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Universal One-pot, One-step Synthesis of Core-shell Nanocomposites with Self-Assembled Tannic Acid Shell and Their Antibacterial and Catalytic Activities

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Abstract

Facile synthesis of metal@polymer nanocomposites were achieved using self-assembled tannic acid shells without cross-linkers. The tannic acid shell was assembled under mildly alkaline conditions in reaction time of 20 min under constant vortexing. Universal synthesis method was demonstrated by the synthesis of Ag@tannic acid and Au@tannic acid nanocomposites. We propose that the shell formation is due to tannic acid undergoing oxidative self-polymerization to poly(tannic acid) or a supramolecular aggregate of oxidized tannic acid held together by charge transfer, hydrogen bond and π - π interactions, similar to dopamine polymerization. Gibbs free energy calculations suggest that polymerization is energetically favorable. Synthesized Ag@tannic acid exhibited antibacterial functionality with *E. coli* Minimum Inhibitory Concentration (MIC) of 100 $\mu\text{g mL}^{-1}$ up to 48 h. The population of *E. coli* was also reduced by 99% within 5 h when incubated with 100 $\mu\text{g mL}^{-1}$ of Ag@tannic acid nanocomposite. Au@tannic acid also functions as a reduction catalyst. It reduces 4-nitrophenol to 4-aminophenol in the presence of NaBH_4 with a rate constant of $k = 0.63 \text{ min}^{-1} \mu\text{mol}^{-1}$. For comparison, using Au nanoparticles yields a rate constant of $0.14 \text{ min}^{-1} \mu\text{mol}^{-1}$. The ease of synthesis renders the nanocomposites superior to others, with potential for large-scale application.

Introduction

Recently, there has been a significantly increasing trend of replacing synthetic polymers with plant polyphenols (PPs) for bionanomaterial synthesis.¹⁻⁵ The use of PPs, specifically tea polyphenol, and tannic acid (TA) for synthesizing core@shell nanocomposites has been reported by Fei et al. and Zeng et al. in 2014. Fei's method,⁶ although a one-step process, requires microwave irradiation, while Zeng's method,⁷ a conventional two-step method,⁸⁻¹¹ needs the addition of Fe^{3+} ions as cross-linkers. In the

1 conventional method, nanoparticles (NPs) are first synthesized through metal salt reduction,
2 such as the Turkevich method,¹² and capped with monomers. Thereafter, polymerization of
3 monomers is induced via UV irradiation or addition of cross-linkers to yield the polymer
4 shell.¹³ Since TA is reported to both reduce metal salt to NPs^{7, 14-15} and undergo oxidative
5 self-polymerization in alkaline pH,¹⁶ we hypothesize that the two steps might be merged into
6 a single step to yield metal@TA nanocomposites. Additionally, because TA contains catechol
7 functional groups, similar to dopamine, we hypothesize that the polymerization of TA may be
8 similar to dopamine's polymerization to poly(dopamine) (PDA).
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11 With the advent of multi-drug-resistant bacteria, it is necessary that alternative means
12 of combating bacteria be found.¹⁷⁻¹⁸ One example is AgNPs.¹⁹⁻²⁵ However, AgNP stability
13 plays a role in bactericidal efficacy.²⁶⁻²⁸ One method for stabilization is to encapsulate the
14 AgNPs in a shell,²⁹ such as our Ag@TA. Furthermore, TA is also reported to exhibit
15 antibacterial properties.³⁰⁻³³ Antibacterial properties of Ag@TA were, therefore, examined by
16 incubating it with *E. coli*.
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19 AuNPs are effective catalysts used for the removal of environmental pollutants.³⁴⁻³⁵
20 These include trichloroethene,³⁶ carbon monoxide,³⁷ and aromatic water pollutants.³⁸ It was
21 reported that when encapsulated in a shell,³⁸ higher stability and better dispersion result in an
22 enhanced catalytic effect. Therefore, we examined the catalytic properties of the Au@TA by
23 applying it to the reduction of 4-nitrophenol to 4-aminophenol with NaBH₄.
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Scheme 1. (a) Schematic depicting the metal@TA nanocomposites formation. The TA shell may be polymerized TA or supramolecular aggregated TA held together via noncovalent interactions such as charge transfer, hydrogen bond and π - π interaction. See Results and Discussion section. (b) Activity of Ag@TA nanocomposite as a bactericidal agent. (c) Activity of Au@TA nanocomposite acting as a catalyst in the reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH_4 .

Experimental Methods

Materials. Silver nitrate (AgNO_3), hydrogen tetrachloroaurate hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), trisodium citrate, TA, sodium borohydride (NaBH_4), 4-nitrophenol and 4-aminophenol were purchased from Sigma-Aldrich. All chemicals were used as received. Phosphate buffer (PB) and sodium salt (pH = 7.8, 10 mM) was used for synthesizing TA-based core@shell

nanocomposites. Water used in all experiments was deionized and ultrafiltered to 18 MΩ·cm using a Milipore Milli-Q gradient system.

Synthesis of core-shell nanocomposites. Ag@TA nanocomposites were prepared by pipetting 50 μL of TA (40 mg mL⁻¹) into 10 mL AgNO₃ (1 mM) in 10 mM PB (pH = 7.8) at room temperature in a 15 mL Corning centrifuge tube. Synthesis using other brands of tubes (e.g. BD Falcon) did not yield any nanoparticles. We surmise that the inner coating of the tubes belonging to other brands have a coating that may interact with metal salts. For higher yields of nanocomposite, 50 mL Corning centrifuge tubes may be used instead, with the volume of TA (40 mg mL⁻¹) pipetted in now adjusted to 150 μL and the volume of AgNO₃ (1 mM) in 10 mM PB (pH = 7.8) is changed to 30 mL. The mixture was then subjected to vigorous vortexing for 20 min. The obtained Ag@TA was collected by centrifugation (9000 x g for 15 min). It was then washed twice with water through resuspension and centrifugation to remove residual TA. Au@TA nanocomposites were prepared using similar procedures, replacing 1 mM AgNO₃ with 1 mM HAuCl₄·3H₂O.

Synthesis of Ag and Au nanoparticles Ag nanoparticles were synthesized by the addition of a mixture of primary reductant NaBH₄ (1mM) and secondary reductant as well as capping agent, trisodium citrate (3.6 mM) into AgNO₃ (1mM). The mixture of NaBH₄ and trisodium citrate were mixed well with vigorous stirring and heated to 60 °C for 30 min in complete darkness. After 30 min, required volumes of AgNO₃ were added dropwise to the mixture. The temperature was then increased to 90 °C and the pH adjusted to 10.5 with the addition of 0.1 M NaOH. Heating continued for 20 min until a color change was observed. Afterward, the mixture was left to cool to room temperature and the Ag nanoparticle suspensions were centrifuged (9000 x g, 20 min) and washed in triplicate, followed by re-dispersion in DI water to ensure all unreacted substances were removed. For Au nanoparticle synthesis, the same technique for synthesizing the nanocomposites was utilized. However, to prevent shell

1 formation, the pH of the reaction was changed from alkaline to neutral by replacing PB with
2 DI water.
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4 **Characterization.** Scanning electron microscopy (FE-SEM, JEOL JSM-6700F) images were
5 taken at an acceleration voltage of 5 kV. Transmission electron microscope images were
6 taken using the Hitachi H-7500. Zeta-potential and hydrodynamic size measurements were
7 conducted in water by Malvern Instruments' Zetasizer, Nano ZS.
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10 **Antibacterial treatment.** *E. coli* strain DH5 α (Zymo Research), transformed with a plasmid
11 expressing ampicillin resistance gene, was grown in 15 mL of lysogeny broth (LB) Lennox in
12 the presence of 100 $\mu\text{g mL}^{-1}$ of ampicillin for 12 h in an orbital shaker incubator. Fresh LB
13 (20 mL), supplemented with 100 $\mu\text{g mL}^{-1}$ of ampicillin, was inoculated with 200 μL of the
14 overnight culture. The same overnight culture was used to inoculate each sample to ensure
15 uniformity of the quantity and growth phase of the bacteria. AgNPs or Ag@TA were added
16 to a final concentration of 10, 25, or 50 $\mu\text{g mL}^{-1}$ (mass is that of Ag only, see Figure S2a),
17 while the control remained nanoparticle free. The samples were further incubated and optical
18 density was measured at 600 nm (OD_{600}) at 2-h intervals for up to 12 h. For optical density
19 measurements, each sample was diluted two times with LB in a cuvette. Fresh LB containing
20 different concentrations of nanoparticles served as blanks. All incubations were carried out at
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43 For finding the minimum inhibitory concentration of Ag@TA, the above
44 experimental procedure was used, except that no ampicillin was added. LB Lennox was also
45 replaced with LB Miller to ensure that the *E. coli* was grown in the most robust conditions.
46 Additionally, concentrations of added Ag@TA were increased to 5, 10, 25, 50, 75, and 100 μg
47 mL^{-1} . Measurements were taken at 2-h intervals up to 12 h, and then at 24, 36, and 48 h.
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56 For the time-kill study, the overnight *E. coli* culture grown in LB Miller was seeded
57 into 20 mL of LB Miller at OD_{600} of 0.001 to 0.01. The value corresponds to *E. coli*
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concentrations between 10^6 to 10^7 CFU mL⁻¹. The same overnight culture was used for the triplicate experiments to ensure uniformity. Ag@TA was then added to the *E. coli* cultures at a concentration of 100 µg mL⁻¹. 200 µL of cell bacteria culture was removed at 1-h intervals for 5 h and diluted 10, 100 or 1000 times, as necessary. 100 µL of the diluted sample was then plated on LB agar and incubated for 18 h at 37 °C. Afterward, the plates were removed, and the number of colonies counted.

Catalytic reduction of 4-nitrophenol. The reduction of 4-nitrophenol in the presence of NaBH₄ was carried out to investigate the catalytic activity of Au@TA. We added 1 mL of deionized water, 0.5 mL of fresh NaBH₄ (0.2 M), and 50 µL 4-nitrophenol (5 mM) sequentially into a cuvette. This was followed by the addition of 50 µL of catalyst (1 mM Au@TA or Au nanoparticles) to the mixture. To monitor the reaction condition, UV-Vis absorption spectra (Shimadzu UV-2450 spectrophotometer) of the reaction was obtained at two-minute intervals as the reaction progressed.

Results and Discussion

Our synthesized Ag@TA and Au@TA nanocomposite was viewed through SEM and TEM. SEM images revealed high monodispersity for the nanocomposites while TEM images showed that the nanocomposite core is ~20 nm in diameter with a shell thickness of $\sim 2 \pm 1$ nm (Figure 1). The hydrodynamic size were measured to be 54.4 ± 0.3 nm and 60.32 ± 0.6 nm for Ag@TA and Au@TA nanocomposite respectively.

Figure 1. (a) SEM image of Ag@TA. (b) TEM image of Ag@TA. (c) SEM image of Au@TA. (d) TEM image of Au@TA.

Thermodynamic calculations were performed to explore the nature of the nanocomposite shell. Using Joback's method, we estimated the Gibbs free energy for reaction (ΔG°) for the dimerization of TA to di-tannic acid to investigate if polymerization of TA to poly(tannic acid) is energetically feasible.³⁹ Depending on the number of $-\text{OH}$ groups between two monomers oxidized into ether groups, the calculated ΔG° values were $-1.28 \text{ kJ mol}^{-1}$ and $51.32 \text{ kJ mol}^{-1}$ for one or two oxidized groups, respectively (Figure 2a and 2b). We speculate that this oxidative self-dimerization may have taken place due to the catalytic effect caused by the reduction of the metal salts to form the metal core. As the polymer increased beyond the size of dimers, our calculation shows that the addition of each monomer to each polymer would have a negative ΔG° regardless of the number of oxidized $-\text{OH}$ groups (Figure 2c). This shows that spontaneous oxidative self-polymerization of TA can

take place as long as the initial reaction of a monomer to dimer is initiated. Nonetheless, our modelling is limited as it assumes that the two –OH groups reacting to form ether groups belong to two different TA monomers. However, due to the high volumes of –OH groups in each TA monomers, adjacent –OH groups within the same TA monomers could also react with each other to form ether groups. This would result in the Gibbs free energy of formation of each TA monomer to increase, thus rendering polymerization to be energetically unfavorable. The reaction between monomers to form dimers has to be initiated before reaction between –OH groups on the same TA monomer takes place for polymerization to occur.

Figure 2. (a) Reaction of monomer tannic acid into dimer with one polymerization bond and corresponding reaction Gibbs free energy. (b) Reaction of monomer tannic acid into dimer with two polymerization bonds and corresponding reaction Gibbs free energy. (c) Graph depicting the value of reaction Gibbs free energy for the addition of one monomer TA to n-mer of TA polymer.

The formation of the TA shell may be explained via the dopamine polymerization mechanism into PDA.⁴⁰⁻⁴² Catechol groups capable of undergoing oxidation to quinone groups are found in both dopamine and TA (Figure 3a and 3b). Although oxidation of dopamine has been reported at varying pH values,⁴³⁻⁴⁴ polymerization of dopamine at atmospheric pressure and room temperature has only been noted to take place at mildly

alkaline pHs.⁴⁵ This includes works by Liu et al. and Choi et al., which describe a PDA shell assembled around AuNPs at mildly alkaline pH to form Au@PDA.⁴⁶⁻⁴⁷ Similarly, our TA shell formation only takes place under mildly alkaline conditions. As such, we propose that TA polymerization into a poly(tannic acid) shell is analogous to that of dopamine to form a PDA shell.

Figure 3. (a) Oxidation of catechol groups in TA to a quinone group before polymerization occurs. (b) Oxidation of catechol groups in dopamine to a quinone group before polymerizing to PDA.

However, because dopamine is unable to reduce metal salts to NPs, Au@PDA synthesis as reported by Liu and Choi still relies on a two-step synthesis method, where AuNPs were first synthesized through metal salt reduction and stabilized with citrate before mixing with dopamine, which polymerizes to PDA and assembles on the AuNPs to form Au@PDA. Whereas, unlike dopamine, TA is known to reduce metal salts to form metal NPs. Hence, a one-step synthesis method is achievable with the use of TA.

The exact chemical structure and polymerization reaction steps for PDA have undergone several revisions. In 2013, Vecchia et al. proposed that quinone oxidized from catechol groups undergoes multiple reaction pathways, such as dimerization, cyclization, and mixed coupling to yield PDA,⁴⁸ while works by Dreyer et al. in 2012 suggests that no covalent bonds between monomeric dopamine were formed during polymerization.⁴⁹ Instead, dopamine oxidation yields a series of quinhydrone held together by noncovalent charge transfer, hydrogen bond and π - π interactions, giving rise to a supramolecular aggregate. This

prompted suggestions that aggregation rather than polymerization is a more accurate description of ‘poly(dopamine)’.² If indeed the model proposed by Dreyer et al. is accurate, then charge transfer, hydrogen bonds between the oxygen in the quinone groups and hydrogen of the –OH groups, or π – π interactions between the aromatic rings of un-oxidized TA catechol groups would be responsible for the aggregation of TA. However, based on our calculations, we postulate that polymerization of TA may follow Vecchia’s model.

After the successful synthesis of Ag@TA, we tested its antibacterial activity by incubating it with *E. coli* at various concentrations. Separately, for comparison, AgNPs were also incubated with *E. coli*, while no AgNP or Ag@TA was added to the negative control sample. To ensure that no other bacteria interfere with our experiment, we used genetically modified *E. coli* that expresses the ampicillin resistance gene with ampicillin added to our samples. At Ag@TA concentrations of 25 and 50 $\mu\text{g mL}^{-1}$, our result show significant growth inhibition of *E. coli* at the 12-h time point as compared to untreated controls and *E. coli* treated with AgNP (Figure 4). Our incubation of TA with *E. coli* shows that TA was not responsible for the antibacterial properties (Figure S3).

Figure 4. Time-dependent turbidity at 600 nm for *E. coli* cultured with and without Ag@TA.

To simulate conditions in real life, we further challenged the Ag@TA antibacterial potency by removing the ampicillin and replacing the growth medium to the more robust lysogeny broth (LB) Miller instead of LB Lennox. Our results show that the minimum inhibitory concentration (MIC) for 12 h is 25 $\mu\text{g mL}^{-1}$ while it is 100 $\mu\text{g mL}^{-1}$ for 48 h (Figure 5a). Next we did a time-kill study and showed that for 100 $\mu\text{g mL}^{-1}$ of Ag@TA, the *E. coli* population is reduced by 99% by the 5-h time point. This means that 100 $\mu\text{g mL}^{-1}$ is also the minimum bactericidal concentration (MBC) (Figure 5b).

Figure 5. (a) Time-dependent turbidity at 600 nm in *E. coli* cultured with different concentrations of Ag@TA in LB Miller culture medium. (b) Time-kill study of *E. coli* incubated with 100 $\mu\text{g mL}^{-1}$ of Ag@TA.

Various stabilizing agents with known biocompatible properties such as citrate, PVP, gallic acid, and Daxad 19, have been used to stabilize AgNPs.^{24, 26, 28, 50} However, a major drawback of using these stabilizing agents is in the preparation techniques. For example, the use of citrate as a stabilizing agent requires heating between 80 and 100 °C.⁵⁰ Stabilization with PVP requires ultrasonic irradiation, rendering large scale production unsuitable, while stabilization with gallic acid requires the solution to be kept under constant stirring.^{24, 28} Finally, stabilization with Daxad 19 requires 2 steps: reduction of silver nitrate with ascorbic acid followed by the addition of Daxad 19.²⁶ Our approach using TA shell to confer stability

is more attractive as it does not require heating to high temperature, ultrasonic irradiation, or constant stirring. Instead, it can be done through a one-step synthesis process without external energy input.

The catalytic effects of Au@TA were then examined by introducing Au@TA into the reaction for the reduction of 4-nitrophenol to 4-aminophenol using NaBH_4 . A color change from yellow to colorless was observed as the reaction progressed (Figure 6a). In addition, monitoring of 4-nitrophenol concentration was also done through examining the absorbance intensity at its characteristic wavelength of 400 nm. Similarly, for 4-aminophenol, monitoring was done at its absorbance wavelength of 312 nm. After addition of AuNP or Au@TA to the reaction mixture, UV-Vis spectra of the mixtures were taken at 2 min intervals. In both cases, the peak at 400 nm decreases over time while the peak at 312 nm increases over time (Figure 6b and 6c). However, the change in the UV-Vis spectrum is faster for the mixture with added Au@TA compared to AuNP, showing that Au@TA performs as a better catalyst.

Figure 6. (a) Photographs of 4-nitrophenol before and after reduction to 4-aminophenol by NaBH_4 in the presence of Au@TA catalyst. UV-Vis absorption spectra at various reaction time points for the 4-nitrophenol catalytic reduction by (b) AuNPs and (c) Au@TA catalyst.

To calculate the rate of reaction, we divided the absorbance at 400 nm for each time point (A_t) with that of time point zero (A_0), giving us the ratio of 4-nitrophenol concentration at each time point (C_t) compared to the initial concentration (C_0). Because excess NaBH_4 was

added into the reaction mixture, the reaction follows pseudo-first-order kinetics. Hence, we plotted the $\ln$ value of the ratio (C_t/C_0) against time (t) and obtained the rate constant K through the gradient of the line (Figure 7a). Our results showed that the reaction rate constant using the Au@TA catalysts was $0.63 \text{ min}^{-1} \mu\text{mol}^{-1}$. This is comparable to other reported values of NP and nanocomposite catalysts (Table S1).⁵¹ It is also 4.5 times higher than our control of AuNPs, with a rate constant of $0.14 \text{ min}^{-1} \mu\text{mol}^{-1}$. Our Au@TA was reused for the catalytic reaction and showed a reaction rate that diminishes no more than 10 % after five cycles of reactions, showing the high reusability of Au@TA as a catalyst (Figure 7b).

Figure 7. (a) Plots of $\ln(C_t/C_0)$ versus reaction time for bare AuNPs and Au@TA. C_t and C_0 represents 4-nitrophenol concentration at reaction time t and the initial reaction time, respectively. (b) Rate constant K of Au@TA nanocomposites after repeated use. The error bars represent the standard deviations of three replicates.

The increase in catalytic activity may be explained through the high abundance of aromatic rings on the TA shell allows for π - π interactions with 4-nitrophenol. This results in the synergistic effect of AuNPs and the TA shells as proposed by Ke et al.⁵² Additionally, the TA shell allows for increased stability, hence reducing aggregation, and could be a contributing factor in preventing the loss of catalytic activity.⁷

Conclusion

In conclusion, we report the formation of TA shells on AgNPs and AuNPs when vortexed for a minimum time of twenty min under mildly alkaline conditions. Our reported work is a significant modification of Fei's work where microwave irradiation is not required.⁶

As both TA and dopamine contain catechol functional groups, we propose that the shell of our nanocomposite may be in fact poly(tannic acid), which formation is analogous to that of dopamine's oxidative self-polymerization. However dopamine's polymerization mechanism is still being studied, with supramolecular aggregation as one of the proposed structure. As such, our TA shell could be also self-assembled TA aggregation. Nonetheless, thermodynamic estimation using Joback's method also shows the feasibility of oxidative self-polymerization.

Furthermore, we showed that Ag@TA exhibits antibacterial activities while Au@TA functions as a catalyst. The MIC of Ag@TA for *E. coli* for 48 h is 100 $\mu\text{g mL}^{-1}$. At an MBC of also 100 $\mu\text{g mL}^{-1}$ Ag@TA, *E. coli* population was reduced by 99% in 5 h. As a catalyst, the Au@TA's reduction of 4-nitrophenol to 4-aminophenol by Au@TA in the presence of NaBH_4 has a rate constant of $0.63 \text{ min}^{-1} \mu\text{mol}^{-1}$, which is much higher than $0.14 \text{ min}^{-1} \mu\text{mol}^{-1}$ for AuNP. With our one-pot, one-step synthesis technique, large production of Ag@TA and Au@TA is achievable, indicating vast potential for industrial applications.

Further studies are required to determine if TA is indeed polymerized in the nanocomposite shell or instead, a supramolecular aggregate. The exact chemical structure and reaction mechanism for polymerization of TA needs to be studied too.

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Scheme 1. (a) Schematic depicting the metal@TA nanocomposites formation. The TA shell may be polymerized TA or supramolecular aggregated TA held together via noncovalent interactions such as charge transfer, hydrogen bond and π - π interaction. See Results and Discussion section. (b) Activity of Ag@TA nanocomposite as a bactericidal agent. (c) Activity of Au@TA nanocomposite acting as a catalyst in the reduction of 4-nitrophenol to 4-aminophenol in the presence of NaBH_4 .

Figure 1. (a) SEM image of Ag@TA. (b) TEM image of Ag@TA. (c) SEM image of Au@TA. (d) TEM image of Au@TA.

Figure 2. (a) Reaction of monomer tannic acid into dimer with one polymerization bond and corresponding reaction Gibbs free energy. (b) Reaction of monomer tannic acid into dimer with two polymerization bonds and corresponding reaction Gibbs free energy. (c) Graph depicting the value of reaction Gibbs free energy for the addition of one monomer TA to n-mer of TA polymer.

Figure 3. (a) Oxidation of catechol groups in TA to a quinone group before polymerization occurs. (b) Oxidation of catechol groups in dopamine to a quinone group before polymerizing to PDA.

Figure 4. Time-dependent turbidity at 600 nm for *E. coli* cultured with and without Ag@TA.

Figure 5. (a) Time-dependent turbidity at 600 nm in *E. coli* cultured with different concentrations of Ag@TA in LB Miller culture medium. (b) Time-kill study of *E. coli* incubated with 100 µg mL⁻¹ of Ag@TA.

Figure 6. (a) Photographs of 4-nitrophenol before and after reduction to 4-aminophenol by NaBH₄ in the presence of Au@TA catalyst. UV-Vis absorption spectra at various reaction time points for the 4-nitrophenol catalytic reduction by (b) AuNPs and (c) Au@TA catalyst.

Figure 7. (a) Plots of $\ln(C_t/C_0)$ versus reaction time for bare AuNPs and Au@TA. C_t and C_0 represents 4-nitrophenol concentration at reaction time t and the initial reaction time, respectively. (b) Rate constant K of Au@TA nanocomposites after repeated use. The error bars represent the standard deviations of three replicates.

20 Minutes Vortex, Mildly Alkaline pH

Tannic Acid Shell formed on metal nanoparticle giving rise to Metal@Tannic Acid nanocomposite

Electronic Supplementary Information

Universal One-pot, One-step Synthesis of Core-shell Nanocomposites with Self-Assembled Tannic Acid Shell and Their Antibacterial and Catalytic Activities

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Estimation of Gibbs free energy through Joback's method

Joback's method assigns each functional group an estimated Gibbs free energy. The total functional group and its assigned Gibbs free energy are summed and 53.88 is added to the value to obtain the estimated Gibbs free energy of formation for each molecule (Figure S6a).

As each addition of a polymerization bond results in the removal of two –OH groups and addition of one ether group, we were able to calculate the Gibbs free energy of formation for n -mers of polymerization by differing numbers of polymerization bonds using the following equation:

$$53.88 + (n)(-4632.22 - 53.88) - (n)(b)(-197.37) + (n - 1)(b)(-105),$$

where n is the degree of polymerization of the polymer and b is the number of polymerization bonds (Figure S6b).

We may also calculate the Gibbs free energy for the reaction of one monomer to each polymer by using the following equation:

$$P + (-237.14)(b) - (I - 4632.22),$$

where P is Gibbs free energy of formation for the product and I is the Gibbs free energy of formation for the initial polymer.

a) Table for calculation of formation Gibbs energy of formation for each molecule

		Monomer			Dimer with one polymerization bond		Dimer with two polymerization bonds	
Bond		Assigned Energy value	Number of functional groups	Functional group Energy	Number of functional groups	Functional group Energy	Number of functional groups	Functional group Energy
-O-	(Non-Ring)	-105	10	-1050	21	-2205	22	-2310
-O-	(Ringed)	-98.22	1	-98.22	2	-196.44	2	-196.44
=CH-		11.3	20	226	40	452	40	452
=C<		54.05	40	2162	80	4324	80	4324
-CH ₂ -		8.42	1	8.42	2	16.84	2	16.84
>C=O	(Non-Ring)	-120.5	10	-1205	20	-2410	20	-2410
>CH	(Ringed)	40.99	5	204.95	10	409.9	10	409.9
-OH		-197.37	25	-4934.25	48	-9473.76	46	-9079.02
Total Energy (kJ mol ⁻¹)				-4632.22		-9028.58		-8738.84

Figure S1. (a) Table showing number of functional groups and the Gibbs free energy of monomer and di(tannic acid), with one and two polymerization bonds. (b) Graph showing the Gibbs free energy of formation for increasing size of tannic acid polymer according to the equation.

Supplementary Experimental Data

Inductive Coupled Plasma Mass Spectroscopy (ICPMS) was done to determine the concentration of Ag present in Ag@TA or Au present in Au@TA. The absorbance value at the peak of the UV spectrum was plotted against the concentration to obtain a standard curve.

Figure S2a. Standard curve of Ag@TA absorbance value at the peak of the UV spectrum plotted against the concentration.

Figure S2b. Standard curve of Au@TA absorbance value at the peak of the UV spectrum plotted against the concentration.

Figure S3. Time-dependent turbidity at 600 nm in *E. coli* cultured with and without PTA nanocomposites.

Figure S4. UV-Vis absorption spectra at various reaction time points for the 4-nitrophenol catalytic reduction by TA.

Table S1. Physicochemical properties of bare AuNPs and Au@PTA nanocomposites[1-11].

Catalyst structure	K (min⁻¹)	K_{nor}(min⁻¹ μmol⁻¹)	Ref. No.
AuNPs/SiO ₂ -NTs	0.64	0.638	1
AuNPs@[Na]- HAMS	0.31	-	2
AuNPs/Fe ₃ O ₄ -NPs	0.01	0.36	3
Fe ₃ O ₄ @SiO ₂ - Au@mSiO ₂	0.35	1.05	4
AuNPs/TWEEN/GO	0.25	1.16	5
AuNPs/GO	0.18	-	6
Au@MIL-100(Fe)	0.33	-	7
Au-EGCG-CF	0.14	0.14	8
Dumbbell-like Fe ₃ O ₄ -Au	0.63	0.33	9
PLAL- AuNPs/CeO ₂ -NTs	0.14	0.84	10
Au@TA-Fe	0.37	3.7	11
Au@PTA	0.63	6.3	This Work

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The following is our point-by-point responses to the comments made by the Reviewers.

Reviewer 1:

“Please include your reviewer’s report that should be sent to the author in this field although this can be considered interesting work, there some major concerns need to be considered for publications.”

1. There are many related literature about TA and their antibacterial and antioxidant properties and TA containing metal nanoparticle including Ag and their utilization as catalyst need to be cited, e.g.,

-COLLOIDS AND SURFACES B BIOINTERFACES, (2016) 142,334-343.

-POLYMER DEGRADATION AND STABILITY, (2016) 133,152-161.

-INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES, (2016) 82,150-159.

-MATERIALS SCIENCE & ENGINEERING C-MATERIALS FOR BIOLOGICAL APPLICATIONS, (2015) 49,824-834. and so on...

Reply: We thank the Reviewer for his/her comments. In this re-submitted version of the manuscript, we have now added these related references in the manuscript. (References 30-33)

“2. As known from literature, TA itself is an antibacterial material and reduction agent. Therefore, in all the related figures and/or tables, the antibacterial properties and 4-NP reduction power of TA should be included.”

Reply: We thank the Reviewer again for his/her comment. We have now added the control experiment of the antibacterial properties (Figure S3) and 4-NP reduction power (Figure S4) of TA.

“3. The exact amounts of Au should be determined by AAS or ICP.”

Reply: We thank the Reviewer again for his/her comment. We have added the ICPMS data for Au in Supplementary Information. (Figure S2b)

In addition, we sincerely thank the Reviewer for looking through our manuscript carefully and for his/her very helpful comments.

Reviewer 2:

“Please include your reviewer's report that should be sent to the author in this field.”

Reply: We thank the Reviewer for his/her helpful comments. We have modified our paper carefully based on the comments.

“1. Authors said that "... TA contains catechol functional groups, similar to dopamine..." in the many place of manuscript. But this statement is not true, because TA contains pyrogallol groups instead of catechol groups.”

Reply: We thank the Reviewer for his/her comment. As it is well known, TA contains pyrogallol (trihydroxyphenyl-containing molecules) groups instead of catechol

(dihydroxyphenyl) groups. Although both pyrogallol and catechol are of different structure, they both contain similar motifs-benzene ring and two hydroxyl groups adjacent to the benzene ring. This kind of structure has similar chemical reduction property. As such, TA-inspired coatings form spontaneously at mildly alkaline pH in the presence of available dissolved oxygen, likely through phenolate ion intermediaries, similar to coatings derived from dopamine polymerization. (*Angew. Chem. Int. Ed.* 2013, 52, 10766.)

"2. Page 9, lines 33-59 and page 10, lines 1-20: Authors speculated that "....the two -OH groups reacting to form ether groups belong to two different TA monomers.". They are also not given any reference and supported from any experimental evidences to prove their speculation. Again, this speculation is not true, because TA is not give the ether formation reaction."

Reply: We thank the Reviewer for his/her comment again. Actually, further studies will be necessary to understand the exact mechanism of coating formation, we surmise that oxidation followed by oligomerization decreases the solubility of TA and combined with their inherent affinity toward the nanoparticles surfaces, ultimately leading to surface deposition forming the shell. In this manuscript, the speculation of ether group formation is a potential mechanism, in reference to the structure found in *Journal Membrane Sci.*2016, 514, 25.