Green Synthesis of Highly Concentrated and Stable Colloidal Dispersion of Core-Shell Silver Nanoparticles (AgNPs-Shell) and their Antimicrobial and Ultra-high Catalytic Properties

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Abstract

The versatile one-pot green synthesis of a highly concentrated and stable colloidal dispersion of AgNPs was carried out using the self-assembled tannic acid without using any other hazardous chemicals. Tannic acid (Plant-based polyphenol) was used as a reducing and stabilizing agent for silver nitrate in a mild alkaline condition. The synthesized AgNPs were characterized for their concentration, capping, size distribution, and shape. The experimental results confirmed the successful synthesis of nearly spherical and highly concentrated (2281 ppm) AgNPs, capped with poly-tannic acid (AgNPs-PTA). The average particle size of AgNPs-PTA was found 9.90 ± 1.60 nm. The colloidal dispersion of synthesized nanoparticles was observed stable for more than 15 months in the ambient environment (25 °C, 65 % relative humidity). The synthesized AgNPs-PTA showed an effective antimicrobial activity against Staphylococcus Aureus Escherichia coli. Ag-PTA also exhibited enhanced catalytic properties. It reduces 4-nitrophenol into 4-aminophenol in the presence of NaBH₄ with a normalized rate constant ($K_{nor} = K/m$) of 615.04 mL·s⁻¹·mg⁻¹. Furthermore, AgNPs-PTA were stable for more than 15 months under ambient conditions. The unique core-shell structure and ease of synthesis render the synthesized nanoparticles superior to others, with potential for large-scale applications, especially in the field of catalysis and biomedical.

KEYWORDS: Biomedical, Green Synthesis, Silver Nanoparticles, Colloidal stability, Antimicrobial and catalytic activity.
1 Introduction

Metallic nanoparticles have attracted the attention of scientists and researchers and have found applications in the emerging fields of nanoscience and biomedical technology [1,2]. Among many metallic nanoparticles, silver nanoparticles (AgNPs) are well known for their wide range use for optical, catalytic, electrical, and biomedical applications [3–5]. Generally, AgNPs are prepared by the chemical [6], and physical [7] synthesis methods. The physical and chemical methods for the synthesis of AgNPs involve the use of toxic, costly, and environmentally hazardous materials. Most recently, the green synthesis methods [5] are introduced that allow the use of eco-friendly, cost-effective and nontoxic preparation of AgNPs. Plant-mediated green synthesis of AgNPs has several advantages over the physical and chemical synthesis methods as it is facile, cost-effective, easy to scale up, and eco-friendly [8]. Furthermore, the green synthesis technique results in higher stable dispersions of nanoparticles without using high energy input, high pressure, high temperature, and toxic chemicals [9].

Tannic acid (TA) contains catechol and galloyl groups, which are well known for their metal chelation and material surface binding properties and play a vital role in the green synthesis of nanoparticles at room temperature by acting as both, reducing and capping agent [10,11]. In alkaline conditions, TA polymerizes and forms a capping layer of poly tannic acid [12]. These two properties of TA make it an ideal candidate for the green synthesis of metallic nanoparticles. In the past, several attempts were reported to fabricate tannic acid-mediated nanoparticles and their potential applications in the field of surface-enhanced Raman scattering [13], catalysis [14], treatment of organic pollutants [15], visual detection of ions [16], toxic gas sensing [17], and biomedical [18].

Due to the multi-drug resistant bacteria, it is vital to find alternative means to kill them [19,20]. Ag NPs are well known due to their antimicrobial activity [21]. However, the stability of nanoparticles plays a unique role in their antibacterial activity [22,23]. One method for stabilizing the Ag NPs is to encapsulate them in a shell [24], like Ag NPs-PTA. Additionally, biocompatible TA also exhibits antibacterial activity [25]. Ag NPs are also reported to exhibit good catalytic properties for the reduction of environmental pollutants. It has been found that higher stability and better dispersion of nanocatalysts, due to the shell, results in enhanced catalytic activity. Therefore, the unique self-polymerization and reducing properties of TA were utilized for the facile synthesis of highly concentrated and stable dispersion of Ag NPs-PTA.

Ag NPs-PTA were characterized for their concentration, capping, size distribution, shape, stability, antibacterial, and catalytic properties. The experimental results show the successful synthesis of nearly spherical and highly concentrated (2281 ppm) Ag NPs, capped with poly-tannic acid (Ag NPs-PTA). The average particle size of Ag NPs-PTA was found 9.90 ± 1.60 nm. The colloidal dispersion of synthesized nanoparticles was observed stable for more than 15 months in the ambient environment. To the best of the authors’ knowledge, it is the first time that such an effective antimicrobial agent and reduction catalyst with high concentration and high colloidal stability are prepared by green synthesis method.
2 Experimental Work

2.1 Materials
Silver nitrate (AgNO₃), tannic acid (C₇₆H₅₂O₄₆, 1701.01 g/mol), sodium borohydride (NaBH₄), 4-nitrophenol (4-NP), and sodium hydroxide (NaOH) were supplied by Sigma-Aldrich. Ultrapure deionized (DI) water, collected from a Milli-Q SP reagent water system (Millipore, Milford, MA), was used during the synthesis process. All the chemicals were used as received without any purification. Luria-Bertani (LB) broth with agar (Lennox) and LB broth (Lennox) was supplied by Merck for anti-bacterial analysis. Freshly prepared solutions of all the chemicals were used during all chemical reactions.

2.2 Synthesis of Ag NPs-PTA
The synthesis of Ag NPs-PTA was carried out by one-pot mixing of 10 ml AgNO₃ (0.147 M), 35 ml TA (1 mM) and 1.35 ml of NaOH (0.2 M) in the ambient environment. The suspension was vigorously mixed using a magnetic stirrer for 10 minutes to produce a homogenous mixture followed by heating at 45 ºC for 30 minutes stirring at 250 RPM. The solution was cooled down to room temperature and the freshly prepared nanoparticles were collected by centrifugal separation (1100 RPM for 15 minutes) and were washed three times using DI water. Figure 1 shows a schematic of the steps involved in this novel method of Ag NPs preparation.

![Schematic diagram for the green synthesis of Ag NPs-PTA](image)

Figure 1. The schematic diagram for the green synthesis of Ag NPs-PTA.

Ag NPs-PTA dispersion was applied to the Activated Carbon Fibre (ACF) sheets (round shape and 1.5 cm in diameter) by drop-coating method followed drying in the vacuum oven at 50 ºC for 2 hours. Four ACF sheets were placed in the tissue culture plate. The aqueous solution of nanoparticles was drop coated in a way to obtain 0.5 mg, 1 mg, 2 mg,
and 4 mg final concentration of nanoparticles on the samples, respectively. The samples coated with nanoparticles were placed overnight in the vacuum oven for drying at 50 ºC.

2.3 Characterization

The successful synthesis of Ag NPs-PTA was confirmed by measuring the ultraviolet-visible (UV-Vis) spectrum using a spectrophotometer (Model: JASCO V-770). The absorption spectrum of the nanoparticle’s dispersion was analyzed in the range of 200 to 700 nm. The size distribution, shape, surface morphology, and other physical properties of the particles were examined by using Schottky Field Emission Scanning Electron Microscopy (FE-SEM, Model: JEOL JSM-7600F) at an accelerating voltage of 15 kV and High-Resolution Transmission Electron Microscopy (HR-TEM, Model: JEM-3010). Samples were prepared by drop coating of aqueous solution on the carbon-coated copper grid for morphological analysis of Ag NPs-PTA by TEM. Elemental analysis of the Ag NPs-PTA was evaluated with the help of an energy dispersive spectrometer (EDS, Model: X-MAX 50).

Zeta-potential analysis of the sample was conducted in water with the help of Zeta sizer Malvern Instruments (Model: Nano-SZ). Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Model: Agilent 7500) was used to determine the actual concentration of the product. The chemical composition of Ag NPs-PTA was also confirmed by an X-Ray Photoelectron Spectrometer (XPS, Model: ESCALAB250).

2.4 Antimicrobial Tests

The Antimicrobial activity of synthesized nanoparticles was analyzed against Gram-negative, Escherichia coli (E. coli, ATCC1129) and Gram-positive, Staphylococcus aureus (S. aureus, ATCC 6538). The AATC147-2004 standard zone of inhibition test was adopted to determine the Antimicrobial performance of synthesized Ag NPs-PTA [26]. The Luria-Bertani (LB) agar solution (25 ml) was added to the agar plates and were placed into a refrigerator for 15 minutes. 50 µl of fresh suspension of bacterial strains (E. coli and S. aureus, 10^5 -10^6 CFU per ml) was transferred to LB agar plates. Bacterial colonies were spread gently in the plate surface with the help of a sterilized glass rod. Round shape ACF samples (1.5×1.5 cm) containing 0.5 mg, 1 mg, 2 mg, and 4 mg concentrations of synthesized Ag NPs-PTA were placed in the LB agar plates along with the reference (control) ACF sample (without Ag NPs-PTA). LB agar plates having ACF samples were placed into the incubator at 37 ºC for 24 hours. The zones of inhibition around the samples were measured to determine the antimicrobial activity of Ag NPs-PTA.

2.5 Catalytic reduction of 4-NP

The catalytic reduction of the 4-NP into 4-AP in the presence of excess NaBH₄ was carried out to analyze the catalytic activity Ag NPs-PTA. Briefly, 2 mL of fresh DI water, 1 mL of freshly prepared NaBH₄ (1 M), and 100 µL 4-NP (5 mM) were added into a cuvette with constant mechanical stirring. To determine the catalytic reduction of the 4-NP, 50 µL of the prepared nanocatalysts (1 mM) was added to the mixture. To monitor the reaction progress, the UV-visible spectrum of the solution was measured at different intervals of time.
3 Results and Discussion

UV-Vis absorption spectrophotometer was used to confirm the successful synthesis of Ag NPs-PTA. Figure 2 represents the characteristic UV-Vis spectrum of the synthesized Ag NPs-PTA nanoparticle dispersion. The concentrated sample was diluted 300 times for UV-Vis analysis. The results, figure 2, shows a sharp absorption at 440 nm, which is a typical surface plasmon resonance absorbance band for Ag NPs-PTA [12].

![UV-Vis spectrum](image)

**Figure 2.** UV-Vis spectrum of the nanoparticle dispersion.

Figures 3(a) and 3(b) represent the FE-SEM and HR-TEM analysis results for the surface morphology of the synthesized Ag NPs-PTA. Spherical-shaped nanoparticles with an average particle size of $\sim 9.90 \pm 1.60$ nm (determined by using ImageJ software) were observed and the corresponding size distribution histogram is shown in figure 3(c). The EDS results, figure 3(d), shows the presence of Ag, C, and O elements and thus confirm the synthesis of pure Ag NPs-PTA nanocomposites. A prominent peak, (figure 3d) was observed at 3 keV due to the characteristic surface plasmon resonance of the silver nanocomposites while the shorter peaks are attributed to the capping agent of the particles and silicon wafer substrate. A similar observation is reported by other researchers while analyzing the EDS results for silver nanoparticles [27].
Figure 3. (a) SEM image of nearly monodispersed Ag NPs-PTA, (inset is the optical images of concentrated (left) and diluted (right) colloidal dispersion of Ag NPs-PTA); (b) HR-TEM image of nanoparticles; (c) Size distribution analysis of Ag NPs-PTA; and (d) EDS pattern of synthesized Ag NPs-PTA.

The Zeta potential value, to analyze the electrostatic stability of the Ag NPs-PTA, was found to be $-18.8 \pm 1.48$ mV, which indicates the high aqueous stability of these nanoparticles. The actual concentration of obtained Ag NPs-PTA, determined by ICP-MS, was found 2281 ppm. To the best of our knowledge, it is the first time that such a high concentration of Ag NPs has been successfully synthesized by a green synthesis process. Characteristics of synthesized nanoparticles are summarized in table 1 and compared with the previously reported data for comparison purposes.

The chemical composition of Ag NPs-PTA was analyzed by the XPS and corresponding results are shown in figure 4 (a & b). Fei et al. analyzed the tannic acid under XPS and reported C and O as the main components of the tannic acid [12]. The XPS results, reveals that AgNPs-PTA sample contains a very small quantity of silver as compared to other elements and confirms the Ag as a core and PTA as a capping layer and hence confirms the synthesis of core-shell (Ag NPs-PTA) nanoparticles. Moreover, the binding energy peaks of C 1s shift from 284.79 to 285.41 and O 1s shifts from 532.23 to 532.79 in Ag NPs-PTA compared to pure TA due to the oxidation of tannic acid [12].
To analyze the long-term stability of the Ag NPs-PTA, the sample was aged for 15 months in ambient conditions. Figure 5 (a) shows the UV-Vis spectra of the freshly prepared Ag NPs-PTA solution and Ag NPs-PTA solution aged for 15 months. The UV-Vis spectrum of the aged Ag NPs-PTA is almost similar to the UV-Vis spectrum of the fresh Ag NPs-PTA indicating that nanoparticles did not aggregate even after 15 months of shelf life. The Zeta potential values and the color of the Ag NPs-PTA dispersion before and after aging were also observed unchanged, figure 5 (b). The analyzed results, Zeta potential, color, and UV-Vis spectra, of the fresh and aged Ag NPs-PTA, confirm their long-term stability. TEM analysis also confirmed that nanoparticles do not aggregate even after 15 months of shelf life (data not shown).

**Figure 4.** (a) X-ray photoelectron (XPS) analysis of Ag NPs-PTA; (b) elemental composition of synthesized silver nanoparticles.

**Figure 5.** (a) UV-Vis spectra of freshly prepared Ag NPs-PTA solution and Ag NPs-PTA solution after 15 months of storage in a dark ambient environment; (b) Concentrated and diluted samples of synthesized Ag NPs-PTA before and after aging of 15 months.
### Table 1. Characteristics of synthesized Ag NPs synthesized in this study in comparison with those synthesized in previous studies

| Initial AgNO₃ Concentration (M) | AgNO₃ Synthesis time/Aqueous stability | Limitation of the synthesis process | Particle size (nm) | Synthesis method | Ref. |
|-------------------------------|---------------------------------------|-------------------------------------|--------------------|-----------------|------|
| 0.147                         | 30 min/ >15 months                    | Relatively lower conversion         | 9                  | Green chemistry | Current Study |
| 1.9                           | 25 h/-                                | Long reaction time under extreme precautions | 30                | Chemical    | [28] |
| 1.65                          | 2 h/3 months                          | Long reaction time, no reproducibility, broad size distribution | 20-230            | Chemical    | [29] |
| 0.94                          | 0.75 h/6 months                      | A relatively high temperature is required. Particles are not stable at low/mild alkaline condition | 5-80              | Chemical    | [30] |
| 0.83                          | 0.75 h/14 months                     | Use of toxic chemicals             | 14                 | Chemical    | [4]  |
| 0.43                          | 10 h/-                                | High energy input (200 W), long reaction time, and use of environmentally hazardous materials | 20-30             | Microwave   | [31] |
| 0.27                          | 7 min/-                               | Not stable at higher concentrations (>0.3M) | 26                | Chemical    | [32] |
| 0.16                          | 4.5 h/-                               | Two-phase, complicated process      | 4                  | Chemical    | [33] |
| 0.02                          | 2 min/-                               | Relatively low concentration and use of hazardous and toxic chemicals | 10                | Chemical    | [34] |
3.1 Antimicrobial Response Analysis

The ACF sheets were drop coated with Ag NPs-PTA dispersion to analyze the antimicrobial response of the synthesized Ag NPs-PTA. In general, nanoparticles easily release from the ACF sheet and they can effectively kill the microbes [35]. Figure 6 represents the SEM images of the ACF sheets drop coated with (b & c) and without (a) AgNPs-PTA dispersion. The results, in figure 6, show that the Ag NPs-PTA are not aggregated and are homogeneously distributed on the ACF sheet surface which is beneficial for antimicrobial applications.

![Figure 6](image)

**Figure 6.** (a) Surface morphology of ACF sheet; (b) Surface morphology of ACF sheet loaded with synthesized Ag NPs; (c) corresponding magnified image of ACF containing dispersed Ag NPs-PTA.

The antimicrobial response of the Ag NPs-PTA was analyzed using the standard Zone of Inhibition test. For this, antimicrobial activity of ACF sheets drop coated with and without Ag NPs-PTA, having different concentration of Ag NPs-PTA (0.0 (Reference/Control), 0.5 mg, 1.0 mg, 2.0 mg, 4.0 mg, respectively) was analysed against S. aureus, figure 7 (a) and E. coli, figure 7 (b), microbes. It was observed that the reference/control sample (C) show no inhibition against the antimicrobe while the ACF sheets drop coated with Ag NPs-PTA dispersion displayed remarkable antimicrobial performance and a clear Zone of Inhibition (ZOI) was noticed. Furthermore, this antimicrobial response lasted for around 8 days. The values of ZOI for each sample are reported in table 2. The results indicate that the Ag NPs-PTA dispersion is more effective towards E. coli compared to S. aureus. This could be due to the thin (7-8 nm) peptidoglycan layer (protecting layer) of E. coli compared to S. aureus (20-80 nm). Several other researchers also reported similar observations [36,37].
Figure 7. Zone of Inhibition (ZOI) of samples (1, 2, 3, 4, and C, containing different concentrations of Ag NPs-PTA) measured against (a) S. aureus and (b) E. coli microbial stains.

Table 2. Antimicrobial activity (ZOI) of the ACF sheet, containing different amount of Ag NPs measured against S. aureus and E. coli.

| Sample | Amount of silver (mg) | Zone of inhibition against E. coli (mm) | Zone of inhibition against S. aureus (mm) |
|--------|------------------------|-----------------------------------------|------------------------------------------|
| Control (C) | 0                      | 0                                       | 0                                        |
| 1      | 0.5                    | 1.5                                     | 0.7                                      |
| 2      | 1                      | 1.5                                     | 1.5                                      |
| 3      | 2                      | 2                                       | 1.5                                      |
| 4      | 4                      | 2                                       | 2.0                                      |

3.2 Catalytic Reduction of 4-NP

In addition to antimicrobial properties, synthesized Ag NPs-PTA nanocomposites also exhibited enhanced catalytic properties. The reduction of 4-NP to 4-AP was analyzed in the presence of excess NaBH₄. This model reduction reaction was monitored by UV-Vis spectroscopy at different intervals of time. As shown in Fig. 8, after the addition of Ag NPs-PTA nanocomposites, the characteristic absorption peak of 4-NP at 400 nm continues to decrease with time, while a new peak at 300 nm, attributed to 4-aminophenol (4-AP), increases slowly and simultaneously. The characteristic yellow color of the 4-NP disappeared completely after the completion of the reaction. It is important to note that, in the absence of synthesized nanocatalyst, characteristics yellow color and absorption peak of 4-NP (λ =400 nm) does not change even after 24 hours of incubation.
Figure 8. (a) UV-Vis spectra of the catalytic conversion of 4-NP to 4-AP in the presence of Ag NPs-PTA; (b) Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-NP into 4-AP in the presence of Ag NPs-PTA nanocatalyst.

The catalytic reaction follows pseudo-first-order kinetics in the presence of excess NaBH$_4$. For the normalization of $C_t$ to $C_0$, $A_t$ was divided by $A_0$ at 400 nm (where $C_0$ is the initial concentration and $C_t$ is the concentration of 4-NP at certain time $t$). Similarly, $A_0$ is the initial absorption and $A_t$ is the absorption of 4-NP at certain time $t$). The rate constant (from slope of dependence $\ln(A_t/A_0)$ on time $t$ obtained by least squares) for this reaction was $8.18 \times 10^{-2}$. A normalized rate constant $K_{nor} = K/m$ (where $m$ is the amount of silver [mg/mL] loaded for catalytic activity) was calculated to nullify the effect of the metal loading concentration. It is evident from the results ($K_{nor}$) summarized in Table 3 that the catalytic activity of synthesized Ag NPs-PTA nanocatalyst for the reduction of organic pollutant 4-NP was superior when compared to previously reported silver-based catalysts.

To the best of our knowledge, this is one of the highest rate constants reported for the reduction of 4-NP. This enhanced catalytic performance can be attributed to the synergistic effect of the silver nanoparticles, PTA shells, and the smaller Ag NPs-PTA nanocomposites compared to the previously reported data. The PTA shell of the nanocatalysts has abundant aromatic rings, which interact and improve the localized concentration of 4-NP and BH$_4^-$ from the aqueous solution through $\pi-\pi$ stacking interactions and thus contribute to the enhanced catalytic efficiency of the nanoparticles in the 4-NP reduction.
Table 3. Catalytic activities of Ag NPs-PTA nanocomposites for the 4-NP reduction in comparison with previously reported silver-based nanocatalysts

| Nanocatalyst structure          | Catalyst (mg/mL) | Rate constant K (s⁻¹) | $K_{\text{nor.}}$ (mL·s⁻¹·mg⁻¹) | Reference |
|---------------------------------|------------------|-----------------------|----------------------------------|-----------|
| Halloysite nanotubes-Ag         | 8.00 × 10⁻³       | 6.96 × 10⁻⁷           | 8.70 × 10⁻⁵                     | [38]      |
| Ag@PAA                          | 2.97 × 10⁻²       | 15.45 × 10⁻³          | 4.59 × 10⁻⁴                     | [39]      |
| Ag-NP/C composite               | 1.00 × 10⁻⁶       | 1.69 × 10⁻³           | 1.69 × 10⁻³                     | [40]      |
| EPS–Ag nanocomposites           | 2.60 × 10⁻²       | 1.26 × 10⁻³           | 4.80 × 10⁻²                     | [41]      |
| Ag NPs@PAA                      | 2.03 × 10⁻⁴       | 7.6 × 10⁻²            | 374.94                          | [4]       |
| TSC-Ag-1.4                      | 1.33 × 10⁻³       | 3.64 × 10⁻⁴           | 2.7 × 10⁻¹                      | [42]      |
| Fe₃O₄/SiO₂-Ag                   | 2.00 × 10⁻²       | 5.50 × 10⁻³           | 2.8 × 10⁻¹                      | [43]      |
| Fe₃O₄-C@Ag                      | 1.00 × 10⁻²       | 3.72 × 10⁻³           | 3.7 × 10⁻¹                      | [44]      |
| TAC-Ag-1.4                      | 1.33 × 10⁻³       | 1.65 × 10⁻³           | 1.24                            | [42]      |
| Fe₃O₄-C@Ag-Au                   | 1.00 × 10⁻²       | 15.80 × 10⁻³          | 1.58                            | [44]      |
| AgNP-PG-5K                      | 4.00 × 10⁻³       | 5.50 × 10⁻³           | 1.38                            | [45]      |
| Ag/SiO₂ 1.08                    | 1.1 × 10⁻³        | 2.53 × 10⁻³           | 2.30                            | [46]      |
| Graphene oxide/Ag NPs–Fe₃O₄    | 8.1 × 10⁻³        | 2.67 × 10⁻²           | 3.30                            | [47]      |
| TAC-Ag-1.0                      | 1.33 × 10⁻³       | 5.19 × 10⁻³           | 3.90                            | [42]      |
| Ag NPs@PGMA-SH composite        | 9.00 × 10⁻⁴       | 3.94 × 10⁻³           | 4.38                            | [48]      |
| AgNPs-PTA                       | 1.33 × 10⁻⁴       | 8.18 × 10⁻²           | 615.04                          | Our work |

4 Conclusion

In this research work, highly concentrated and stable colloidal dispersion of Ag NPs-PTA was synthesized using a novel, one-pot, and cost-effective green synthesis method. Nontoxic tannic acid was used for the fabrication of Ag NPs, as a strong reducing and capping agent under mild alkaline conditions. The synthesized nanoparticles displayed excellent colloidal stability in the ambient environment (more than 15 months). The synthesized Ag NPs-PTA were characterized, which confirmed the formation of nearly spherical shaped Ag NPs, with the average particle size of $\sim 9.90 \pm 1.60$ nm and capped with PTA. The Zeta Potential and UV-Vis analysis showed electrostatic and compositional stability of the synthesized Ag NPs-PTA dispersion before and after 15 months aging. The ACF sheet
samples drop coated with Ag NPs-PTA displayed remarkable Antimicrobial response when analyzed against S. aureus, and E. coli microbes. The synthesized Ag NPs-PTA nanocatalyst also displayed an enhanced catalytic performance for the reduction 4-NP to 4-AP with rate constant of \( K_{\text{cat}} = 63.71 \text{ mL} \cdot \text{s}^{-1} \cdot \text{mg}^{-1} \). This study may offer a unique opportunity for the fabrication of multifunctional metal-PTA nanocomposites, which will have many unique futures uses like catalytic, metal detection, and biomedical applications.

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