

NANO REVIEW

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Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles for Chemical Sensing

Chen Chen¹, Yongan Tang², Branislav Vlahovic² and Fei Yan^{1*} 

Abstract

The integration of different noble metal nanostructures, which exhibit desirable plasmonic and/or electrocatalytic properties, with electrospun polymer nanofibers, which display unique mechanical and thermodynamic properties, yields novel hybrid nanoscale systems of synergistic properties and functions. This review summarizes recent advances on how to incorporate noble metal nanoparticles into electrospun polymer nanofibers and illustrates how such integration paves the way towards chemical sensing applications with improved sensitivity, stability, flexibility, compatibility, and selectivity. It is expected that further development of this field will eventually make a wide impact on many areas of research.

Keywords: Electrospinning, Polymer nanofibers, Noble metal nanoparticles, Sensing

Review

Background

The rapid development of nanoscience and nanotechnology has led to a wide variety of practical applications, including air filtration, wound dressings, drug delivery, detection, energy production, and food packaging [1–10]. Nanomaterials often have physical and chemical properties that are very different from the same materials at larger scales. Many different strategies have been developed for the synthesis and construction of nanostructured materials [11–13]. Based on dimensionality, nanomaterials may be classified into four categories: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). 1D nanomaterials such as nanowires, nanorods, and nanotubes have been widely investigated in the last few decades. Among the aforementioned materials, 1D nanofibers have attracted tremendous attention due to their unique structural and physical properties such as small diameters, large surface area per unit mass, small pore size, and flexibility in surface functionalities [14, 15]. There are many processing techniques that have been utilized to produce

1D nanofibers such as template synthesis [16], self-assembly [17], and electrospinning [18, 19]. Among these methods, electrospinning appears to be the most versatile and simplest one for preparing nanofibers [15]. It is notable that by adjusting the parameters of the polymer solution or the electrospinning setup, most of the known polymers such as polyacrylonitrile (PAN) [20, 21], polyvinylidene fluoride (PVdF) [18], and polyvinylalcohol (PVA) [22] can be successfully electrospun into ultrafine fibers. Therefore, due to the significant simplicity and versatility of electrospinning, electrospun polymer nanofibers have garnered substantial attention in recent years, particularly in the field of chemical sensors.

The field of plasmonics that deals with light-matter interactions between adsorbed molecules and noble metal structures at nanoscale dimensions has recently emerged as a rapidly growing area of interest, as evidenced by the explosive growth in various fields including surface-enhanced Raman scattering (SERS) [23–25], surface-enhanced infrared absorption spectroscopy [26, 27], surface-enhanced fluorescence spectroscopy [28–30], surface plasmon resonance spectroscopy [31–34], and plasmonic colorimetry [35]. The fascinating optical properties of plasmonic nanostructures are dominated by collective oscillations of the conduction band electrons in the noble metal (e.g., Au, Ag, and Pt) nanostructures known as

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surface plasmons. The quest for simple methods to fabricate reproducible plasmonic nanostructures has spurred much interest in a variety of scientific disciplines; however, it has remained a big challenge to hierarchically assemble individual noble metal nanostructures with desirable long-range order at predefined sites on a substrate. Templated synthesis and assembly of nanoscale plasmonic building blocks to form rationally designed architectures have emerged as an overarching strategy for addressing this challenge [36–38]. Electrospun polymer nanofibers have been shown to be one of the most promising templates to pack noble metal nanostructures with great precision. The controlled incorporation of noble metal nanostructures with desired plasmonic properties into electrospun polymer nanofibers paves the way towards sensing applications with improved sensitivity, stability, flexibility, compatibility, and selectivity.

This review highlights recent advances in integrating electrospun polymer nanofibers with noble metal nanoparticles and their applications for chemical sensing. We summarize the following: (1) the basic setup and process parameters for electrospinning, (2) different strategies for the synthesis of Au or Ag nanostructures, (3) preparation of electrospun polymer nanofibers decorated with Au or Ag nanoparticles, and (4) examples of chemical sensing applications of electrospun polymer nanofibers decorated with Au or Ag nanoparticles.

Electrospinning: Basic Set-up and Process Parameters

The electrospinning system generally consists of four main parts: a direct current power supply with high voltage, a syringe that contains polymer solution, a metallic needle with a blunt tip, and a grounded conductive collector, as shown in Fig. 1. During the electrospinning process, the polymer solution in the syringe will be pumped out through the metallic needle tip at a specific

rate. A high voltage is applied to create charges on the surfaces of the polymer droplet forming a Taylor cone, and when the repulsive electrostatic force is sufficiently strong to overcome the surface tension of the polymer droplet, the polymer droplet will be elongated into a conical shape [39]. Subsequently, the polymer jets will undergo an elongation process, during which the polymer will be stretched and the polymer solution solvent will evaporate, leaving the long and thin polymer nanofibers collected on the grounded conductive collector.

One of the great advantages of electrospinning is that by changing the parameters during the electrospinning process, the morphology of the electrospun nanofibers can be easily controlled. These parameters include polymer concentration, solution viscosity, solution conductivity, flow rate, applied voltage, the working distance between the collector and tip of the needle, and air humidity [12]. Polymer concentration is an important parameter as it determines the morphology of the electrospun nanofibers, because the surface tension can be dominant as the polymer concentration decreases, which will lead to polymer bead formation [39]. In addition, solution viscosity is another critical parameter, which determines if the polymer can be electrospun into nanofibers or not. The solution viscosity is highly dependent on the polymer concentration and the molecular weight of the polymer used for the electrospinning. In principle, a polymer with higher molecular weight has, on average, longer molecular chains, and it will form more entanglements leading to a higher viscosity of the polymer solution. Therefore, for a solution made with high molecular weight polymers, even though the polymer concentration is low, it still can produce a uniform jet due to a sufficient level of solution viscosity. Conversely, if the molecular weight is too low, an appropriate polymer solution viscosity cannot be guaranteed even with a high polymer concentration and the polymer tends to form a bead structure on the collector [40]. Comparatively, the processing conditions such as applied voltage and flow rate also play a significant role in nanofiber formation during electrospinning. For applied voltage, it has been proven that varied applied voltage will not change the nanofiber morphology dramatically. According to the past work, both larger and smaller fiber diameters can be obtained when a higher voltage is applied [40].

Synthesis and Assembly of Au Or Ag Nanostructures

During the last few decades, great advances have been made in the synthesis of Ag and Au nanostructures with different sizes and shapes. It is worth noting that different nanostructures can give rise to significantly different optical, electronic, magnetic, or chemical properties, which may be suitable for different applications. Generally, based

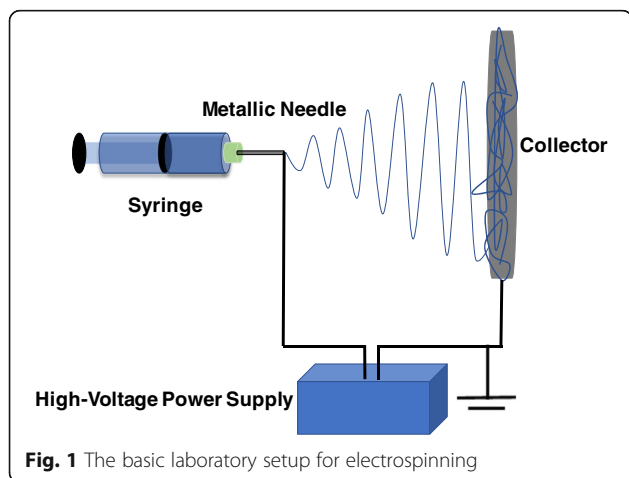


Fig. 1 The basic laboratory setup for electrospinning

on the different mechanisms, the reductive approaches to Au or Ag nanostructures can be approximately classified into chemical and physical methods. Typically, the way to obtain Au or Ag nanostructures is to mix Au or Ag precursors with a reducing agent and/or a colloidal stabilizer, and nanostructured Au or Ag with different sizes and shapes can be generated under specific conditions. AgNO_3 and HAuCl_4 are the most commonly used precursors for Ag and Au nanostructure synthesis, and various reducing agents such as sodium borohydride, alcohols, sodium citrate, and poly(vinyl pyrrolidone) (PVP) can reduce Ag/Au ions into Ag/Au atoms with exceptional control over their sizes and shapes. It has been proved that the plasmon resonance frequencies of the Au or Ag nanoparticles depend on their sizes. For example, Xia and coworkers have synthesized Ag nanocubes ranging from 60 to 100 nm and compared their SERS with respect to both size and shape (sharp vs. truncated) [39]. It demonstrates that larger particles (90 and 100 nm) were found to have higher SERS efficiencies (90 and 100 nm), which is primarily attributed to the overlap between the laser source and plasmon resonance band. Additionally, particles with sharper corners also gave more intense SERS signals than their truncated counterparts.

Synthesis of Au Nanostructures

Based on Turkevich's research in 1951, HAuCl_4 could be reduced in a water solution in the presence of citrate, which has been one of the most commonly used methods for Au nanoparticle synthesis [41]. By changing the amount of citrate, the mean size of the Au nanoparticles can be easily manipulated and citrate plays a role as a nucleating agent and a growth agent at the same time [41]. It has been proven that the citrate reduction method can produce relatively narrow size distributions of the Au nanoparticles. Subsequent studies demonstrated that the mechanism of the control on different Au nanoparticle sizes as a function of the amount of citrate is intimately related to the pH values, because different pH values will determine the formation process of the Au nanoparticles [42].

In 1994, Brust and Schiffrin made a great contribution to the Au nanostructure synthesis by inventing a two-phase synthetic strategy. In this approach, AuCl_4^- was transferred from aqueous solution to toluene using tetrabutylammonium bromide as the phase-transfer reagent and strong thiol-gold interactions were utilized to protect AuNPs with thiol ligands. Au clusters with a size range between 1 and 3 nm (Fig. 2) were obtained through the reduction reaction by sodium borohydride (NaBH_4) in the presence of dodecanethiol [41]. As NaBH_4 was added into the organic phase, the color of the solution turned into deep brown immediately. Several parameters including gold/thiol ratio, temperature,

and reduction rate can be varied to control the size of the resulting Au nanoparticles. For example, larger thiol/gold mole ratios led to Au nanoparticles with smaller average core sizes [43]. Different ligands were utilized to form monolayer-protected gold clusters and the ratio between thiol and AuCl_4^- could be adjusted in the synthesis to control the size of the AuNPs. Seed-mediated growth, developed by Jana et al. has also shown great promise for generating Au nanoparticles with controlled and monodispersed particle size [44–47]. In a typical process, high-quality seeds are required and then the cylindrical Au nanostructures are grown in multiple steps. In the seed-mediated growth approach, the yield of Au nanostructures is relatively low and high-quality seeds are necessary [48].

Various polymers have been reported for the stabilization of Au nanoparticles, which include PVP, poly(ethylene glycol) (PEG), PVA, poly(vinyl methyl ether) (PVME), chitosan, and polyethyleneimine (PEI) [49–57]. Different polymers exhibit different formation processes for Au nanostructures; for example, the reduction between gold ions and PVP may involve a solid-liquid (S-L) mechanism and the nitrogen and oxygen atom heterocyclic ring can contribute to the reducing ability of the PVP [56]. In the reduction reaction, PVP plays the roles of both a reducing agent and a steric stabilizer; therefore, by varying the concentration or ratio between PVP and Au ions, different Au nanostructures with different shapes and sizes can be achieved (as shown in Fig. 3).

In addition to the chemical synthesis strategies of Au nanostructures, several physical methods have also been used to improve the quality of the Au nanostructures, including photochemistry (UV, Near-IR), sonochemistry, radiolysis, thermolysis, and microwave irradiation [58–65]. In the microwave irradiation synthesis process, the addition of different amounts of oleic acid not only increases the growth rate but also controls the morphology of the resulting Au nanostructures as shown in Fig. 4 [65]. In addition, oleylamine could also be added as the reducing agent and the nucleated Au functions as the catalyst to initiate the reaction between oleic acid and oleylamine to form dioleamide, which plays a role as the capping agent for the as-prepared Au nanoparticles.

Synthesis of Ag Nanostructures

Use of citrate as the reducing agent for Ag colloid synthesis in an aqueous solution has been discovered for decades. Typically, a set amount of sodium citrate solution is added into a boiling aqueous solution of AgNO_3 and the Ag nanocrystals will be obtained after keeping the system boiling for 1 h. During the reaction, the citrate ions serve as both a reducing agent and a stabilizer and they can complex with the silver seeds, thereby influence the particle growth, leading

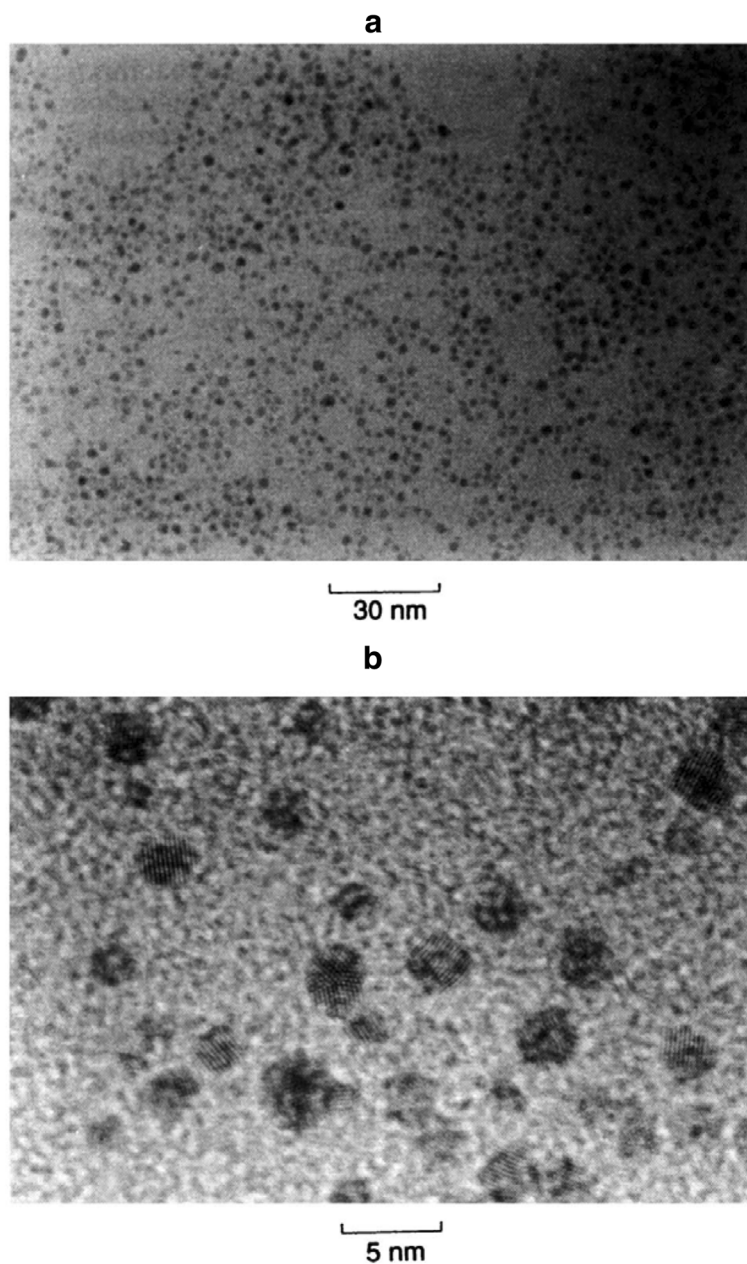


Fig. 2 TEM pictures of the thiol derivatized gold nanoparticles at **a** low and **b** high magnification [147]. Reprinted with permission from [147]. Copyright {2010} Royal Society of Chemistry

to formation of larger clusters of silver [66]. Furthermore, by varying the pH of the solution or the concentration of citrate ions, different protonation states associated with citrate ion can be achieved, resulting in different growth mechanisms and morphologies of Ag clusters [13].

Another commonly used method for synthesizing Ag nanostructures is the polyol process, which can lead to the formation of Ag nanostructures with a wide variety of sizes and shapes [67–71]. In the

polyol reduction process, the nucleation, growth process and the resultant Ag nanostructure morphology are sensitive to reaction conditions, such as temperature, reagent concentration, and presence of trace ions [13]. In a typical polyol reduction process, a Ag precursor with a capping agent is injected into a preheated polyol such as ethylene glycol; 1,2-propylene glycol; or 1,5-pentanediol, which plays a dual role as a solvent and a reducing agent [13, 66]. The exact mechanism during the polyol reduction process

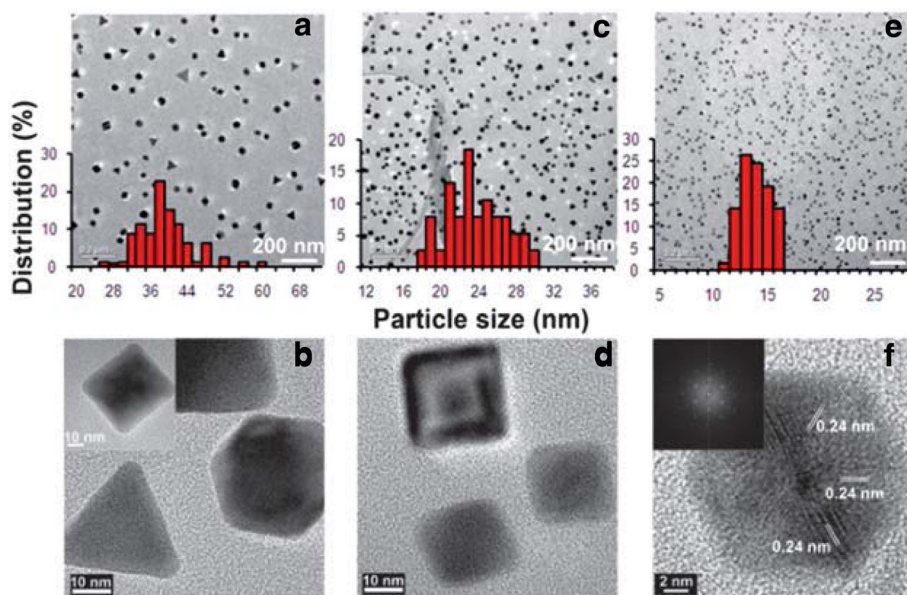


Fig. 3 TEM images and histograms of AuNPs from AuNPs-PVP nanocomposite films with weight ratios of HAuCl₄ to PVP, [HAuCl₄/PVP] = 1:1.5 (a, b), 1:2 (c, d), and 1:4 (e, f) [88]. Reprinted with permission from ref. [67]. Copyright {2010} Royal Society of Chemistry

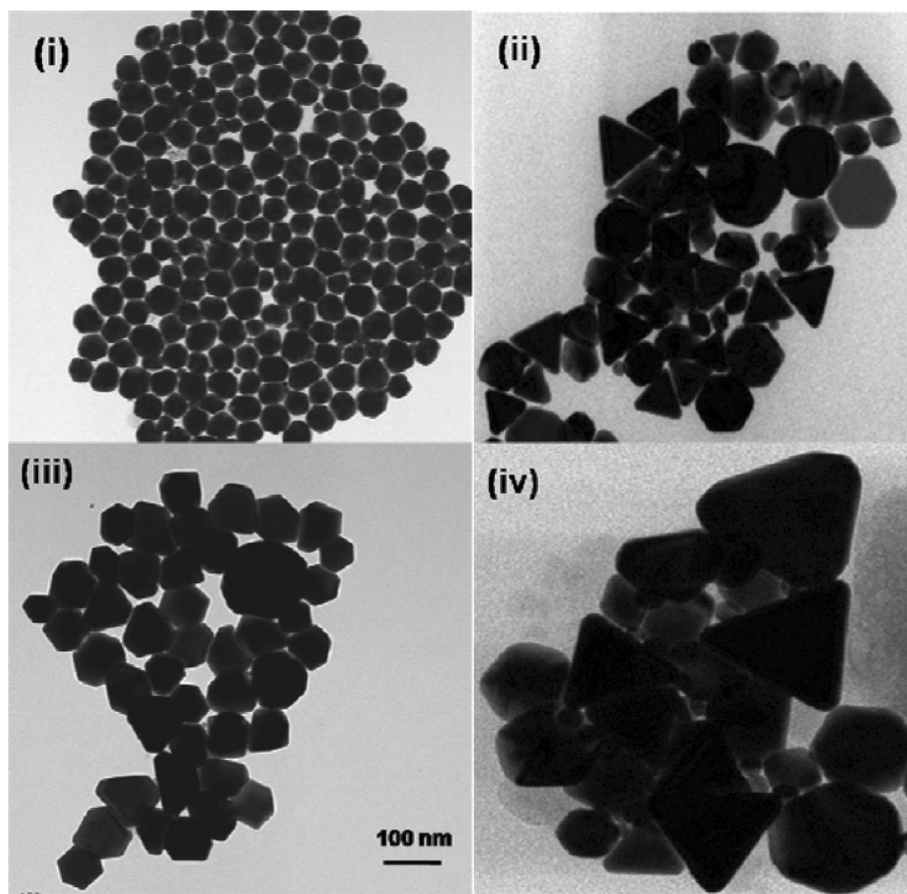
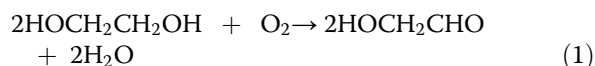


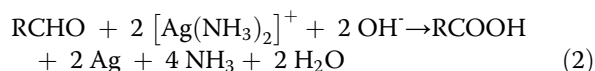
Fig. 4 TEM images of the gold nanoparticles prepared in **i** 60, **ii** 70, **iii** 80, and **iv** 90% oleic acid [65]. Reprinted with permission from ref. [65]. Copyright {2010} American Chemical Society

is still largely unknown due to its complex nature, and one of the possible reactions is as follows:



By using a spectroscopic method, the formation of glycolaldehyde (GA) has been confirmed and it is the intermediate product of ethylene glycol and a stronger reductant that can effectively reduce AgNO_3 into Ag [72]. This may also explain why the polyol process is highly dependent on the reaction temperature [13]. During the polyol reaction, Ag atoms initially form small clusters and later grow into stable and bigger clusters. Finally, Ag nanostructures with different shapes and sizes will be formed after continuous growth.

Moreover, silver nitrate, in the presence of aldehyde-containing compounds (or sugar, e.g., glucose), can form Tollen's reagent and subsequently transform into elemental Ag through the reduction reaction:



This reaction is also called the silver mirror reaction, which will produce a shiny mirror coating on the inner surface of a reaction container [13]. However, no shape control can be achieved through this reaction, which limits its use in synthesizing Ag nanostructures.

Seed-mediated growth, which uses nanocrystals as seeds for further growth, has attracted a lot of attention and become another popular synthetic approach for Ag nanostructures. Basically, there are two main steps involved: the seed nucleation and the growth of the nanostructures. These two steps are essentially separate, enabling great control over the final morphology of Ag nanostructures [13, 67]. For Ag nanostructures synthesized by this method, the final shape of the nanostructure not only depends on the initial seed but is also governed by the growth rates of different crystallographic facets [13]. It has been found that the growth rates of specific facets are significantly influenced by the capping agent. For example, when used as the capping agent, citrate has been shown to bind more strongly to {111} than {100} crystal facets, tending to form nanoplates. However, for PVP, it binds more strongly to {100} than {111} crystal facets and can thereby reduce the growth rate along the [73] direction, leading to different morphology formation. These studies demonstrate that by changing the reaction conditions including capping agents and seed types, binding strengths with different facets can be simply manipulated, leading to precise control over the morphology of the Ag nanostructures [13].

A long time ago, people found that a silver precursor (e.g., AgNO_3) could interact with light leading to the formation of elemental silver. Therefore, in the presence of appropriate chemical species, Ag nanostructures can be formed under laser irradiation of a sample of Ag colloids [13]. Early studies found when ultrafast (femto- or nano-second) laser pulses were applied to Ag nanostructures, these nanostructures would melt and tend to form rough spheres due to the low surface energy and thermodynamic stability of this shape [13, 74, 75]. Inspired by these early studies, later investigations revealed that light excitation could also be utilized to grow or modify nanostructures in a controllable fashion and the size and shape of the resultant nanostructures are found to be dependent on applied laser wavelength and power [76–79]. Recent studies indicate that citrate, oxygen, and light are necessary for the reaction. The mechanism behind the light-mediated synthesis is as follows: the Ag seeds that absorb/scatter light weakly reduce dioxygen and release Ag^+ into solution; in the presence of light and Ag^+ , citrate will degrade into acetoacetate, and the resulting electrons are transferred into the Ag nanostructure, accelerating the rate of silver deposition on the surface [13, 78, 80]. By increasing irradiation light intensity, the photochemical process can be significantly enhanced which increases the photoreaction rate and the yield of Ag nanoprisms [78].

Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles

Ag and Au nanostructures have proven to be versatile platforms for various application such as plasmonics, biomedical research, sensing, and catalysis [81–86]. Taking advantage of the flexibility, uniform distribution, controllable morphology, and free-standing properties of electrospun polymer nanofibers, the combination of Au or Ag nanostructures with polymer nanofibers have great potential to improve the reusability and widen the current applications. For example, it is notable that encapsulation of Ag nanoparticles into polymer fiber matrix can efficiently prevent the sulfuration on the surface of Ag nanoparticles. The addition of Au or Ag nanostructures into electrospun nanofibers can also change the nanofiber morphology. Kim and coworkers synthesized Au NP/PEO composites and found that there was a 50-nm increase of fiber diameter after addition of Au NPs to PEO (poly (ethylene oxide)) [87].

Preparation of Electrospun Polymer Nanofibers Decorated with Ag Nanoparticles

Based on the sequence of the reduction process of Ag^+ to Ag nanostructure, the preparation of electrospun polymer nanofibers decorated with Ag nanoparticles can be classified into two different methods. In the first

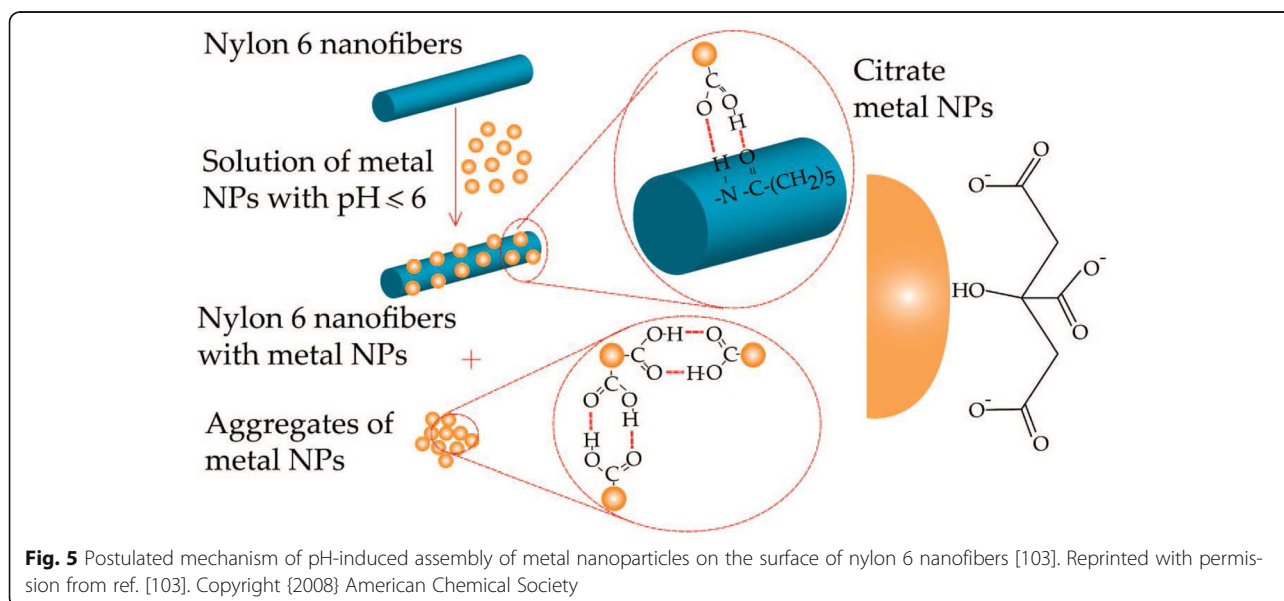
method, the Ag nanostructure with different morphologies is either prepared first or the Ag precursor is reduced into Ag nanostructures inside the polymer precursor solution. If the reduction reaction is conducted in a separate solution, the as-prepared Ag nanostructures will be separated and added into the polymer precursor solution subsequently. In this way, because the Ag nanostructure reduction takes place before the electrospun nanofiber formation, it does not require a solvent that can dissolve and stabilize the Ag precursor. In addition, it is not necessary for the polymer to be able to reduce the Ag precursor and it means suitable polymers can be utilized for the composite without limitation. Furthermore, since it is easier to control the Ag nanostructure morphology in a dependent reduction process, the separate synthesis processes permit Ag nanostructure/electrospun nanofiber composites with more Ag nanostructure morphologies.

The other method to prepare electrospun polymer nanofibers decorated with Ag nanoparticles involves first dissolving the Ag precursor into the polymer precursor solution or attaching it onto the surface of the electrospun polymer nanofibers, followed by a reduction process which transforms the Ag precursor into Ag nanostructures. This method is also called the in situ growth of plasmonic nanoparticles. Generally, to perform the reduction reaction, one of the approaches is to utilize a reducing polymer or mixed polymer that contains a reducing polymer as the electrospun nanofiber precursor such as chitosan and PVP [88, 89–91]. The exact mechanism of how the PVP reduces Ag precursor into Ag nanoparticles is still not fully understood, and it has been hypothesized that the aldehyde functional groups, resulting from the oxidation of the hydroxyl end

group, might reduce the metal ions in a similar way to that of Tollen's reagent [92]. Furthermore, it is worth pointing out that the metal formation capacity is highly dependent on the molecule weight of PVP when the same mass of polymer is used [88]. Other approaches to reduce Ag^+ in or outside the polymer nanofibers include heating, UV irradiation, microwave irradiation, or hydrogen reduction [93–97]. Leonard et al. prepared tourmaline nanoparticles/polyurethane nanofiber composite and decorated with silver nitrite on the surface [98]. After the irradiation treatment for 4 h, silver nitrate was reduced into Ag nanoparticles which exhibited a wire-like structure on the surface of the composites.

Preparation of Electrospun Polymer Nanofibers Decorated with Au Nanoparticles

Similar to the strategies to encapsulate Ag nanostructures, most researchers demonstrate that electrospun polymer nanofibers decorated with Au nanoparticles could firstly be synthesized using a regular Au nanostructure method such as citrate reduction and seed-mediated approach and then disperse the as-prepared Au nanostructures into the electrospinning polymer precursor solution [73, 99–102]. For some specific applications, Au nanostructures are required to decorate on the surface of the nanofibers and Au nanostructures are found to be attracted by some specific functional groups on the polymers. By adjusting the Ag or Au solution pH, Dong et al. found that one of the three COONa groups from the surface-bound citrate on the NPs would become COOH, which could bridge the amide group on the surface of the nylon 6 fibers through two intermolecular hydrogen bonds and bond the Ag or Au NPs on the surface of the nylon 6 nanofibers as shown in Fig. 5 [103].



Some polymers contain functional groups on their backbones that can be easily modified with other materials such as 3-mercaptopropyltrimethoxysilane (MPTES) to provide stronger binding sites to attract the Au nanoparticles [99]. In addition, some polymers can be used to stabilize Au nanostructures and function as the electron donor in the reduction process of Au^{3+} to Au^0 . Pucci et al. found that under irradiation, the RCH_2OH in the PVA with available α hydrogen atoms could be transformed into RCHO while releasing H^+ and e^- [52]. Subsequently, the produced e^- might be trapped by the Au^{3+} to produce Au^0 making PVA additives more efficient photo-reduction reactions [104].

Sensing Applications of Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles

Some recent examples of sensing applications based on electrospun polymer nanofibers decorated with noble metal nanoparticle (e.g., Au and Ag NPs) are illustrated in Table 1. From Table 1, it is seen that the metal particle/nanofiber composites have many advantages such as simplicity, high sensitivity, and high selectivity in detecting various biological and chemical specimens. Through electrospinning, the metal particle/nanofiber composites can be easily fabricated with a high surface area, which can provide easy access for the detection

molecules leading to excellent activities for SERS. Therefore, many metal particle/nanofiber composites show low limit of detection. In addition, based on the results in Table 1, it can be concluded that the density and size of metal particles have an important impact on the SERS activity/sensitivity because enhancement of Raman signals result from the presence of hot spots between/among metal particles.

Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles for Chemical Sensing Based on SERS

Surface-enhanced Raman scattering (SERS) has emerged as one of the most promising and powerful analytical tools for probing single molecules, ions, biomolecules, and for cell studies [105–111]. Since the mid-1980s, more researchers began to focus on the exploration of promising analytical applications of SERS instead of the fundamental understanding of the phenomenon [112]. Organized Au or Ag nanostructures have attracted tremendous attention due to their signal-amplifying function as SERS substrates, which have been attributed to a local electromagnetic field enhancement induced by the metallic nanostructures. The SERS enhancement factor (ratio between the Raman signals from a given number of molecules in the presence and in the absence of the nanostructure) is closely related to the size and shape of the nanostructures that give rise to the effect [113].

Table 1 Examples of sensing applications of electrospun polymer nanofibers decorated with noble metal nanoparticles

Detection mode	Nanofiber materials	Au or Ag nanostructures	Limit of detection	Reference
SERS	Cellulose	Ag NPs	1 ppm thiabendazole	[118]
SERS	PVA	Au nanorods with Ag nanowires	10^{-4} M 3,3'-diethylthiatricarbocyanine iodide	[117]
SERS	PVA	Au nanorods	10^{-4} M 3,3'-diethylthiatricarbocyanine iodide	[100]
SERS	PVA	Ag NPs	1 μM 4-mercaptobenzoic acid (4-MBA)	[116]
SERS	PVA	Au and Ag NPs	4-MBA (2 mM) and thiophenol (1 mM)	[123]
SERS	PAA/PVA	Au NPs	10^{-8} Rhodamine 6G (R6G) and 10^{-9} 4-Aminothiophenol (4-ATP)	[115]
SERS	Poly(2-vinyl pyridine)	Au nanorods	1 mM 1,4-benzenedithiol	[73]
SERS	PVP	Ag nanowires	5 mg/mL 4,4'-bipyridine	[122]
SERS	PAN	Ag nanoparticles	10^{-4} p-Aminothiophenol	[148]
SERS	PAN	Ag NPs	10 ppb R6G	[114]
SERS	Silica	Au and Ag NPs	1 mM MBA	[121]
SERS	Chitosan	Ag NPs	1 μM R6G and 0.001 mg/mL D-glucose	[106]
SERS	PMMA	Au NPs	0.1 nM malachite green isothiocyanate	[119]
SERS	PMMA	Ag NPs	1 mM 4-MBA	[149]
Electrochemical	Bacteria cellulose	Au NPs	1 μM H_2O_2	[150]
Electrochemical	PAN	Ag–Pt Bimetallic NPs	0.11 μM dopamine (DA)	[151]
Electrochemical	PVA	Au NPs	0.5 μM H_2O_2	[99]
Electrochemical	PVA/poly(ethyleneimine)/glucose oxidase	Au NPs	0.9 μM glucose	[146]

Typically, the Au, Ag, or AuAg-mixed nanostructures are arranged on rigid materials as the SERS substrate and these methods are either complicated and time consuming in synthesis processes or require strict synthetic conditions.

Recently, a flexible substrate fabricated by combining electrospun nanofibers with Au, Ag, or AuAg-mixed nanostructures has become popular due to their excellent SERS performance and, compared with the rigid substrate, these flexible structures are adaptable to a rough substrate in terms of wrapping and bending [106, 114]. These metal/nanofiber composites demonstrated a 3D structure, which can provide high density of “hot spots”, which refers to the regions of highly enhanced local electromagnetic field [115]. In addition, the polymer outside the nanostructures can protect them from the surrounding environment especially for Ag nanostructures, which gives the composite long lifetime and high sensitivity [116].

Different polymers or ceramic nanofibers, such as PVA [100, 116, 117], cellulose [118], poly(methyl methacrylate) (PMMA) [119], chitosan [106], poly (acrylic acid) (PAA)/PVA [120], and silica [121] have been utilized to combine with different Ag or Au nanostructures to fabricate the flexible substrate for SERS. PVA is a nontoxic, biocompatible polymer, which has good electrospinability, and it is a popular material for electrospinning. When it is used as the supporting material for Ag nanostructures for SERS, it functions not only as the host matrix but also as an organic additive inducing the aggregation of individual Ag nanostructures [116]. In a typical process, the Au or Ag nanostructures are produced in specific morphologies first and these nanostructures are added into the polymer solution as the precursor solution. He et al. synthesized nearly monodispersed Ag NPs via a microwave-assisted method and then these as-prepared silver dimers and aggregates were mixed into a 7% aqueous PVA solution for electrospinning [116]. In order to reduce the specific surface area and the surface Gibbs free energy of individual nanofibers, Ag NPs were self-assembled inside the PVA nanofibers. The assembly of Ag dimers or aligned aggregates within PVA nanofibers was confirmed using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses. Moreover, Ag NPs tended to form a linear chain-like structure along the axial direction of fibers (Fig. 6) because when a high voltage was applied to the solution, Ag NPs became positively charged on one side and negatively charged on the other, leading to a self-alignment by electrostatic attraction in the direction of the electric field [116].

As the amount of Ag NPs increased in the PVA nanofibers, the enhancement factor did not increase accordingly, which indicated that different morphology of Ag

NP aggregation had a great influence on the enhancement effects of SERS [116]. When 4-mercaptobenzoic acid (4-MBA) was used as a probing molecule to study the Raman enhancement effects, the Ag/PVA nanofibers showed excellent detection reproducibility (i.e., the average relative standard deviation values of the major Raman peak were less than 0.07). Taking advantage of the same nanoparticle alignment in the polymer nanofibers, Ag nanowires (NWs) were also synthesized and electrospun into PVA nanofibers [122]. The Ag NW/PVA nanofibers showed similar morphology and the NWs were “frozen-up” within the polymer fibers. In addition, the electrospun Ag NW/PVA nanofibers were arranged into different structures and stronger SERS intensities were obtained from the arranged samples [122]. Besides Ag nanostructures, Au nanostructures were also encapsulated into the PVA electrospun nanofibers as SERS substrates [100]. Zhang et al. used a seed-mediated surfactant-directed approach to synthesize Au nanorods (AuNRs), and these Au NRs exhibited good alignment along the axial direction of the nanofibers, which demonstrates that electrospinning is a powerful tool to assemble anisotropic nanorods on a large scale [100]. Ag and Au nanostructures can be co-assembled into the PVA nanofibers [117, 123]. Different SERS effects can be obtained by varying the Au/Ag ratio and the excitation wavelength due to the different activities of Au and Ag nanostructures under different wavelengths [124]. In spite of the different morphologies of Ag and Au nanostructures, both Au/PVA and Ag/PVA composites showed excellent SERS performance.

Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles for Chemical Sensing Based on Electrochemical Techniques

Nowadays, metal nanoparticles (such as Au, Ag, Cu, and Ni) have become widely utilized in electrochemical sensing applications, which can be attributed to their rich electronic properties, high surface area, and excellent chemical stability [125, 126]. Au NPs can decrease the overpotentials of many electroanalytical reactions and maintain the reversibility of redox reactions [41, 127]. The Au NP platform can be used for detection of different kinds of analytes including small molecules such as glucose [128, 129], dopamine [130–133], bisphenol A [134], toxic chemicals and drugs such as mercury [135–138], antimony [139], and hydrogen peroxide [140]. Au NPs hold great promise as substrates for designing electrochemical biosensors, which benefit from their ability to provide a stable immobilization of biomolecules retaining their bioactivity, ease of use in chemical synthesis, narrow size distribution, and their convenient labeling of biomolecules [141–143]. Furthermore, both Ag and Au NPs have good biocompatibility

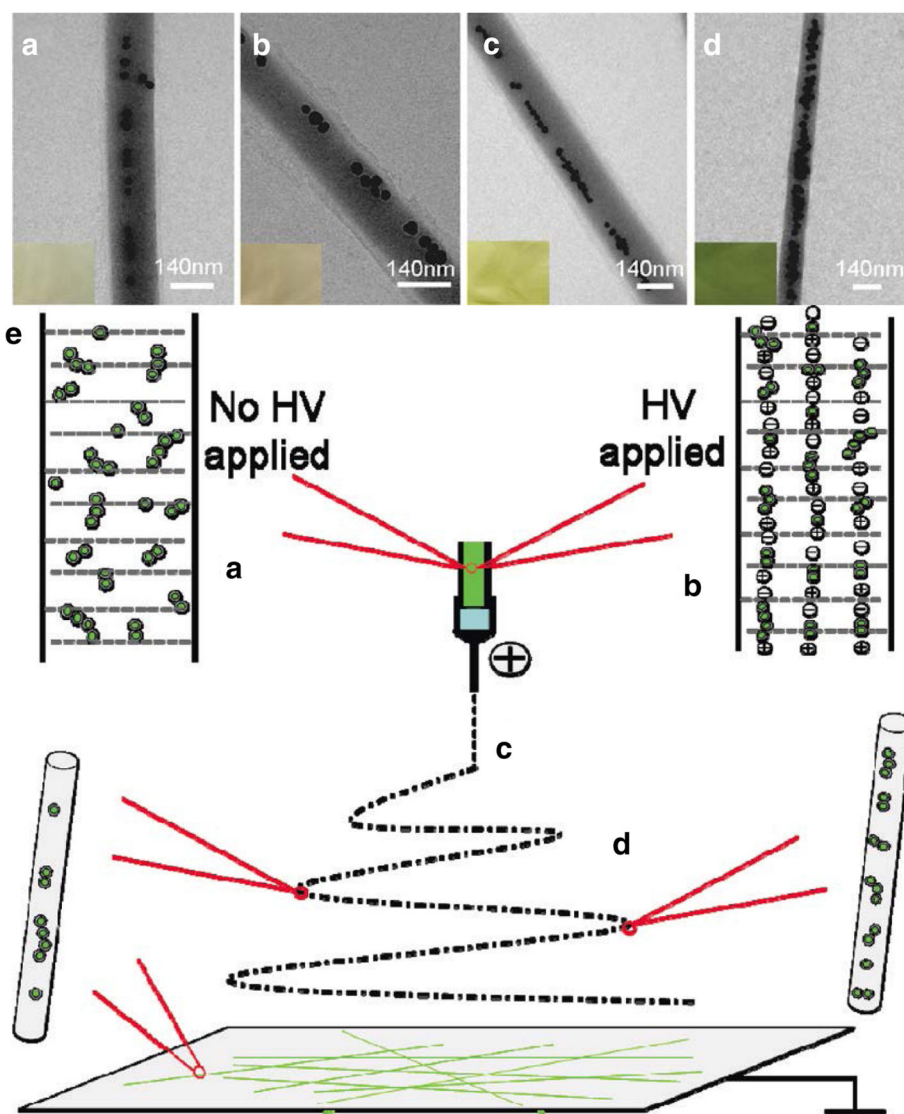


Fig. 6 a–d Typical TEM image of Ag/PVA nanofibers with the molar ratio of PVA/Ag 530:1 (a), 530:2 (b), 530:3 (c), and 530:4 (d). The increase of the molar ratio of Ag/PVA in the Ag/PVA solution led to stronger aggregation state and a larger distribution in the sizes of the aggregated Ag NPs. **e** Schematic representation of the formation of chain-like arrays of Ag NP aggregates within PVA nanofibers [116]. Reprinted with permission from ref. [116]. Copyright {2009} American Chemical Society

and large surface area which can help adsorb biomolecules strongly and play an important role in the immobilization of biomolecules [144]. Accordingly, combining Au or Ag NPs with large-surface-area polymer nanofibers, which provide a large loading capacity for nanoparticles, can further enhance the sensitivity of the sensors [145].

Sapountzi et al. decorated the PVA/poly(ethyleneimine) (PEI)/glucose oxidase nanofibers with Au NPs to further improve the conductivity of the mat and used these composites as electrochemical biosensors [146]. However, both PVA and PEI are water soluble polymers and it may weaken the stability of the composite. Therefore, the researchers conducted a post-electrospinning

cross-linking step by exposing the NFs to glutaraldehyde (GA) vapors and the morphology of the fibers was still well retained, suggesting a successful chemical cross-linking reaction induced by GA vapors [146]. The same treatment was also performed by other researchers and the cross-linked PVA nanofiber mat maintained its morphology even after being soaked in water for 15 days [99]. After obtaining the water soluble PVA nanofiber mat, 3-mercaptopropyltrimethoxysilanes (MPTES) were first modified on the surface of electrospun PVA nanofibers. Then, the modified PVA nanofiber mat was immersed into the as-prepared Au NPs aqueous solutions and Au NPs were strongly bonded onto the surface of the modified

PVA nanofibers due to the strong affinity between the thiol groups and Au NPs [99]. Au NPs were homogeneously decorated on the surface of the modified PVA nanofibers for different Au NP concentrations, leading to highly sensitive detection of H₂O₂ and the Au NPs/modified PVA also showed more advantages such as fast response, broad linear range, and low detection limit [99].

Conclusions

Extensive research has been carried out to study the properties and applications of both Au or Ag nanostructures and electrospun nanofiber materials in recent years. Taking advantage of the flexibility, large surface area, ease of production, and surface modification of the electrospun polymer nanofibers, the combination of Au/Ag nanostructures with nanofibers makes these composites versatile platforms for various applications in optics, antibacterial coatings, photovoltaics, and chemical and biological sensors etc. The adaptable functionalization of both electrospun nanofibers and Au or Ag nanostructures can lead to unique morphologies and structures for Au or Ag nanostructure/electrospun nanofiber composites, followed by more applications with enhanced performance.

Despite the increasing number of publications using electrospun polymer nanofibers decorated with noble metal nanoparticles for sensing applications, the field is in its infancy. The rational integration of noble metal nanoparticles to nanofiber matrices to achieve desirable plasmonic properties will bring unprecedented strategies for sensor development. Further investigations are required to better understand the morphology control, formation mechanism, and applications to specific applications. It is expected that further development of this field will eventually make a wide impact on many areas of research.

Abbreviations

GA: Glutaraldehyde; MPTEs: 3-Mercaptopropyltrimethoxysilane; NWS: Nanowires; PAA: Poly (acrylic acid); PAN: Polyacrylonitrile; PEG: Poly(ethylene glycol); PEI: Polyethyleneimine; PEO: Poly (ethylene oxide); PVA: Polyvinyl alcohol; PVdF: Polyvinylidene fluoride; PVME: Poly(vinyl methyl ether); PVP: Polyvinylpropylene; SERS: Surface-enhanced Raman scattering; TEM: Transmission electron microscopy; XPS: X-ray photoelectron spectroscopy

Acknowledgements

This work was supported in part by the U.S. NSF (DMR-1523617) and ARO: W911NF-13-0165. FY thanks Dr. Guy D. Griffin (Oak Ridge, TN) for proofreading the manuscript.

Authors' Contributions

FY jointly conceived the study with YT and BV. CC and FY conducted a thorough literature review on the topic. CC wrote the original draft of the manuscript. YT and FY reviewed and edited the manuscript. All authors reviewed the manuscript. All authors read and approved the final manuscript.

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Competing Interests

The authors declare that they have no competing interests.

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Received: 22 April 2017 Accepted: 28 June 2017

Published online: 11 July 2017

References

- Zhu, C., Chen, Y., Lu, Y., Ge, H., Jiang, K., Fu, X., Zhang, Nitrogen-doped carbon nanofibers derived from polyacrylonitrile for use as anode material in sodium-ion batteries. *Carbon* N. Y. 94 (2015) 189–195. doi:10.1016/j.carbon.2015.06.076
- Chen C, Li G, Lu Y, Zhu J, Jiang M, Hu Y, Cao L, Zhang X (2016) Chemical vapor deposited MoS₂/electrospun carbon nanofiber composite as anode material for high-performance sodium-ion batteries. *Electrochim Acta* c. doi:10.1016/j.electacta.2016.11.170
- Jing X, Mi HY, Peng J, Peng XF, Tung LS (2015) Electrospun aligned poly(propylene carbonate) microfibers with chitosan nanofibers as tissue engineering scaffolds. *Carbohydr Polym* 117:941–949. doi:10.1016/j.carbpol.2014.10.025
- Wen P, Zhu D-H, Wu H, Zong M-H, Jing Y-R, Han S-Y (2016) Encapsulation of cinnamon essential oil in electrospun nanofibrous film for active food packaging. *Food Control* 59:366–376. doi:10.1016/j.foodcont.2015.06.005
- GhavamiNejad A, Rajan Unnithan A, Ramachandra Kurup Sasikala A, Samarikhajaj M, Thomas RG, Jeong YY, Nasser S, Murugesan P, Wu D, Hee Park C, Kim CS (2015) Mussel-inspired electrospun nanofibers functionalized with size-controlled silver nanoparticles for wound dressing application. *ACS Appl Mater Interfaces* 7:12176–12183. doi:10.1021/acsami.5b02542
- Zhang R, Liu C, Hsu PC, Zhang C, Liu N, Zhang J, Lee HR, Lu Y, Qiu Y, Chu S, Cui Y (2016) Nanofiber air filters with high-temperature stability for efficient PM_{2.5} removal from the pollution sources. *Nano Lett* 16:3642–3649. doi:10.1021/acs.nanolett.6b00771
- Jiang S, Hou H, Agarwal S, Greiner A (2016) Polyimide nanofibers by "Green" electrospinning via aqueous solution for filtration applications. *ACS Sustain Chem Eng* 4:4797–4804. doi:10.1021/acsschemeng.6b01031
- Xu J, Liu C, Hsu PC, Liu K, Zhang R, Liu Y, Cui Y (2016) Roll-to-roll transfer of electrospun nanofiber film for high-efficiency transparent air filter. *Nano Lett* 16:1270–1275. doi:10.1021/acs.nanolett.5b04596
- Liu C, Hsu P-C, Lee H-W, Ye M, Zheng G, Liu N, Li W, Cui Y (2015) Transparent air filter for high-efficiency PM_{2.5} capture. *Nat Commun* 6:6205. doi:10.1038/ncomms7205
- Chen C, Fu K, Lu Y, Zhu J, Xue, L, Hu Y, Zhang X (2015) Tin antimony alloy-filled porous carbon nanofiber composite for use as anode in sodium-ion batteries. *RSC Adv* 39: 30793–30800. doi:10.1039/C5RA01729G.
- Liang HW, Liu S, Yu SH (2010) Controlled synthesis of one-dimensional inorganic nanostructures using pre-existing one-dimensional nanostructures as templates. *Adv Mater* 22:3925–3937. doi:10.1002/adma.200904391
- Zhang C-L, Yu S-H (2014) Nanoparticles meet electrospinning: recent advances and future prospects. *Chem Soc Rev* 43:4423–48. doi:10.1039/c3cs60426h

13. Rycenga M, Cobley CM, Zeng J, Li W, Moran CH, Zhang Q, Qin D, Xia Y (2011) Controlling the synthesis and assembly of silver nanostructures for plasmonic applications. *Chem Rev* 111:3669–3712. doi:10.1021/cr100275d
14. Palmqvist AEC (2003) Synthesis of ordered mesoporous materials using surfactant liquid crystals or micellar solutions. *Curr Opin Colloid Interface Sci* 8:145–155. doi:10.1016/S1359-0294
15. Huang Z, Zhang Y, Kotaki M, Ramakrishna S (2003) A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos Sci Technol*. <http://www.sciencedirect.com/science/article/pii/S0266353803001787>.
16. Feng L, Li S, Li H, Zhai J, Song Y, Jiang L, Zhu D (2002) Super-hydrophobic surface of aligned polyacrylonitrile nanofibers. *Angew Chem Int Ed* 41:1221–1223. doi:10.1002/1521-3773(20020402)41:7<1221::AID-ANIE1221>3.0.CO;2-G
17. Whitesides GM, Grzybowski B (2002) Self-assembly at all scales. *Science* 295:2418–21. doi:10.1126/science.1070821
18. Yanilmaz M, Chen C, Zhang X (2013) Fabrication and characterization of SiO₂/PVDF composite nanofiber-coated PP nonwoven separators for lithium-ion batteries. *J Polym Sci B Polym Phys* 51:1719–1726. doi:10.1002/polb.23387
19. Ge Y, Jiang H, Fu K, Zhang C, Zhu J, Chen C, Lu Y, Qiu Y, Zhang X (2014) Copper-doped Li₄Ti₅O₁₂/carbon nanofiber composites as anode for high-performance sodium-ion batteries. *J Power Sources* 272:860–865. doi:10.1016/j.jpowsour.2014.08.131
20. Li S, Chen C, Fu K, White R, Zhao C, Bradford PD, Zhang X (2014) Nanosized Ge@CNF, Ge@C@CNF and Ge@CNF@C composites via chemical vapour deposition method for use in advanced lithium-ion batteries. *J Power Sources* 253:366–372. doi:10.1016/j.jpowsour.2013.12.017
21. Li S, Chen C, Fu K, Xue L, Zhao C, Zhang S, Hu Y, Zhou L, Zhang X (2014) Comparison of Si/C, Ge/C and Sn/C composite nanofiber anodes used in advanced lithium-ion batteries. *Solid State Ion* 254:17–26. doi:10.1016/j.ssi.2013.10.063
22. Koski A, Yim K, Shivkumar S (2004) Effect of molecular weight on fibrous PVA produced by electrospinning. *Mater Lett* 58:493–497. doi:10.1016/S0167-577X(03)00532-9
23. Zhang C, Jiang SZ, Yang C, Li CH, Huo YY, Liu XY, Liu AH, Wei Q, Gao SS, Gao XG, Man BY (2016) Gold@silver bimetal nanoparticles/pyramidal silicon 3D substrate with high reproducibility for high-performance SERS. *Sci Rep* 6:25243. doi:10.1038/srep25243
24. Sivanesan A, Witkowska E, Adamkiewicz W, Dziewit Ł, Kamińska A, Waluk J (2014) Nanostructured silver-gold bimetallic SERS substrates for selective identification of bacteria in human blood. *Analyst* 139:1037–43. doi:10.1039/c3an01924a
25. Dong X, Zhou J, Liu X, Lin D, Zha L (2014) Preparation of monodisperse bimetallic nanorods with gold nanorod core and silver shell and their plasmonic property and SERS efficiency. *J Raman Spectrosc* 45:431–437. doi:10.1002/jrs.4495
26. Perry DA, Razer TM, Primm KM, Chen T, Shamburger JB, Golden JW, Owen AR, Price AS, Borchers RL, Parker WR (2013) Surface-enhanced infrared absorption and density functional theory study of dihydroxybenzene isomer adsorption on silver nanostructures. *J Phys Chem C* 117:8170–8179. doi:10.1021/jp3121462
27. Brown LV, Yang X, Zhao K, Zheng BY, Nordlander P, Halas NJ (2015) Fan-shaped gold nanoantennas above reflective substrates for surface-enhanced infrared absorption (SEIRA). *Nano Lett* 15:1272–1280. doi:10.1021/nl504455s
28. Zhang Z, Yang P, Xu H, Zheng H (2013) Surface enhanced fluorescence and Raman scattering by gold nanoparticle dimers and trimers. *J Appl Phys* 113:033102. doi:10.1063/1.4776227
29. Shtoyko T, Raut S, Rich RM, Sronce RJ, Fudala R, Mason RN, Akopova I, Gryczynski Z, Gryczynski I (2014) Preparation of plasmonic platforms of silver wires on gold mirrors and their application to surface enhanced fluorescence. *ACS Appl Mater Interfaces* 6:18780–18787. doi:10.1021/am504431j
30. Damm S, Lordan F, Murphy A, McMillen M, Pollard R, Rice JH (2014) Application of AAO matrix in aligned gold nanorod array substrates for surface-enhanced fluorescence and Raman scattering. *Plasmonics* 9:1371–1376. doi:10.1007/s11468-014-9751-y
31. Zeng S, Baillargeat D, Ho H-P, Yong K-T (2014) Nanomaterials enhanced surface plasmon resonance for biological and chemical sensing applications. *Chem Soc Rev* 43:3426–52. doi:10.1039/c3cs60479a
32. Juvé V, Cardinal MF, Lombardi A, Crut A, Maioli P, Pérez-Juste J, Liz-Marzán LM, Del Fatti N, Vallée F (2013) Size-dependent surface plasmon resonance broadening in nonspherical nanoparticles: single gold nanorods. *Nano Lett* 13:2234–2240. doi:10.1021/nl400777y
33. Huang YF, Zhang M, Bin Zhao L, Feng JM, Wu DY, Ren B, Tian ZQ (2014) Activation of oxygen on gold and silver nanoparticles assisted by surface plasmon resonances. *Angew Chem Int Ed* 53:2353–2357. doi:10.1002/anie.201310097
34. Cao J, Sun T, Grattan KTV (2014) Gold nanorod-based localized surface plasmon resonance biosensors: a review. *Sensors Actuators B Chem* 195:332–351. doi:10.1016/j.snb.2014.01.056
35. Guo Y, Wu J, Li J, Ju H (2016) A plasmonic colorimetric strategy for biosensing through enzyme guided growth of silver nanoparticles on gold nanostars. *Biosens Bioelectron* 78:267–273. doi:10.1016/j.bios.2015.11.056
36. Zhang L, Liu T, Liu K, Han L, Yin Y, Gao C (2015) Gold nanoframes by nonepitaxial growth of Au on AgI nanocrystals for surface-enhanced Raman spectroscopy. *Nano Lett* 15:4448–4454. doi:10.1021/acs.nanolett.5b01544
37. Li C, Jamison AC, Rittikulsittichai S, Lee T, Lee TR (2014) In situ growth of hollow gold–silver nanoshells within porous silica offers tunable plasmonic extinctions and enhanced colloidal stability. *ACS Appl Mater Interfaces* 6:19943–19950. doi:10.1021/am505424w
38. Gao X, Lu F, Dong B, Liu Y, Gao Y, Zheng L (2015) Facile synthesis of gold and gold-based alloy nanowire networks using wormlike micelles as soft templates. *Chem Commun* 51:843–846. doi:10.1039/C4CC08549C
39. Agarwal S, Greiner A, Wendorff JH (2013) Functional materials by electrospinning of polymers. *Prog Polym Sci* 38:963–991. doi:10.1016/j.progpolymsci.2013.02.001
40. Tan SH, Inai R, Kotaki M, Ramakrishna S (2005) Systematic parameter study for ultra-fine fiber fabrication via electrospinning process. *Polymer (Guildf)* 46:6128–6134. doi:10.1016/j.polymer.2005.05.068
41. Saha K, Agasti SS, Kim C, Li X, Rotello VM (2012) Gold nanoparticles in chemical and biological sensing. *Chem Rev* 112:2739–2779. doi:10.1021/cr2001178
42. Ji X, Song X, Li J, Bai Y, Yang W, Peng X (2007) Size control of gold nanocrystals in citrate reduction: the third role of citrate. *J Am Chem Soc* 129:13939–13948. doi:10.1021/ja074447k
43. Daniel MCM, Astruc D (2004) Gold nanoparticles: assembly, supramolecular chemistry, quantum-size related properties and applications toward biology, catalysis and nanotechnology. *Chem Rev* 104:293–346. doi:10.1021/cr030698
44. Jana NR, Gearheart L, Murphy CJ (2001) Seeding growth for size control of 5–40 nm diameter gold nanoparticles. *Langmuir* 17:6782–6786. doi:10.1021/la0104323
45. Jana NR, Jana NR, Gearheart L, Gearheart L, Murphy CJ, Murphy CJ (2001) Wet chemical synthesis of high aspect ratio cylindrical gold nanorods. *J Phys Chem B* 105:4065–4067. doi:10.1021/jp0107964
46. Johnson CJ, Dujardin E, Davis SA, Murphy CJ, Mann S (2002) Growth and form of gold nanorods prepared by seed-mediated, surfactant-directed synthesis. *J Mater Chem* 12:1765–1770. doi:10.1039/b200953f
47. Gole A, Murphy CJ (2004) Seed-mediated synthesis of gold nanorods: Role of the size and nature of the seed. *Chem Mater* 16:3633–3640. doi:10.1021/cm0492336
48. Nik B, El Sayed A (2003) Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method. *Chem Mater* 15:1957–1962. doi:10.1021/Cm020732l
49. Tracy JB, Kalyuzhny G, Crowe MC, Balasubramanian R, Choi JP, Murray RW (2007) Poly(ethylene glycol) ligands for high-resolution nanoparticle mass spectrometry. *J Am Chem Soc* 129:6706–6707. doi:10.1021/ja071042r
50. Susumu K, Mei BC, Mattoussi H (2009) Multifunctional ligands based on dihydroliipoic acid and polyethylene glycol to promote biocompatibility of quantum dots. *Nat Protoc* 4:424–436. doi:10.1038/nprot.2008.247
51. Sun X, Dong S, Wang E (2004) One-step synthesis and characterization of polyelectrolyte-protected gold nanoparticles through a thermal process. *Polymer (Guildf)* 45:2181–2184. doi:10.1016/j.polymer.2004.01.010
52. Pucci A, Bernabò M, Elvati P, Meza LI, Galebeck F, de Paula Leite CA, Tirelli N, Ruggeri G (2006) Photoinduced formation of gold nanoparticles into vinyl alcohol based polymers. *J Mater Chem* 16:1058. doi:10.1039/b511198f
53. Oh E, Susumu K, Goswami R, Mattoussi H (2010) One-phase synthesis of water-soluble gold nanoparticles with control over size and surface functionalities. *Langmuir* 26:7604–7613. doi:10.1021/la904438s
54. Krishna Rao KSV, Ramasubba Reddy P, Lee YI, Kim C (2012) Synthesis and characterization of chitosan-PEG-Ag nanocomposites for antimicrobial application. *Carbohydr Polym* 87:920–925. doi:10.1016/j.carbpol.2011.07.028
55. Harnish B, Robinson JT, Pei Z, Ramström O, Yan M (2005) UV-cross-linked poly(vinylpyridine) thin films as reversibly responsive surfaces. *Chem Mater* 17:4092–4096. doi:10.1021/cm050144i

56. Carotenuto G (2001) Synthesis and characterization of poly(N-vinylpyrrolidone) filled by monodispersed silver clusters with controlled size. *Appl Organomet Chem* 15:344–351. doi:10.1002/aoc.165
57. Pal T, Sau TK, Jana NR (1997) Reversible formation and dissolution of silver nanoparticles in aqueous surfactant media. *Langmuir* 13:1481–1485. doi:10.1021/la960834o
58. Pol VG, Gedanken A, Calderon-Moreno J (2003) Deposition of gold nanoparticles on silica spheres: a sonochemical approach. *Chem Mater* 15:1111–1118. doi:10.1021/cm021013+
59. Gachard E, Remita H, Khatouri J, Keita B, Nadjo L, Belloni J (1998) Radiation-induced and chemical formation of gold clusters. *New J Chem* 22:1257–1265. doi:10.1039/a804445g
60. Chen W, Cai WP, Liang CH, Zhang LD (2001) Synthesis of gold nanoparticles dispersed within pores of mesoporous silica induced by ultrasonic irradiation and its characterization. *Mater Res Bull* 36:335–342. doi:10.1016/S0025-5408(01)00497-4
61. Moessner S, Spatz JP, Moeller M, Aberle T, Schmidt J, Burchard W (2000) Solution behavior of poly(styrene)-. *Macromolecules* 33:4791–4798
62. Okitsu K, Yue A, Tanabe S, Matsumoto H, Yobiko Y (2001) Formation of colloidal gold nanoparticles in an ultrasonic field: control of rate of gold(III) reduction and size of formed gold particles. *Langmuir* 17:7717–7720. doi:10.1021/la010414l
63. Zhou Y, Wang CY, Zhu YR, Chen ZY (1999) A novel ultraviolet irradiation technique for shape-controlled synthesis of gold nanoparticles at room temperature. *Chem Mater* 11:2310–2312. doi:10.1021/cm990315h
64. Mallick K, Wang ZL, Pal T (2001) Seed-mediated successive growth of gold particles accomplished by UV irradiation: a photochemical approach for size-controlled synthesis. *J Photochem Photobiol A Chem* 140:75–80. doi:10.1016/S1010-6030(01)00389-6
65. Mohamed MB, Abouzeid KM, Abdelsayed V, Aljarash AA, El-Shall MS (2010) Growth mechanism of anisotropic gold nanocrystals via microwave synthesis: formation of dioleamide by gold nanocatalysis. *ACS Nano* 4:2766–2772. doi:10.1021/nn9016179
66. Pillai ZS, Kamat PV (2004) What factors control the size and shape of silver nanoparticles in the citrate ion reduction method? *J Phys Chem B* 108:945–951. doi:10.1021/jp037018r
67. Xia Y, Xiong Y, Lim B, Skrabalak SE (2009) Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? *Angew Chem Int Ed* 48:60–103. doi:10.1002/anie.200802248
68. Wiley B, Herricks T, Sun Y, Xia Y (2004) Polyol synthesis of silver nanoparticles: use of chloride and oxygen to promote the formation of single-crystal, truncated cubes and tetrahedrons. *Nano Lett* 4:1733–1739. doi:10.1021/nl048912c
69. Wiley BJ, Wang Z, Wei J, Yin Y, Cobden DH, Xia Y (2006) Synthesis and electrical characterization of silver nanobeams. *Nano Lett* 6:2273–2278. doi:10.1021/nl061705n
70. Sun Y, Mayers B, Herricks T, Xia Y (2003) Polyol synthesis of uniform silver nanowires: a plausible growth mechanism and the supporting evidence. *Nano Lett* 3:955–960. doi:10.1021/nl034312m
71. Tao A, Sinsersuksakul P, Yang P (2006) Polyhedral silver nanocrystals with distinct scattering signatures. *Angew Chem Int Ed* 45:4597–4601. doi:10.1002/anie.200601277
72. Skrabalak SE, Wiley BJ, Kim M, Formo EV, Xia Y (2008) On the polyol synthesis of silver nanostructures: glycolaldehyde as a reducing agent. *Nano Lett* 8:2077–2081. doi:10.1021/nl800910d
73. Lee CH, Tian L, Abbas A, Kattumenu R, Singamaneni S (2011) Directed assembly of gold nanorods using aligned electrospun polymer nanofibers for highly efficient SERS substrates. *Nanotechnology* 22:275311. doi:10.1088/0957-4484/22/27/275311
74. Kawasaki M, Hori M (2003) Laser-induced conversion of noble metal-island films to dense monolayers of spherical nanoparticles. *J Phys Chem B* 107:6760–6765. doi:10.1021/jp034768s
75. Tsuji T, Kakita T, Tsuji M (2003) Preparation of nano-size particles of silver with femtosecond laser ablation in water. *Appl Surf Sci* 206:314–320. doi:10.1016/S0169-4332(02)01230-8
76. Zhang J, Li S, Wu J, Schatz GC, Mirkin CA (2009) Plasmon-mediated synthesis of silver triangular bipyramids. *Angew Chem Int Ed* 48:7787–7791. doi:10.1002/anie.200903380
77. Jin R, Cao Y, Mirkin CA, Kelly KL, Schatz GC, Zheng JG (2001) Photoinduced conversion of silver nanospheres to nanoprisms. *Science* 294:1901–1903. doi:10.1126/science.1066541
78. Xue C, Métraux GS, Millstone JE, Mirkin CA (2008) Mechanistic study of photomediated triangular silver nanoprism growth. *J Am Chem Soc* 130:8337–8344. doi:10.1021/ja8005258
79. Zheng X, Xu W, Corredor C, Xu S, An J, Zhao B, Lombardi JR (2007) Laser-induced growth of monodisperse silver nanoparticles with tunable surface plasmon resonance properties and a wavelength self-limiting effect. *J Phys Chem C* 111:14962–14967. doi:10.1021/jp074583b
80. Wu X, Redmond PL, Liu H, Chen Y, Steigerwald M, Brus L (2008) Photovoltage mechanism for room light conversion of citrate stabilized silver nanocrystal seeds to large nanoprisms. *J Am Chem Soc* 130:9500–9506. doi:10.1021/ja8018669
81. Shang L, Chen H, Dong S (2007) Electrochemical preparation of silver nanostructure on the planar surface for application in metal-enhanced fluorescence. *J Phys Chem C* 111:10780–10784. doi:10.1021/jp068713c
82. Le Ru EC, Meyer M, Etchegoin PG (2006) Proof of single-molecule sensitivity in surface enhanced Raman scattering (SERS) by means of a two-analyte technique. *J Phys Chem B* 110:1944–1948. doi:10.1021/jp054732v
83. Pakizeh T, Käll M (2009) Unidirectional ultracompact optical nanoantennas. *Nano Lett* 9:2343–2349. doi:10.1021/nl900786u
84. Fantuzzi, G, Pengo P, Gomila R, Ballester P, Hunter CA, Itm CNR, Padova U, Uk S, Multivalent recognition of bis- and tris-Zn-porphyrins by N-methylimidazole functionalized gold nanoparticles. *Chem Comm* 8:1004–1005
85. Devilez A, Stout B, Bonod N (2010) Compact metallo-dielectric optical antenna for ultra directional and enhanced radiative emission. *ACS Nano* 4:3390–3396. doi:10.1021/nn100348d
86. Blackie EJ, Le Ru EC, Etchegoin PG (2009) Single-molecule surface-enhanced Raman spectroscopy of nonresonant molecules. *J Am Chem Soc* 131:14466–14472. doi:10.1021/ja905319w
87. Kim G-M, Wutzler A, Radsch H-J, Michler GH, Simon P, Sperling RA, Parak WJ (2005) One-dimensional arrangement of gold nanoparticles by electrospinning. *Chem Mater* 17:4949–4957. doi:10.1021/cm0508120
88. Jeon SH, Xu P, Zhang B, Mack NH, Tsai H, Chiang LY, Wang HL (2011) Polymer-assisted preparation of metal nanoparticles with controlled size and morphology. *J Mater Chem* 21:2550–2554. doi:10.1039/C0JM02340J
89. Patakfalvi R, Virányi Z, Dékány I (2004) Kinetics of silver nanoparticle growth in aqueous polymer solutions. *Colloid Polym Sci* 283:299–305. doi:10.1007/s00396-004-1138-8
90. Laudenslager MJ, Schiffman JD, Schauer CL (2008) Carboxymethyl chitosan as a matrix material for platinum, gold, and silver nanoparticles. *Biomacromolecules* 9:2682–2685. doi:10.1021/bm800835e
91. Zhao Y, Zhou Y, Wu X, Wang L, Xu L, Wei S (2012) A facile method for electrospinning of Ag nanoparticles/poly(vinyl alcohol)/carboxymethyl-chitosan nanofibers. *Appl Surf Sci* 258:8867–8873. doi:10.1016/j.apsusc.2012.05.106
92. Washio I, Xiong Y, Yin Y, Xia Y (2006) Reduction by the end groups of poly(vinyl pyrrolidone): a new and versatile route to the kinetically controlled synthesis of Ag triangular nanoplates. *Adv Mater* 18:1745–1749. doi:10.1002/adma.200600675
93. Nguyen TH, Lee KH, Lee BT (2010) Fabrication of Ag nanoparticles dispersed in PVA nanowire mats by microwave irradiation and electro-spinning. *Mater Sci Eng C* 30:944–950. doi:10.1016/j.msec.2010.04.012
94. Sengupta R, Chakraborty S, Bandyopadhyay S, Dasgupta S, Mukhopadhyay R, Auddy K, Deuri AS (2007) A short review on rubber/clay nanocomposites with emphasis on mechanical properties. *Engineering* 47:21–25. doi:10.1002/pen
95. Hiep NT, Khon HC, Niem WT, Toi W, Quyen TN, Hai ND, Anh MNT (2016) Microwave-assisted synthesis of chitosan/polyvinyl alcohol silver nanoparticles gel for wound dressing applications. *Int J Polym Sci* 2016:1–11. doi:10.1155/2016/1584046
96. Hang AT, Tae B, Park JS (2010) Non-woven mats of poly(vinyl alcohol)/chitosan blends containing silver nanoparticles: fabrication and characterization. *Carbohydr Polym* 82:472–479. doi:10.1016/j.carbpol.2010.05.016
97. Dong G, Xiao X, Liu X, Qian B, Liao Y, Wang C, Chen D, Qiu J (2009) Functional Ag porous films prepared by electrospinning. *Appl Surf Sci* 255:7623–7626. doi:10.1016/j.apsusc.2009.04.039
98. Tijing LD, Amarjargal A, Jiang Z, Ruelo MTG, Park CH, Pant HR, Kim DW, Lee DH, Kim CS (2013) Antibacterial tourmaline nanoparticles/polyurethane hybrid mat decorated with silver nanoparticles prepared by electrospinning and UV photoreduction. *Curr Appl Phys* 13:205–210. doi:10.1016/j.cap.2012.07.011
99. Wang J, Bin Yao H, He D, Zhang CL, Yu SH (2012) Facile fabrication of gold nanoparticles-poly(vinyl alcohol) electrospun water-stable nanofibrous mats:

- efficient substrate materials for biosensors. *ACS Appl Mater Interfaces* 4: 1963–1971. doi:10.1021/am300391j
100. Zhang CL, Lv KP, Cong HP, Yu SH (2012) Controlled assemblies of gold nanorods in PVA nanofiber matrix as flexible free-standing SERS substrates by electrospinning. *Small* 8:647–653. doi:10.1002/sml.201290030
101. Zhang H, Hu Z, Ma Z, Gecevičius M, Dong G, Zhou S, Qiu J (2016) Anisotropically enhanced nonlinear optical properties of ensembles of gold nanorods electrospun in polymer nanofiber film. *ACS Appl Mater Interfaces* 8:2048–2053. doi:10.1021/acsami.5b10411
102. Bai J, Li Y, Yang S, Du J, Wang S, Zheng J, Wang Y, Yang Q, Chen X, Jing X (2007) A simple and effective route for the preparation of poly(vinylalcohol) (PVA) nanofibers containing gold nanoparticles by electrospinning method. *Solid State Commun* 141:292–295. doi:10.1016/j.ssc.2006.10.024
103. Dong H, Wang D, Sun G, Hinestroza JP (2008) Assembly of metal nanoparticles on electrospun nylon 6 nanofibers by control of interfacial hydrogen-bonding interactions. *Chem Mater* 20:6627–6632. doi:10.1021/cm801077p
104. Tanahashi I, Kanno H (2000) Temperature dependence of photoinduced Au particle formation in polyvinyl alcohol films. *Appl Phys Lett* 77:3358. doi:10.1063/1.1328092
105. Rodríguez-Lorenzo L, Alvarez-Puebla RA, Pastoriza-Santos I, Mazzucco S, Stéphane O, Kociak M, Liz-Marzán LM, de Abajo FJ G (2009) Zeptomol detection through controlled ultrasensitive surface-enhanced raman scattering. *J Am Chem Soc* 131:4616–4618. doi:10.1021/ja809418t
106. Severyukhina AN, Parakhonskiy BV, Prikhozhdenko ES, Gorin DA, Sukhorukov GB, Möhwald H, Yashchenok AM (2015) Nanoplasmonic chitosan nanofibers as effective SERS substrate for detection of small molecules. *ACS Appl Mater Interfaces* 7:15466–15473. doi:10.1021/acsami.5b03696
107. Yashchenok A, Masic A, Gorin D, Shim BS, Kotov NA, Fratzi P, Möhwald H, Skirtach A (2013) Nanoengineered colloidal probes for raman-based detection of biomolecules inside living cells. *Small* 9:351–356. doi:10.1002/sml.201201494
108. Xu LJ, Zong C, Zheng XS, Hu P, Feng JM, Ren B (2014) Label-free detection of native proteins by surface-enhanced Raman spectroscopy using iodide-modified nanoparticles. *Anal Chem* 86:2238–2245. doi:10.1021/ac403974n
109. Li J, Chen L, Lou T, Wang Y (2011) Highly sensitive SERS detection of As³⁺ ions in aqueous media using glutathione functionalized silver nanoparticles. *ACS Appl Mater Interfaces* 3:3936–3941. doi:10.1021/am200810x
110. Khlebtsov BN, Khanadeev VA, Panfilova EV, Bratashov DN, Khlebtsov NG (2015) Gold nanoisland films as reproducible SERS substrates for highly sensitive detection of fungicides. *ACS Appl Mater Interfaces* 7:6518–6529. doi:10.1021/acsami.5b01652
111. Drescher D, Büchner T, McNaughton D, Kneipp J (2013) SERS reveals the specific interaction of silver and gold nanoparticles with hemoglobin and red blood cell components. *Phys Chem Chem Phys* 15:5364–73. doi:10.1039/c3cp43883j
112. Vo-Dinh T, Yan F, MB Wabuyele WB (2005) Surface-enhanced Raman scattering for medical diagnostics and biological imaging. *J Raman Spectrosc* 36:640–647. doi:10.1002/jrs.1348
113. Fan M, Andrade GFS, Brolo AG (2011) A review on the fabrication of substrates for surface enhanced Raman spectroscopy and their applications in analytical chemistry. *Anal Chim Acta* 693:7–25. doi:10.1016/j.aca.2011.03.002
114. Zhang L, Gong X, Bao Y, Zhao Y, Xi M, Jiang C, Fong H (2012) Electrospun nanofibrous membranes surface-decorated with silver nanoparticles as flexible and active/sensitive substrates for surface-enhanced Raman scattering. *Langmuir* 28:14433–14440. doi:10.1021/la302779q
115. Yang T, Ma J, Zhen S, Huang C (2016) Electrostatic assemblies of well-dispersed AgNPs on the surface of electrospun nanofibers as highly active SERS substrates for wide-range pH sensing. *ACS Appl Mater Interfaces* 8: 14802–14811. doi:10.1021/acsami.6b03720
116. He D, Hu B, Yao Q, Wang K, Yu S (2009) Large-scale synthesis of flexible free-standing SERS substrates with high sensitivity: electrospun PVA nanofibers embedded with controlled alignment of silver nanoparticles. *ACS Nano* 3:3993–4002. doi:10.1021/nn900812f
117. Zhang C-L, Lv K-P, Huang H-T, Cong H-P, Yu S-H (2012) Co-assembly of Au nanorods with Ag nanowires within polymer nanofiber matrix for enhanced SERS property by electrospinning. *Nanoscale* 4:5348. doi:10.1039/c2nr30736g
118. Liou P, Nayigiziki FX, Kong F, Mustapha A, Lin M (2017) Cellulose nanofibers coated with silver nanoparticles as a SERS platform for detection of pesticides in apples. *Carbohydr Polym* 157:643–650. doi:10.1016/j.carbpol.2016.10.031
119. Zhong L, Yin J, Zheng Y, Liu Q, Cheng X, Luo F (2014) Self-assembly of Au nanoparticles on PMMA template as flexible, transparent, and highly active SERS substrates. *Anal Chem* 86:6262–6267. doi:10.1021/ac404224f
120. Liu Z, Yan Z, Jia L, Song P, Mei L, Bai L, Liu Y (2017) Gold nanoparticle decorated electrospun nanofibers: a 3D reproducible and sensitive SERS substrate. *Appl Surf Sci* 403:29–34. doi:10.1016/j.apsusc.2017.01.157
121. Zhang S, Ni W, Kou X, Yeung MH, Sun L, Wang J, Yan C (2007) Formation of gold and silver nanoparticle arrays and thin shells on mesostructured silica nanofibers. *Adv Funct Mater* 17:3258–3266. doi:10.1002/adfm.200700366
122. Zhang CL, Lv KP, Hu NY, Yu L, Ren XF, Liu SL, Yu SH (2012) Macroscopic-scale alignment of ultralong Ag nanowires in polymer nanofiber mat and their hierarchical structures by magnetic-field-assisted electrospinning. *Small* 8:2936–2940. doi:10.1002/sml.201201353
123. Wu H, Lin D, Pan W (2010) High performance surface-enhanced Raman scattering substrate combining low dimensional and hierarchical nanostructures. *Langmuir* 26:6865–6868. doi:10.1021/la1000649
124. Li X, Cao M, Zhang H, Zhou L, Cheng S, Yao JL, Fan LJ (2012) Surface-enhanced Raman scattering-active substrates of electrospun polyvinyl alcohol/gold-silver nanofibers. *J Colloid Interface Sci* 382:28–35. doi:10.1016/j.jcis.2012.05.048
125. Li D, Lv P, Zhu J, Lu Y, Chen C, Zhang X, Wei Q (2015) Nicu alloy nanoparticle-loaded carbon nanofibers for phenolic biosensor applications. *Sensors (Switzerland)* 15:29419–29433. doi:10.3390/s151129419
126. Wang B, Akiba U, Anzai J (2017) Recent progress in nanomaterial-based electrochemical biosensors for cancer biomarkers: A review. *Molecules* 22: 1048, 1–20. doi:10.3390/molecules22071048
127. Li Y, Schluesener HJ, Xu S (2010) Gold nanoparticle-based biosensors. *Gold Bull* 43:29–41. doi:10.1007/BF03214964
128. Chen M, Diao G (2009) Electrochemical study of mono-6-thio- β -cyclodextrin/ferrocene capped on gold nanoparticles: characterization and application to the design of glucose amperometric biosensor. *Talanta* 80: 815–820. doi:10.1016/j.talanta.2009.07.068
129. Li Y, Song YY, Yang C, Xia XH (2007) Hydrogen bubble dynamic template synthesis of porous gold for nonenzymatic electrochemical detection of glucose. *Electrochem Commun* 9:981–988. doi:10.1016/j.elecom.2006.11.035
130. Li J, Lin X (2007) Simultaneous determination of dopamine and serotonin on gold nanocluster/overoxidized-polypropylene composite modified glassy carbon electrode. *Sensors Actuators, B Chem* 124:486–493. doi:10.1016/j.snb.2007.01.021
131. Raj CR, Okajima T, Ohsaka T (2003) Gold nanoparticle arrays for the voltammetric sensing of dopamine. *J Electroanal Chem* 543:127–133. doi:10.1016/S0022-0728(02)01481-X
132. Li M, Gao F, Yang P, Wang L, Fang B (2008) Conveniently assembling dithiocarbamate and gold nanoparticles onto the gold electrode: a new type of electrochemical sensors for biomolecule detection. *Surf Sci* 602:151–155. doi:10.1016/j.susc.2007.10.006
133. Zhang L, Jiang X (2005) Attachment of gold nanoparticles to glassy carbon electrode and its application for the voltammetric resolution of ascorbic acid and dopamine. *J Electroanal Chem* 583:292–299. doi:10.1016/j.jelechem.2005.06.014
134. Yin H, Zhou Y, Ai S, Han R, Tang T, Zhu L (2010) Electrochemical behavior of bisphenol a at glassy carbon electrode modified with gold nanoparticles, silk fibroin, and PAMAM dendrimers. *Microchim Acta* 170:99–105. doi:10.1007/s00604-010-0396-z
135. Domínguez-Renedo O, Alonso-Lomillo MA, Ferreira-Gonçalves L, Arcos-Martínez MJ (2009) Development of urease based amperometric biosensors for the inhibitive determination of Hg (II). *Talanta* 79:1306–1310. doi:10.1016/j.talanta.2009.05.043
136. Zhu Z, Su Y, Li J, Li D, Zhang J, Song S, Zhao Y, Li G, Fan C (2009) Highly sensitive electrochemical sensor for mercury (II) ions by using a mercury-specific oligonucleotide probe and gold nanoparticle-based amplification. *Work* 81:7660–7666. doi:10.1021/ac9010809
137. Xu H, Zeng L, Xing S, Shi G, Xian Y, Jin L (2008) Microwave-radiated synthesis of gold nanoparticles/carbon nanotubes composites and its application to voltammetric detection of trace mercury(II). *Electrochem Commun* 10:1839–1843. doi:10.1016/j.elecom.2008.09.030
138. Abollino O, Giacomino A, Malandrino M, Piscionieri G, Mentasti E (2008) Determination of mercury by anodic stripping voltammetry with a gold nanoparticle-modified glassy carbon electrode. *Electroanalysis* 20:75–83. doi:10.1002/elan.200704044
139. Domínguez Renedo O, Arcos Martínez MJ (2007) Anodic stripping voltammetry of antimony using gold nanoparticle-modified carbon screen-printed electrodes. *Anal Chim Acta* 589:255–260. doi:10.1016/j.aca.2007.02.069

140. Xu S, Peng B, Han X (2007) A third-generation H₂O₂ biosensor based on horseradish peroxidase-labeled Au nanoparticles self-assembled to hollow porous polymeric nanospheres. *Biosens Bioelectron* 22:1807–1810. doi:10.1016/j.bios.2006.07.008
141. Kerman K, Saito M, Tamiya E, Yamamura S, Takamura Y (2008) Nanomaterial-based electrochemical biosensors for medical applications. *TrAC - Trends Anal Chem* 27:585–592. doi:10.1016/j.trac.2008.05.004
142. Pingarrón JM, Yáñez-Sedeño P, González-Cortés A (2008) Gold nanoparticle-based electrochemical biosensors. *Electrochim Acta* 53:5848–5866. doi:10.1016/j.electacta.2008.03.005
143. Siangproh W, Dungchai W, Rattanarat P, Chailapakul O (2011) Nanoparticle-based electrochemical detection in conventional and miniaturized systems and their bioanalytical applications: a review. *Anal Chim Acta* 690:10–25. doi:10.1016/j.aca.2011.01.054
144. Luo X, Morrin A, Killard AJ, Smyth MR (2006) Application of nanoparticles in electrochemical sensors and biosensors. *Electroanalysis* 18:319–326. doi:10.1002/elan.200503415
145. Che X, Yuan R, Chai Y, Li J, Song Z, Wang J (2010) Amperometric immunosensor for the determination of α -1-fetoprotein based on multiwalled carbon nanotube-silver nanoparticle composite. *J Colloid Interface Sci* 345:174–180. doi:10.1016/j.jcis.2010.01.033
146. Sapountzi E, Braiek M, Vocanson F, Chateaux JF, Jaffrezic-Renault N, Lagarde F (2017) Gold nanoparticles assembly on electrospun poly(vinyl alcohol)/poly(ethyleneimine)/glucose oxidase nanofibers for ultrasensitive electrochemical glucose biosensing. *Sensors Actuators, B Chem* 238:392–401. doi:10.1016/j.snb.2016.07.062
147. M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, Synthesis of thiol-derivatised gold nanoparticles in, *Chem. Commun.* (1994) 801–802. doi:10.1039/c39940000801
148. Ren S, Dong L, Zhang X, Lei T, Ehrenhauser F, Song K, Li M, Sun X, Wu Q (2017) Electrospun nanofibers made of silver nanoparticles, cellulose nanocrystals, and polyacrylonitrile as substrates for surface-enhanced Raman scattering. *Materials (Basel)* 10:68. doi:10.3390/ma10010068
149. Bao Y, Lai C, Zhu Z, Fong H, Jiang C (2013) SERS-active silver nanoparticles on electrospun nanofibers facilitated via oxygen plasma etching. *RSC Adv* 3: 8998. doi:10.1039/c3ra41322e
150. Zhang T, Wang W, Zhang D, Zhang X, Yurong M, Zhou Y, Qi L (2010) Biotemplated synthesis of cold nanoparticle-bacteria cellulose nanofiber nanocomposites and their application in biosensing. *Adv Funct Mater* 20: 1152–1160. doi:10.1002/adfm.200902104
151. Huang Y, Miao YE, Ji S, Tjiu WW, Liu T (2014) Electrospun carbon nanofibers decorated with Ag-Pt bimetallic nanoparticles for selective detection of dopamine. *ACS Appl Mater Interfaces* 6:12449–12456. doi:10.1021/am502344p

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