moiety can combine non-covalently with host molecules. An example of this was established by Stoddart, J. F. et al. in which tetrathiafulvalene acted as a guest molecule and tetracationic cyclophane has shown interaction for guest molecules by interaction with it as host molecule [148].

The oxidation and reduction due to the host–guest interaction prompted the assembly and disassembly of nanoparticles attached with guest molecule –see Fig. 16A while another aspect related to Au NPs redox reaction based assembly and disassembly was reported and in some cases, the same host–guest interactions cause assembly and disassembly of nanoparticles under light irradiation [25,149]. For example, Au NPs modified with cyclodextrin due to electrostatic interactions cause the attachment and detachment from the surface of carbon nanotubes upon the use of UV light [150].

Importantly, the particle size, electrostatic interaction, and Van der Waal forces are significant factors that can determine the reversible assembly of Au NPs. Basically, the reversible assembly behavior for complex shapes of Au NPs (cube, nanowires, triangles, and stars) has not been studied well. The reason behind such kind of behavior relates to size, complex geometries and multiple forces such as electrostatic forces and Van der Waal Forces (Fig. 16B) [151]. Mostly, it has been estimated that the particle size to induce reversible aggregation is about 5 to 8 nm [152].

Literature on the stimuli-responsive reversible assembly of Au NPs is in agreement with this range. Basically, the problem with the bigger size nanoparticles can be explained well with the DLVO theory and surface interactions of uncapped Au NPs which leads to coalescence and even further transformation like nanorods to nanowires [153–156]. Disassembly behavior of large Au NPs has not been achieved successfully because it is difficult to break the attractive forces. The magnitude and range of the repulsive forces are of the order wires > rods > spheres. Another crucial parameter is the successful functionalization of Au NPs. In some case, the unsuccessful modification of Au NPs with SP, azobenzene, PNIPAm or some other polymer can lead to aggregation of Au NPs. Various factors need to be considered to achieve reversible assembly of Au NPs for pH-responsive systems like the ratio of pH-responsive moiety and Au NPs, the molecular weight of the polymer (pH-responsive) and size of particles. In case of PNIPAm the higher the concentration of PNIPAm will also lead to the unsuccessful reversible assembly of Au NPs and it will initiate aggregation. Other relevant parameters are well explained by Israelachvili et al. and include capillary forces, friction and lubrication forces, connective forces, solvation, depletion and structural forces, repulsive steric and confining forces [151]. Hence, all the reversible assembly processes required some kind of stimuli to go from aggregation to dispersion and vice versa as explained by Ling et al. [1] who have articulated detailed mechanisms of nanoparticles assembly and disassembly behavior for the biomedical applications.

#### 5. Summary and outlook

Although many examples have been explained in detail for the reversible assembly of Au NPs in solution induced by external stimuli, the field is underdeveloped compared to just single directional assembly of Au NPs. Continued efforts to advance applications in plasmonics, SERS, sensors, and catalysis still require exploration of the reversible assembly of Au NPs. We finish this review with some research opportunities/new approaches to achieving advanced applications in this area of research. Firstly, in case of light-mediated assembly of Au NPs, the light responsive polymers and monomers are limited somewhat to azobenzene and spiropyran. The modification of azobenzene and spiropyran with other stimuli-responsive monomeric system to initiate further

polymerization is still undiscovered. Reversible assembly under selective condition (different light wavelengths) can also be induced by using ligand exchange techniques. Utilization of only UV light also imparts a limitation, to expand further IR and other light regions responding materials like donor–acceptor stenoise adducts and hydrazone-based switches are still not completely developed for reversible assembly of Au NPs.

Another important factor is the different shapes of Au NPs. In the context of synthesis, different shapes of Au NPs like stars, cubes, nanowires, and rods have been successfully prepared but less attention has been paid toward their reversible assembly. The surfactant modification is the same as for spherical Au NPs but due to complex shapes, it can generate special effects of assembly and disassembly. Additionally, as regards to surfactant modification, the improper size distribution of Au NPs can lead to unbalanced stimuli-responsive surfactant modification of Au NPs that can cause selective size based reversible assembly of Au NPs. In the case of Au NRs, the selective modification of sides and ends of Au NRs can give rise to a dual response to different stimuli like pH and temperature induced end to end and side-by-side assembly/disassembly of Au NRs.

Synthetic chemists have devoted extensive efforts for the synthesis of new molecular switches that can respond to light, pH, temperature and other stimuli. In the future, it is possible to carry out the organic reaction in the presence of Au NPs and in response to the reaction the assembly and disassembly of Au NPs can be observed. From a broader materials science perspective, dynamic systems and networks comprising nanoparticles and functional surface ligands represents an excellent starting point for designing and realization of the dynamic assemblies that apart from storing information, would perform programmed tasks related to sensing or spatiotemporal catalysis. In the near future, such systems will cause employ dynamic reversible assemblies that could not only store the information but possible perform programmable tasks.

### CRediT authorship contribution statement

**M. Zubair Iqbal:** Visualization, Formal analysis, Investigation, Methodology, Data curation, Writing - original draft. **Israt Ali:** Visualization, Formal analysis, Data curation, Writing - original draft. **Waheed S. Khan:** Visualization, Methodology, Writing - review & editing. **Xiangdong Kong:** Conceptualization, Investigation, Funding acquisition, Methodology, Project administration, Supervision, Validation, Visualization, Writing - review & editing. **Eithne Dempsey:** Conceptualization, Investigation, Funding acquisition, Methodology, Project administration, Supervision, Validation, Visualization, Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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