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# Rapid and selective detection of aluminum ion using 1,2,3-triazole-4,5-dicarboxylic acid-functionalized gold nanoparticle-based colorimetric sensor†

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A highly selective, sensitive, rapid, low-cost, simple and visual colorimetric system for  $\text{Al}^{3+}$  ion detection was developed based on gold nanoparticles (AuNPs) modified with 1,2,3-triazole-4,5-dicarboxylic acid (TADA). The modified gold nanoparticles (TADA-AuNPs) were first prepared by sodium citrate ( $\text{Na}_3\text{Ct}$ ) reduction of chloroauric acid ( $\text{HAuCl}_4$ ) and then capped with a TADA ligand. Five TADA-AuNPs sensors were constructed with sodium citrate ( $\text{Na}_3\text{Ct}$ )/chloroauric acid ( $\text{HAuCl}_4$ ) under different molar ratios. Results showed that the molar ratio of  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$ , TADA-AuNPs concentration, pH range and detection time had obvious influences on the performance of this colorimetric method. The optimal detection conditions for  $\text{Al}^{3+}$  ions were as follows:  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio of 6.4 : 1, 0.1 mM of TADA-AuNPs concentration, 4–10 pH range and 90 s of detection time. Under the optimal conditions and using diphenyl carbazone (DPC) as a  $\text{Cr}^{3+}$  masking agent, this colorimetric sensor exhibited outstanding time efficiency, selectivity and sensitivity for  $\text{Al}^{3+}$  detection. In particular, the detection limits of this sensor obtained via UV-vis and the naked eye were 15 nM and 1.5  $\mu\text{M}$ , respectively, which were much lower than the current limit (3.7  $\mu\text{M}$ ) for drinking water in WHO regulation and better than the previous reports. Moreover, this colorimetric sensing system could be used to for on-site, trace level and real-time rapid detection of  $\text{Al}^{3+}$  in real water samples.

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## 1. Introduction

Aluminum (Al) is one of the richest metals in nature, and it is widely used in modern industry and everyday life, such as in packaging foils, containers, cooking utensils, and food additives. However, aluminum products will release aluminum ion ( $\text{Al}^{3+}$ ) slowly, contaminating food, drinking water or soil. Moreover,  $\text{Al}^{3+}$  can also accumulate in the human body through the food chain. An increasing level of  $\text{Al}^{3+}$  in the human body can trigger a series of diseases, including senile dementia and Parkinson's disease. Therefore,  $\text{Al}^{3+}$  has been restricted as a toxic metal by the World Health Organization (WHO) with a maximum consumption limit of 7 mg per kilogram body weight weekly, or 3.7  $\mu\text{M}$  (0.1 mg  $\text{L}^{-1}$ ) and 7.4  $\mu\text{M}$  (0.2 mg  $\text{L}^{-1}$ ) in

drinking water for large and small water treatment facilities, respectively.<sup>1–4</sup>

Several traditional detection methods, such as atomic absorption spectrometry (AAS),<sup>5</sup> inductively coupled plasma optical emission spectroscopy (ICP-OES)<sup>6</sup> and inductively coupled plasma mass spectrometry (ICP-MS),<sup>7</sup> have been employed to monitor trace levels of  $\text{Al}^{3+}$  in food or in the environment. Although these methods can provide high sensitivity and accurate results, the detection process is time-consuming and generally requires costly sophisticated instrumentation and skilled professionals, which limit their applications, especially for on-site and real-time detection. Thus, it is urgent to develop an inexpensive, highly efficient, instrument-free and easily operated method for trace level  $\text{Al}^{3+}$  detection.

Colorimetric sensors based on gold nanoparticles (AuNPs) have attracted widespread attention because of their fast and visual output, as well as no need for expensive instruments. Taking advantages of unique surface plasmon resonance (SPR) absorption, easy surface functionalization and variable solution colors, AuNPs have been used for colorimetric sensing in food security, environmental monitoring, and health care.<sup>8–11</sup> Potential applications include the determination of metal ions,<sup>12–18</sup> pesticide residues,<sup>19,20</sup> bisphenol A (BPA),<sup>21,22</sup>

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phosphate,<sup>23</sup> azodicarbonamide (ADA),<sup>24</sup> antibiotics,<sup>25–27</sup> adenosine and nucleic acids,<sup>28–30</sup> dopamine,<sup>31</sup> bacteria,<sup>32,33</sup> and virus.<sup>34,35</sup>

In recent years, rapid detection of  $\text{Al}^{3+}$  using AuNPs as a colorimetric sensor have been reported, in which the AuNPs' surface were functionalized by different  $\text{Al}^{3+}$  recognition ligands, such as diaminodiphenyl sulfone,<sup>36</sup> ascorbic acid,<sup>37</sup> 11-mercaptoundecanoic acid,<sup>38</sup> 5-mercaptomethyltetrazole,<sup>39</sup> poly(acrylic acid),<sup>40</sup> triazole ether,<sup>41</sup> catechol,<sup>42</sup> and xylene orange.<sup>43</sup> Their detection limits *via* UV-vis and the naked eye, detection time, and interference ions are summarized in Table 1. It is clear that different ligands have great influence on the sensitivity and selectivity of the sensors. However, most of these sensors show low sensitivity with naked eye detection, which is higher than the current limit (3.7  $\mu\text{M}$ ) in drinking water,<sup>36–41</sup> need long detection time<sup>38–41</sup> or suffer from interferences.<sup>36</sup> Some efforts have been made to decrease the naked eye detection limits to 3.5  $\mu\text{M}$ ,<sup>42</sup> and 2.8  $\mu\text{M}$ ,<sup>43</sup> which can almost meet the limit requirement in drinking water. 1,2,3-Triazole-4,5-dicarboxylic acid (TADA), with both triazole and carboxyl groups in the structure, was found to have strong binding force to AuNPs.<sup>44</sup> In addition, abundant lone pair electrons in the TADA may possess it of superior capability in coordinating with metal cations.

We herein for the first time constructed a colorimetric sensor based on TADA-modified AuNPs for highly efficient detection of  $\text{Al}^{3+}$  ion. The TADA-AuNPs were easily synthesized from the pre-synthesized citrate-covered AuNPs (citrate-AuNPs), as the triazole group of TADA more readily binds to Au, compared to the carboxyl group.<sup>44</sup> The principle of this colorimetric sensing method is that TADA on the surface of AuNPs can specifically recognize  $\text{Al}^{3+}$ , resulting in an aggregation-induced color change from dark red to violet or blue. This change was confirmed by Fourier transform infrared (FTIR), Raman spectroscopy, UV-visible spectrophotometer (UV-vis), transmission electron microscopy (TEM), and dynamic light scattering (DLS). Several TADA-AuNPs sensors with different particle sizes were prepared under different molar ratios of sodium citrate ( $\text{Na}_3\text{Ct}$ )/chloroauric acid ( $\text{HAuCl}_4$ ). The selectivity and sensitivity of the method were evaluated using optimized detection parameters, including  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio, TADA-AuNPs concentration, pH range, and detection time. The detection time is 90 s

and the detection limits *via* UV-vis and the naked eye were determined to be 15 nM and 1.5  $\mu\text{M}$ , respectively, better than the previous reports.<sup>36–43</sup> We propose that this TADA-AuNPs colorimetric method might be suitable for real-time rapid detection of  $\text{Al}^{3+}$  ion in water, milk, soil, and other foods.

## 2. Materials and methods

### 2.1. Chemicals

Chloroauric acid ( $\text{HAuCl}_4$ ), sodium citrate ( $\text{Na}_3\text{Ct}$ ), and 1,2,3-triazole-4,5-dicarboxylic acid (TADA) were analytical grade and purchased from Lab Network (Shanghai, China). Sodium hydroxide (NaOH), phosphate buffered saline (PBS), hydrochloric acid (HCl),  $\text{AlCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrCl}_3$ ,  $\text{InCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , NaCl, KCl,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_3\text{PO}_4$  were analytical grade and purchased from Aladdin (Shanghai, China).  $\text{GaCl}_3$  was analytical grade and purchased from Bidepharm (Shanghai, China).  $\text{Al}^{3+}$  standard solution was purchased from Macklin (Shanghai, China). Diphenyl carbazone (DPC), analytical grade, was used as a  $\text{Cr}^{3+}$  masking agent and purchased from Macklin (Shanghai, China). Ultrapure water, 18.2  $\text{M}\Omega\text{ cm}$  at 25  $^\circ\text{C}$ , was used for preparing solutions.

### 2.2. Synthesis of TADA-functionalized AuNPs (TADA-AuNPs) sensor

The TADA-AuNPs were prepared using a previously reported method, with some improvement.<sup>18</sup> To synthesize citrate-terminated AuNPs (citrate-AuNPs), 100 mL of 0.25 mM chloroauric acid ( $\text{HAuCl}_4$ ) aqueous solution were boiled, followed by the rapid addition of 4 mL of 40 mM sodium citrate ( $\text{Na}_3\text{Ct}$ ) solution. The  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio was 6.4 : 1. The solution was kept boiling for 30 min with stirring and then cooled to room temperature. The solution color changed from light yellow to dark red, indicating that citrate-AuNPs had formed in the solution. To modify citrate-AuNPs with TADA, 100 mL synthesized citrate-AuNPs solution was transferred to a 500 mL round bottom flask and then mixed with 145 mL of 0.25 mM TADA solution and 5 mL PBS solution. The pH was adjusted to 7.41 with 0.5 mM NaOH solution. The mixed solution was heated to 60  $^\circ\text{C}$ , incubated for 1 h with stirring, and then cooled to room temperature. The mixed solution was centrifuged for

Table 1 Comparison of ligand-functionalized gold nanoparticles-based colorimetric sensors for  $\text{Al}^{3+}$  detection

Ligand	Detection limit ( $\mu\text{M}$ )		Detection time (s)	Interference ions	Eliminating interference method	Ref.
	UV-vis	Naked eye				
Diaminodiphenyl sulfone	0.62	—	—	$\text{Fe}^{3+}$ , $\text{Cr}^{3+}$	—	36
Ascorbic acid	0.46	—	120	$\text{Ca}^{2+}$	Using anion exchange resin	37
11-Mercapto-undecanoic acid	0.57	20	1800	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Pb}^{2+}$	Using EDTA masking agent	38
5-Mercapto-methyltetrazole	0.53	10	900	—	—	39
Poly(acrylic acid)	2	8	900	—	—	40
Triazole ether	0.018	5	600	—	—	41
Catechol	0.81	3.5	60	—	—	42
Xylene orange	0.44	2.8	—	—	—	43
1,2,3-Triazole-4,5-dicarboxylic acid	0.015	1.5	90	$\text{Cr}^{3+}$	Using DPC masking agent	This work



25 min at 15 000 rpm to remove the excess NaOH, TADA, and sodium citrate. The TADA-AuNPs precipitate was resuspended in 10 mL of ultrapure water to obtain the stock solution. A series of TADA-AuNPs solutions with concentrations ranged from 0.025 mM to 0.55 mM were prepared by diluting the stock solution with appropriate amount of ultrapure water. Five TADA-AuNPs solutions with different particle size were obtained by controlling the  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio as follows: 0.8 : 1, 1.6 : 1, 3.2 : 1, 6.4 : 1, and 12.8 : 1, respectively. The synthesis process is shown in Scheme 1.

### 2.3. Characterization

UV-vis absorption spectra were measured *via* a Shimadzu UV-2700 UV-vis spectrophotometer. The transmission electron microscopy (TEM) images were obtained on a ThermoFisher Tecnai G2 Spirit TEM microscope. The Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu IRAffinity-1S spectrophotometer. The dynamic light scattering (DLS) images were generated on a Malvern ZEN3700 DLS and Zeta Sizer. The Raman spectra were measured by a Renishaw's inVia Raman spectrometer.

## 3. Results and discussion

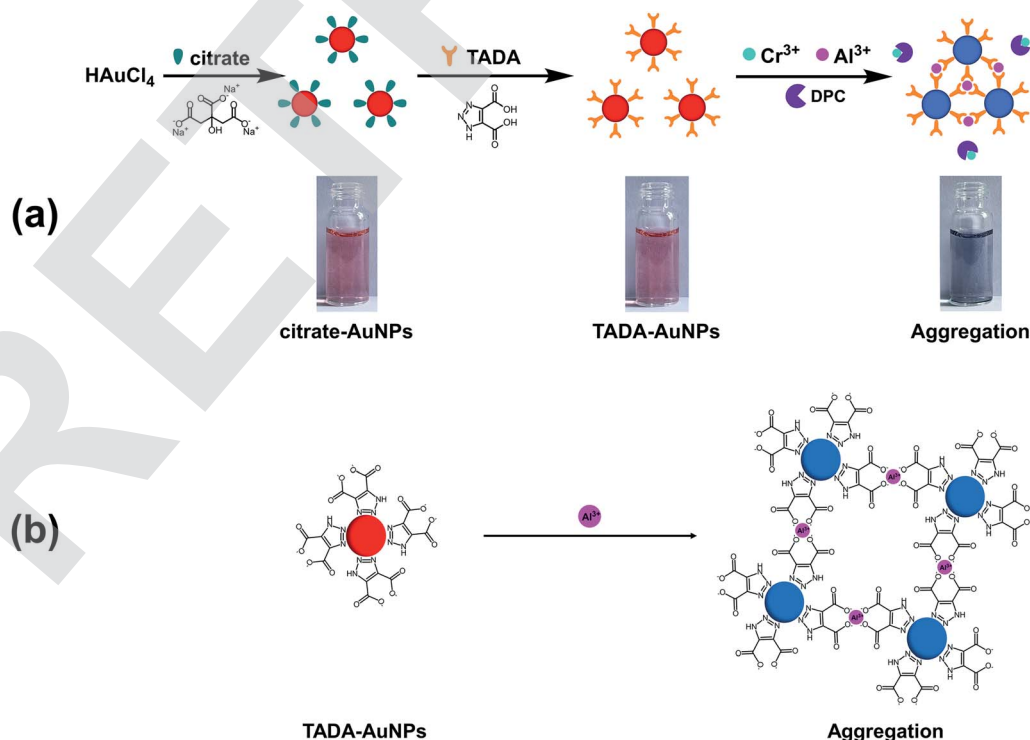
### 3.1. Construction and characterization of $\text{Al}^{3+}$ colorimetric sensor

A main advantage of TADA-AuNPs for target analytes ( $\text{Al}^{3+}$ ) is their excellent selective colorimetric response, through which the ion content can be visualized by the naked eye or detected by UV-vis spectrophotometer.

The design strategy for the  $\text{Al}^{3+}$  colorimetric sensor is illustrated in Scheme 1. First, stable dark red citrate-AuNPs solution was obtained by reducing  $\text{HAuCl}_4$  with  $\text{Na}_3\text{Ct}$ . Then, citrate-AuNPs were functionalized by TADA, and well-dispersed dark red AuNPs capped with TADA (TADA-AuNPs) were obtained. The solution color changes from dark red to violet or blue due to the aggregation of TADA-AuNPs induced by  $\text{Al}^{3+}$  in the presence of a masking agent (DPC) to eliminate the interference of  $\text{Cr}^{3+}$  (Scheme 1a). The triazole groups on TADA-AuNPs function as metal ion binding ligands. Since  $\text{Al}^{3+}$  was bound between the triazoles which from TADA, the TADA-AuNPs aggregated (Scheme 1b).

Fig. 1 gives the FTIR and Raman spectra of citrate-AuNPs and TADA-AuNPs. As shown in Fig. 1a, with the exception of the citrate-AuNPs characteristic peaks at  $1655\text{ cm}^{-1}$  (was,  $\text{C}=\text{O}$ ) and  $3300\text{--}3600\text{ cm}^{-1}$  ( $\text{O-H}$ ), there exhibited two new characteristic peaks at  $1570\text{ cm}^{-1}$  ( $\text{N}=\text{N}$ ) and  $3480\text{ cm}^{-1}$  ( $\text{N-H}$ ) in the TADA-AuNPs spectra, which belong to the triazole groups in TADA. Thus, this result indicates that TADA ligand was attached to the citrate-AuNPs surface successfully.<sup>45</sup> To further confirm the binding mode of the ligand TADA on the surface of citrate-AuNPs, Raman spectra of citrate-AuNPs and TADA-AuNPs are measured. As shown in Fig. 1b, TADA-AuNPs has an obvious new characteristic peak at  $560\text{ cm}^{-1}$  compared with citrate-AuNPs, which belongs to Au-N bond.<sup>46</sup> Therefore, combining FTIR and Raman spectroscopy, it clearly demonstrates that the ligand TADA was modified to the surface of citrate-AuNPs through its triazole group's N atom.

In order to explore the response of TADA-AuNPs to  $\text{Al}^{3+}$ , the photographs and UV-vis absorption spectra of citrate-AuNPs, TADA-AuNPs and their corresponding solutions containing  $\text{Al}^{3+}$



Scheme 1 Schematic of the design strategy for the  $\text{Al}^{3+}$  colorimetric sensor.

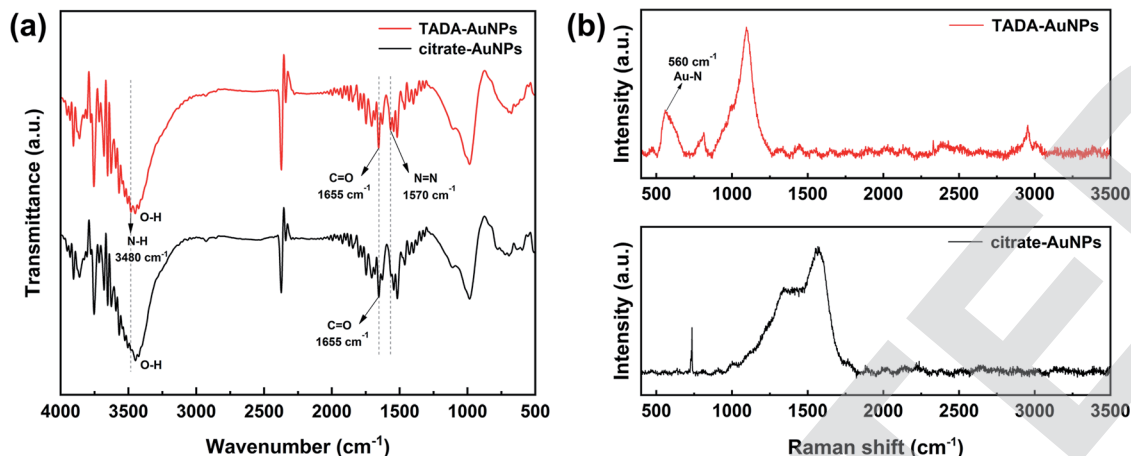


Fig. 1 (a) Fourier infrared (FTIR) and (b) Raman spectra of citrate-AuNPs and TADA-AuNPs.

are obtained. As shown in Fig. 2, the appearance of dark red color and the shift in the peak at 520 nm to 525 nm in the UV-vis absorption spectra (Fig. 2b), compared to citrate-AuNPs (Fig. 2a), indicate the formation of AuNPs and surface functionalization with TADA. When 2  $\mu\text{M}$  of  $\text{Al}^{3+}$  was added to the TADA-AuNPs solution, the solution color changed from red to blue, and a new absorption peak at 625 nm appeared along with weaker absorption found at 525 nm in the UV-vis spectrum (Fig. 2c). In comparison, the UV-vis spectrum and the solution color of citrate-AuNPs mixed with 5  $\mu\text{M}$   $\text{Al}^{3+}$  were nearly the same with those of citrate-AuNPs (Fig. 2a and d). These results illustrate that the TADA-modification possesses the AuNPs with specific  $\text{Al}^{3+}$  recognition, resulting in the color change of the solution from red to blue.

This result can be further confirmed by TEM and DLS measurements. Fig. 3a and b show that both citrate-AuNPs and TADA-AuNPs are well-dispersed, spherical nanoparticles with

a hydrodynamic average particle size of about 30 nm (Fig. 3a' and b'). Upon the addition of 2  $\mu\text{M}$   $\text{Al}^{3+}$  to TADA-AuNPs, obvious particle aggregation can be observed in TEM image and the hydrodynamic average particle size increases to about 192 nm (Fig. 3c'). These results may be due to the large number of carboxyl groups present on the surface of TADA-AuNPs, causing its zeta potential to be  $-43.9$  mV in pH = 6.3 (see Fig. S1 in ESI<sup>†</sup>) and making it exhibit a specific and strong targeting force to  $\text{Al}^{3+}$ .<sup>47</sup> At the same time, "interparticle cross-linking mechanism" will occur between  $\text{Al}^{3+}$  and TADA-AuNPs, resulting in induced aggregation of TADA-AuNPs (Scheme 1b).<sup>37,47</sup> Conversely, for citrate-AuNPs, the addition of  $\text{Al}^{3+}$  had no effects on the shape or size of AuNPs, indicating no interaction between  $\text{Al}^{3+}$  ions and citrate-AuNPs.

It is well known that the color change of AuNPs is closely related to the factors such as particle size, shape, aggregation state, shape, capping agent, and solvent refractive index.<sup>48</sup> Thus, according to Fig. 2 and 3, it is likely that  $\text{Al}^{3+}$  induced the aggregation of TADA-AuNPs, causing a significant change in particle size, resulting in the solution color change from red to blue.

To estimate the optimum particles size of TADA-AuNPs, five different molar ratios of  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  (0.8 : 1, 1.6 : 1, 3.2 : 1, 6.4 : 1, and 12.8 : 1) were introduced for the preparation of TADA-AuNPs, and the  $\text{HAuCl}_4$  concentration was 0.25 mM. Particle morphologies and solution colors were obtained from TEM and digital camera (Fig. 4). The average sizes of TADA-AuNPs decreased from 56 nm to 14 nm when the  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio ranged from 0.8 : 1 to 3.2 : 1 (Fig. 4 a-c). Then, the particle size became stable when further increasing the  $\text{Na}_3\text{Ct}$  proportion (Fig. 4 d and e), which was similar to a previous report.<sup>49</sup> Meanwhile, the solution colors of the obtained TADA-AuNPs changed from purple to red along with the  $\text{Na}_3\text{Ct}$  ratio increase (Fig. 4f). As mentioned above, the detection of  $\text{Al}^{3+}$  ion bases on the color change of TADA-AuNPs, the color difference between red and blue is more obvious than that between purple and blue. Therefore, dark red-colored TADA-AuNPs solutions synthesized with  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio larger than 6.4 : 1 are suitable for the colorimetric detection of  $\text{Al}^{3+}$ . Subsequently,

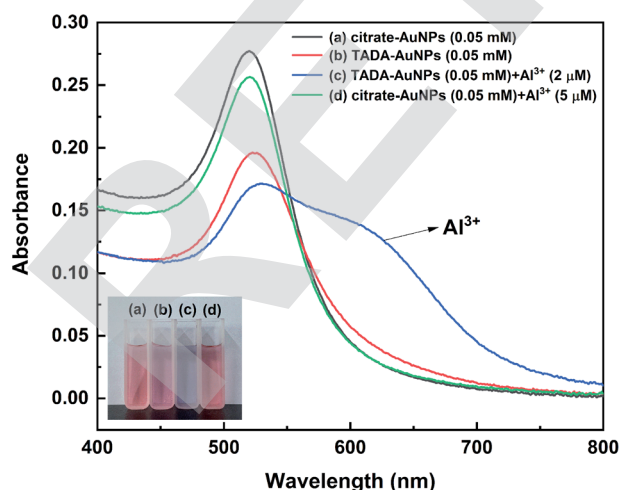


Fig. 2 UV-vis spectra and photographs (inset) of (a) citrate-AuNPs (0.05 mM), (b) TADA-AuNPs (0.05 mM), (c) TADA-AuNPs (0.05 mM) mixed with 2  $\mu\text{M}$   $\text{Al}^{3+}$  and (d) citrate-AuNPs (0.05 mM) mixed with 5  $\mu\text{M}$   $\text{Al}^{3+}$ .





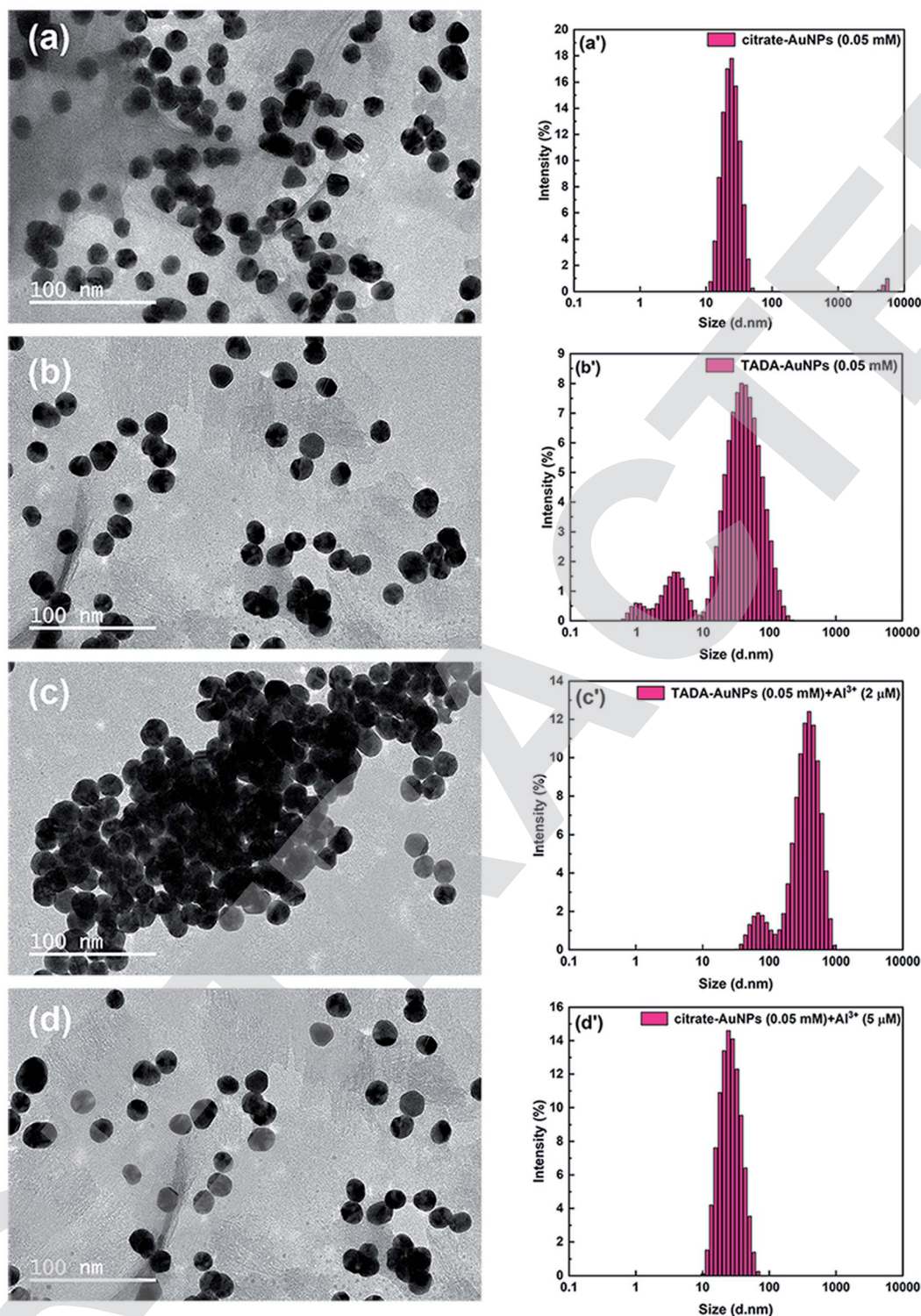


Fig. 3 TEM and DLS images of (a and a') citrate-AuNPs (0.05 mM), (b and b') TADA-AuNPs (0.05 mM), (c and c') TADA-AuNPs (0.05 mM) mixed with  $2 \mu\text{M}$   $\text{Al}^{3+}$  and (d and d') citrate-AuNPs (0.05 mM) mixed with  $5 \mu\text{M}$   $\text{Al}^{3+}$ .

TADA-AuNPs synthesized under different  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molecular ratios were used as  $\text{Al}^{3+}$  colorimetric detection sensors, and the detection limits of  $\text{Al}^{3+}$  determined by the naked eye (naked eye detection limit of  $\text{Al}^{3+}$ ) are illustrated in Table 2. While purple-colored TADA-AuNPs showed no

obvious response to  $\text{Al}^{3+}$ , the red-colored TADA-AuNPs turned blue by adding  $\text{Al}^{3+}$  and had detection limits of 1.5 and  $2.0 \mu\text{M}$  for  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratios 6.4 : 1 and 12.8 : 1 synthetic NPs, respectively. This phenomenon may be due to the different surface area-volume ratio of gold nanoparticles in different



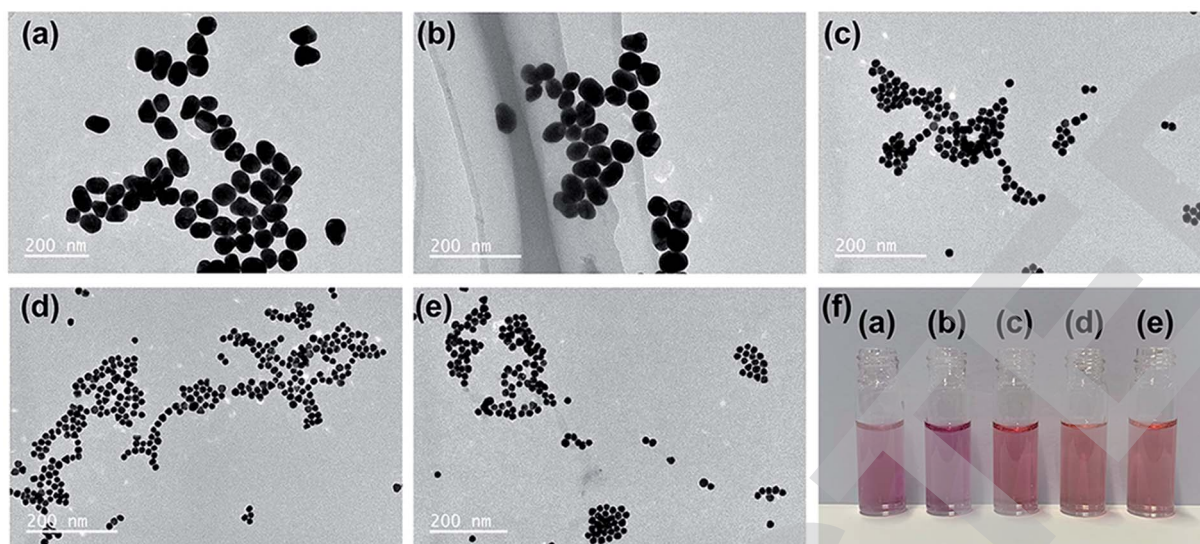


Fig. 4 TEM images (a–e) and photographic images (f) of synthesized TADA–AuNPs solutions in different  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratios using an initial  $\text{HAuCl}_4$  concentration of 0.25 mM. The  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratios in a, b, c, d, and e are 0.8 : 1, 1.6 : 1, 3.2 : 1, 6.4 : 1, and 12.8 : 1, respectively.

sizes (see Fig. S2 in ESI<sup>†</sup>). Since the smaller the diameter, the larger the surface area-volume ratio, which may affect the optical properties of gold nanoparticles, thereby influencing the detection sensitivity.<sup>50</sup> The TADA–AuNPs synthesized with  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  (molar ratio of 6.4 : 1) had a lower naked eye detection limit, and therefore was selected as the  $\text{Al}^{3+}$  colorimetric detection sensor. The effect of the TADA–AuNPs concentration on the naked eye detection limit of  $\text{Al}^{3+}$  was further investigated, and the results are exhibited in Table 3. The naked eye detection limit of  $\text{Al}^{3+}$  increased with the increase of TADA–AuNPs concentration. For enhanced detection sensitivity, 0.1 mM TADA–AuNPs synthesized using 6.4 : 1  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molecular ratio was chosen to construct the colorimetric sensor for  $\text{Al}^{3+}$  detection and used in the following studies.

### 3.2. Method selectivity

In order to evaluate the method selectivity, the UV-vis absorption spectra of TADA–AuNPs solution reacting with  $\text{Al}^{3+}$  and 21 common interference ions, including 18 metal ions ( $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,

$\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and 3 non-metal ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) ions were tested. In addition, 10 mM diphenyl carbazone (DPC) was used as a  $\text{Cr}^{3+}$  masking agent. As shown in Fig. 5a, both  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$  can induce the TADA–AuNPs aggregation without DPC, leading to a color change from dark red to blue and an SPR absorption peak shift from 525 nm to 650 nm. While in the presence of DPC, the interference of  $\text{Cr}^{3+}$  is eliminated and only  $\text{Al}^{3+}$  can induce TADA–AuNPs aggregation (Fig. 5b). Other ions do not influence the solution color and the SPR absorption spectra in the presence or absence of the masking agent, illustrating no aggregation occurred. For quantitative testing of  $\text{Al}^{3+}$ , DPC was used as a  $\text{Cr}^{3+}$  masking agent, and the competitive experiments of  $\text{Al}^{3+}$  (4  $\mu\text{M}$ ) with the 21 interference ions (50  $\mu\text{M}$ ) mentioned above were carried out, using the relative UV-vis absorption ratio ( $A_{650\text{ nm}}/A_{525\text{ nm}}$ ) to evaluate the degree of AuNPs aggregation under various parameters. The higher the ratio of  $A_{650\text{ nm}}/A_{525\text{ nm}}$ , the more severe aggregation of TADA–AuNPs was observed. The results in Fig. 5c illustrate that the UV-vis absorption ratios ( $A_{650\text{ nm}}/A_{525\text{ nm}}$ ) of TADA–AuNPs binding with 21 interference ions are much lower than that of  $\text{Al}^{3+}$ . Additionally, the  $A_{650\text{ nm}}/A_{525\text{ nm}}$  ratios (black bars) in the presence of interfering ions are almost consistent with that of the absence interfering ions, which further showed that only  $\text{Al}^{3+}$  can induce TADA–AuNPs aggregation. This  $\text{Al}^{3+}$  colorimetric detection method shows excellent selectivity.

Table 2 Optimization of  $\text{Na}_3\text{Ct}/\text{HAuCl}_4$  molar ratio for  $\text{Al}^{3+}$  determination via the naked eye

$\text{Na}_3\text{Ct}/\text{HAuCl}_4$ molar ratio	TADA–AuNPs solution color	Naked eye detection limit of $\text{Al}^{3+}$ ( $\mu\text{M}$ )
0.8 : 1	Purple	No obvious color change
1.6 : 1	Purple	No obvious color change
3.2 : 1	Slight purple	No obvious color change
6.4 : 1	Dark-red	1.5
12.8 : 1	Dark-red	2.0

### 3.3. Optimization of detection parameters for $\text{Al}^{3+}$ ion

According to the principle of the  $\text{Al}^{3+}$  colorimetric sensor, the experimental conditions of pH and detection time had great effects on the performance of the test method. In order to explore the effective pH range for  $\text{Al}^{3+}$  detection, a pH titration test of TADA–AuNPs without  $\text{Al}^{3+}$  was conducted. The SPR absorption of TADA–AuNPs in the pH range of 1–13 was



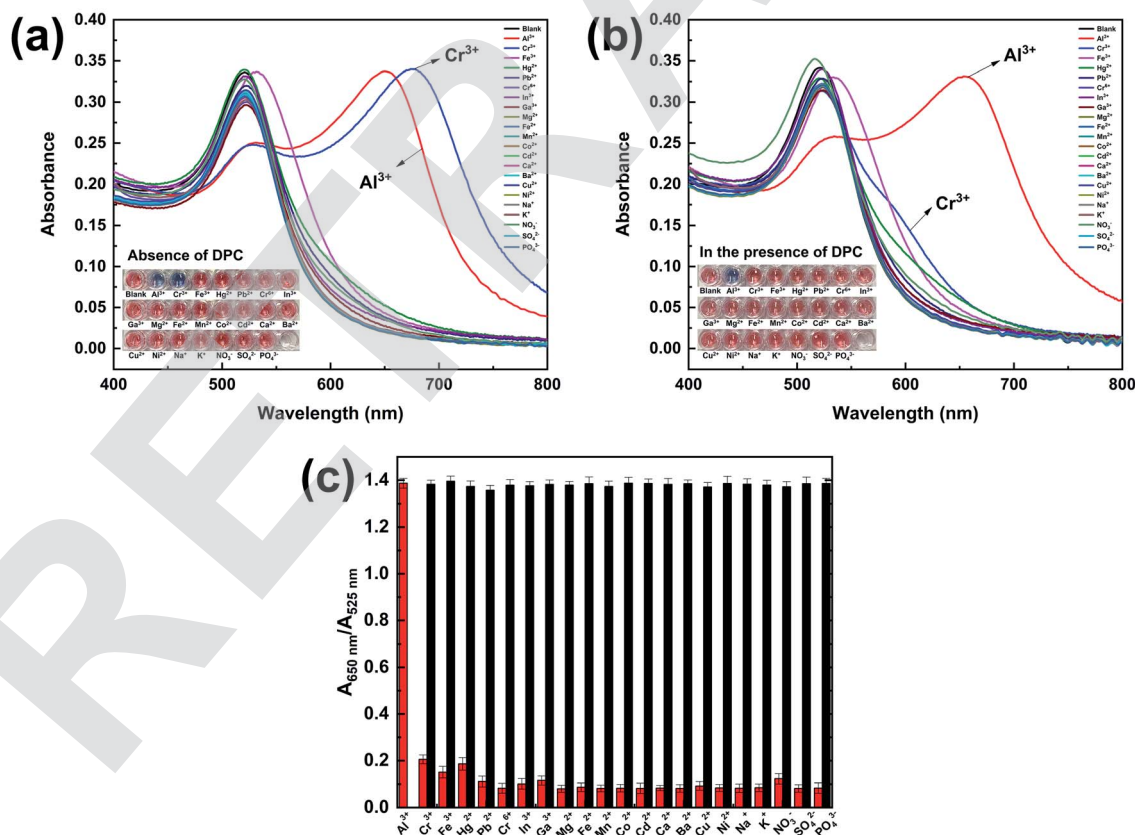


**Table 3** Optimization of TADA–AuNPs concentration ( $\text{Na}_3\text{Cit}/\text{HAuCl}_4 = 6.4 : 1$ ) for  $\text{Al}^{3+}$  determination via the naked eye

Concentration of TADA–AuNPs (mM)	Naked eye detection limit of $\text{Al}^{3+}$ ( $\mu\text{M}$ )
0.025	Too light color, not suitable for sensor
0.05	1
0.1	1.5
0.2	2.5
0.3	3.5
0.4	4.5
0.5	5.5
0.55	Too dark color, not suitable for sensor

performed, and the corresponding photographic images are shown in Fig. 6a. When the pH ranged from 4 to 12, the UV-vis absorption spectra of TADA–AuNPs exhibited a single peak at 525 nm, and the colors of the corresponding solutions were dark red. This indicates that TADA–AuNPs are stable under these pH conditions. Conversely, when the pH was  $< 4$  or  $> 12$ , the UV-vis absorption spectra of TADA–AuNPs exhibited a red-shifted new peak. Additionally, the color of the corresponding solution became blue, illustrating that the TADA–AuNPs under

these pHs formed aggregates. The reason why aggregation happens in strongly acidic and basic conditions may be because of the chemical changes on the surface of the gold nanoparticles. When  $\text{pH} < 4$ , after being protonated, negatively charged citrate may reduce its binding ability with AuNPs, resulting in a decrease in the electrostatic repulsion ability of the AuNPs; At the same time, the protonated TADA may reduce its coordination ability with AuNPs, making it unable to protect AuNPs. Under the combined effect of the two, AuNPs aggregated.<sup>51</sup> When  $\text{pH} > 12$ , under strong alkaline conditions, the carboxyl groups of citrate and TADA may be deprotonated, and their coordination ability with AuNPs may decrease, making them unable to protect AuNPs, leading to aggregation of AuNPs covered with hydroxyl groups.<sup>18</sup> Thus, the effects of the pH range from 4 to 12 on the relative UV-vis absorption ratio ( $A_{650 \text{ nm}}/A_{525 \text{ nm}}$ ) was further studied in the presence of  $\text{Al}^{3+}$ , and the results are shown in Fig. 6b. At pH 4–10, the stable TADA–AuNP solution underwent “interparticle cross-linked” aggregation in the presence of  $\text{Al}^{3+}$  ( $4 \mu\text{M}$ ). The color changed from dark red to blue and the  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  ratio increased. While at pH 11–12, the TADA–AuNPs solution still stabled, with the appearance of a dark red color and a decrease in the  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  ratio. This is due to the interaction between  $\text{OH}^-$  and  $\text{Al}^{3+}$ , forming the



**Fig. 5** UV-vis absorption spectra and photographic images (inset) of TADA–AuNPs solution in the presence of various ions (a) without and (b) with DPC masking agent (10 mM); (c) UV-vis absorption ratios ( $A_{650 \text{ nm}}/A_{525 \text{ nm}}$ ) of TADA–AuNP solutions reacting individually with various inference ions. The red bars and the black bars represent the individual ions and the single interference ion mixed with  $\text{Al}^{3+}$ , respectively. The concentration of  $\text{Al}^{3+}$  was  $4 \mu\text{M}$ . The concentration of the other ions was  $50 \mu\text{M}$ .

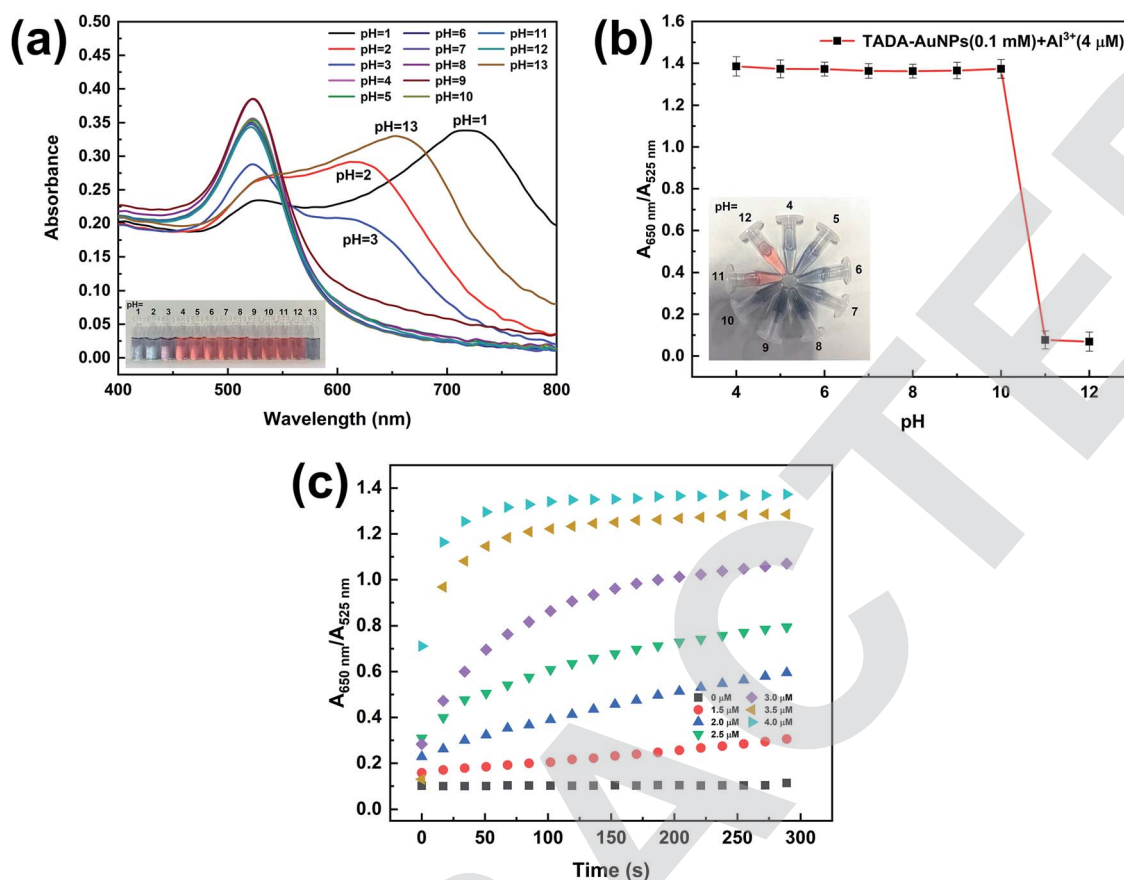


Fig. 6 (a) The change in UV-vis absorption spectra of TADA-AuNPs solution (0.1 mM) with pH and the corresponding photographic images (inset); (b) changes in UV-vis absorption ratios ( $A_{650 \text{ nm}}/A_{525 \text{ nm}}$ ) of the mixed solution of TADA-AuNPs (0.1 mM) and  $\text{Al}^{3+}$  ( $4 \mu\text{M}$ ) as a function of pH and the corresponding photographic images (inset); (c) changes in UV-vis absorption ratios ( $A_{650 \text{ nm}}/A_{525 \text{ nm}}$ ) of the mixed solution of TADA-AuNPs (0.1 mM) and  $\text{Al}^{3+}$  ( $4 \mu\text{M}$ ) as a function of pH and the corresponding photographic images (inset). All of the above are in the presence of the DPC masking agent (10 mM).

$\text{Al}(\text{OH})_3$  colloid. Therefore, the optimal pH range for the  $\text{Al}^{3+}$  assay is 4–10. The pH of 6.3 was selected for the following studies.

The effect of detection time on the relative UV-vis absorption ratio ( $A_{650 \text{ nm}}/A_{525 \text{ nm}}$ ) of TADA-AuNPs mixed with different concentrations of  $\text{Al}^{3+}$  (0–4  $\mu\text{M}$ ) was investigated. As shown in Fig. 6c, the value of  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  depends on the concentration of  $\text{Al}^{3+}$ .  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  increased rapidly with the increase of detection time and then became steady. Additionally, with the increase in  $\text{Al}^{3+}$  concentration, the detection time to saturation decreased. For 4  $\mu\text{M}$   $\text{Al}^{3+}$ , the  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  ratio reached saturation when the detection time was 90 s, which means that  $\text{Al}^{3+}$  has induced the aggregation of TADA-AuNPs completely. Thus, the optimal detection time is 90 s.

### 3.4. Detection sensitivity

Under the optimal detection parameters, the detection sensitivity of this colorimetric sensor for  $\text{Al}^{3+}$  was studied, and the results are outlined in Fig. 7. There is a good linear correlation between  $A_{650 \text{ nm}}/A_{525 \text{ nm}}$  and  $\text{Al}^{3+}$  concentration in the range of 1.5–4.0  $\mu\text{M}$  ( $R^2 = 0.9976$ ), from which the detection limit of  $\text{Al}^{3+}$

was determined to be 15 nM (Fig. S3 in ESI,† 3 times signal to noise ratio (S/N)). More importantly, this colorimetric assay can be used for visual determination of  $\text{Al}^{3+}$ . As shown in the inset photograph in Fig. 7, when the  $\text{Al}^{3+}$  concentration was 1.5  $\mu\text{M}$ , the color of the TADA-AuNP solution began to turn from dark red to violet, and this change could be easily identified and detected by the naked eye. Thus, the detection limit of  $\text{Al}^{3+}$  via naked eye is 1.5  $\mu\text{M}$ , which is much lower than the current limit (3.7  $\mu\text{M}$ ) for drinking water in the WHO regulation and better than the previous reports.

### 3.5. Application in environmental water samples

Recovery experiments performed on spiked river water samples were carried out to determine the practical application effect of the as-constructed  $\text{Al}^{3+}$  colorimetric sensor. The water samples were spiked with four concentration levels of  $\text{Al}^{3+}$  (1.50, 2.50, 3.50, and 4.00  $\mu\text{M}$ ) after filtration through a 0.2  $\mu\text{m}$  membrane. The  $\text{Al}^{3+}$  concentration in each sample was analyzed by the colorimetric sensor through UV-vis spectra (Fig. S4†) and the calculated results are shown in Table 4. The recoveries ranged from 95%–109%, and the relative standard deviations (RSD)





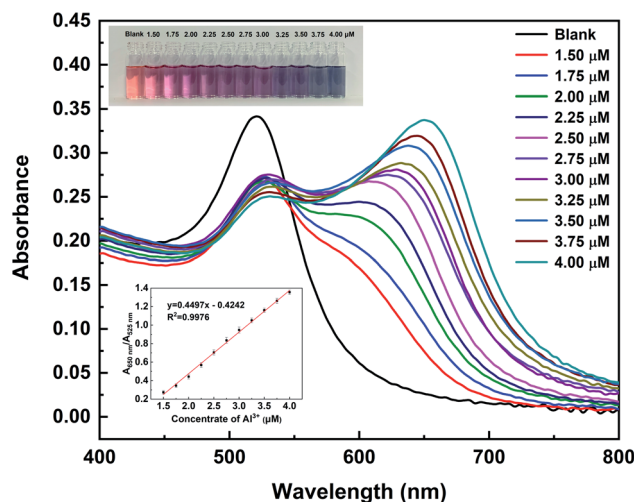


Fig. 7 UV-vis absorption spectra of TADA-AuNPs bound with various  $\text{Al}^{3+}$  concentrations (0, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, 3.50, 3.75, and 4.00  $\mu\text{M}$ ) in the presence of the DPC masking agent (10 mM) and the corresponding photographic images (inset) and the linear relationship between  $A_{650\text{ nm}}/A_{525\text{ nm}}$  absorbance ratio and  $\text{Al}^{3+}$  concentration.

Table 4 Detection of  $\text{Al}^{3+}$  in spiked real water samples

Added concentration of $\text{Al}^{3+}$ ( $\mu\text{M}$ )	Found concentration of $\text{Al}^{3+}$ <sup>a</sup> ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
0	—	—	—
1.50	$1.63 \pm 0.046$	108.7	2.8
2.50	$2.54 \pm 0.086$	101.6	3.4
3.50	$3.58 \pm 0.11$	102.3	3.1
4.00	$3.82 \pm 0.057$	95.5	1.5

<sup>a</sup> Detection based on three independent samples ( $n = 3$ ); values: mean  $\pm$  SD.

were less than 3.5% ( $n = 3$ ). This indicates that the designed TADA-AuNPs sensor is applicable for  $\text{Al}^{3+}$  detection in water samples.

## 4. Conclusions

A selective, sensitive, rapid, low-cost and simple colorimetric system for the visual detection of  $\text{Al}^{3+}$  based on 1,2,3-triazole-4,5-dicarboxylic acid (TADA)-functionalized gold nanoparticles (TADA-AuNPs) has been successfully developed. This sensing system shows high selectivity for  $\text{Al}^{3+}$  quantitative detection using diphenyl carbazone (DPC) as a  $\text{Cr}^{3+}$  masking agent. Moreover, the sensing system has the advantages of fast response (90 s) and low detection limits, which are 15 nM and 1.5  $\mu\text{M}$  for UV-vis detection and naked eye identification, respectively. The detection limits are much lower than the current limit (3.7  $\mu\text{M}$ ) for drinking water in the WHO regulation. In addition, this colorimetric sensing system can be used to accurately detect the  $\text{Al}^{3+}$  in real water samples, and it shows

great potential for rapid, *in situ* and real-time determination of trace  $\text{Al}^{3+}$ . More significantly, this colorimetric assay can be easily modified to detect other element ions or restricted substances. Simply changing the ligand to recognize the target analyte allows for versatile and broad application. The sensor shows great potential for food safety, agriculture, and environmental monitoring applications.

## Conflicts of interest

There are no conflicts of interest to declare.

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