

## Supporting Information

### **One-pot preparation of pomegranate-like polydopamine stabilized small gold nanoparticles with superior stability for recyclable nanocatalysts**

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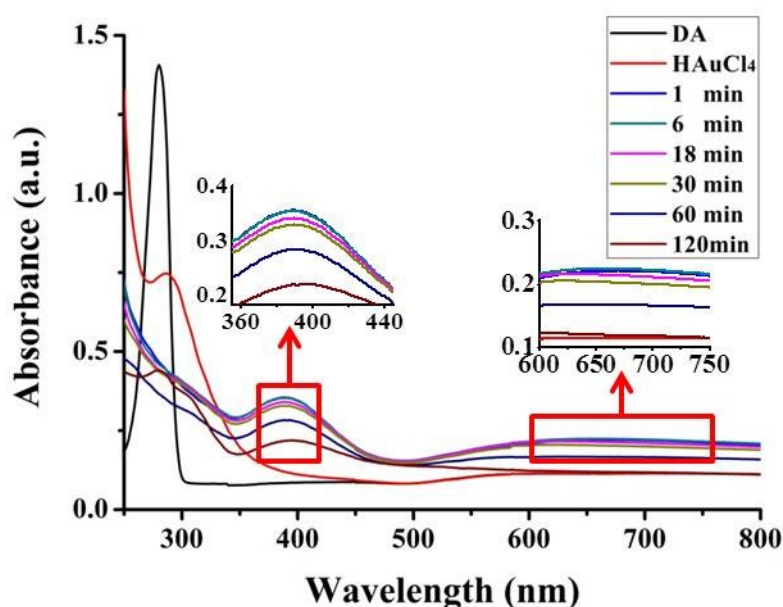
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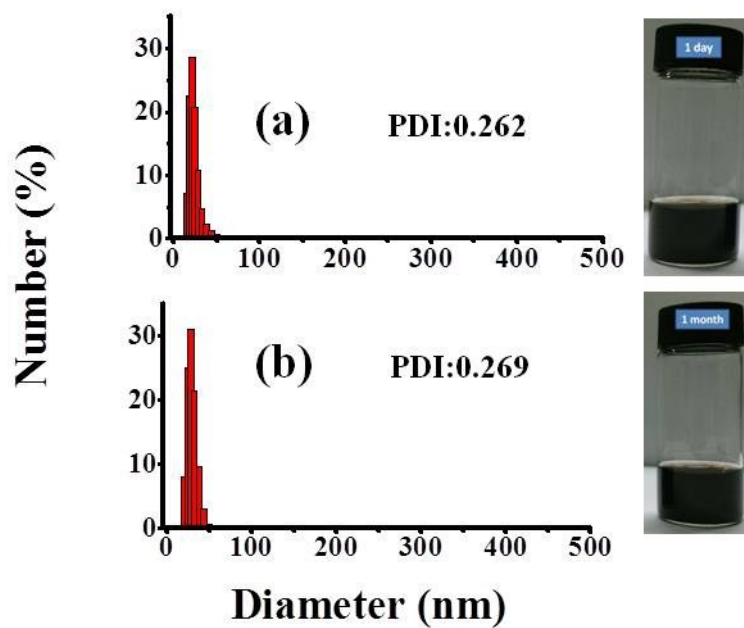
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### Optimization of the premixing time of DA and H<sub>AuCl</sub><sub>4</sub>.

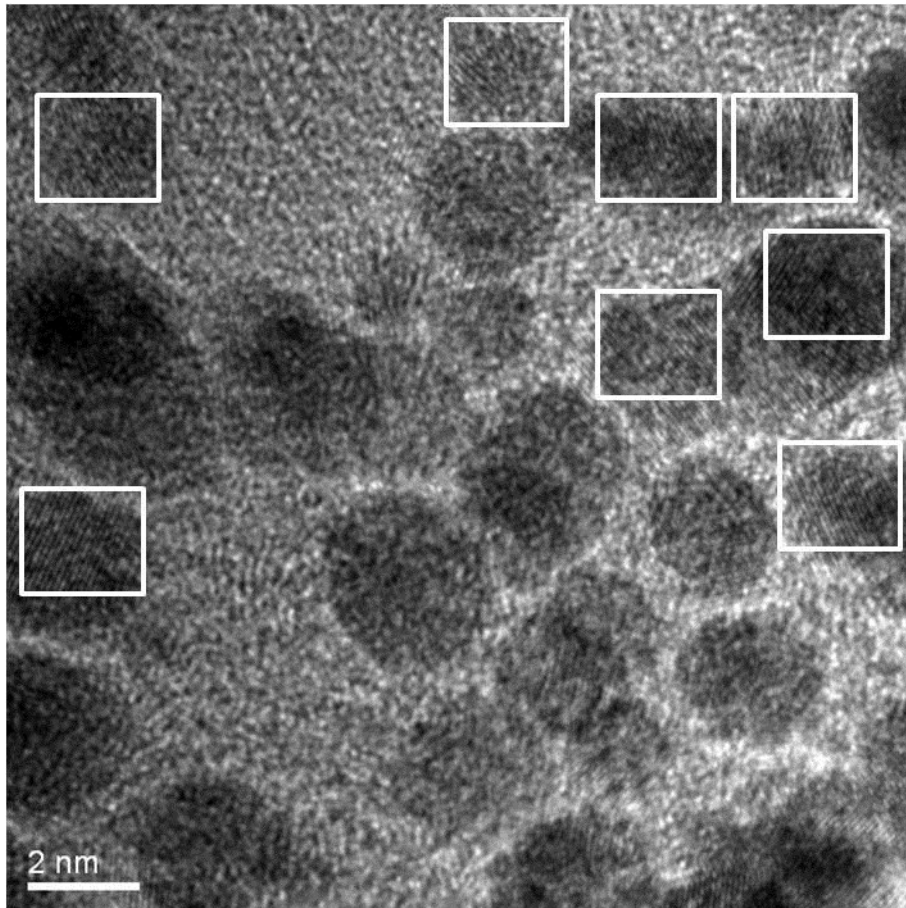
In order to get the small seeds for the preparation of PDA stabilized small AuNPs, the pre-mixing time of DA and H<sub>AuCl</sub><sub>4</sub> was optimized at first. The UV-vis spectra were employed to monitor the kinetics of the mixture of DA and H<sub>AuCl</sub><sub>4</sub>. Initially, DA and H<sub>AuCl</sub><sub>4</sub> showed typical absorption peak at 280 nm and 290 nm separately. When dopamine and H<sub>AuCl</sub><sub>4</sub> were mixed together for 1 min, these two peaks declined and two new peaks (inset of Figure S1) around 390 nm and 670 nm appeared, indicating the formation of very small Au clusters. The adsorption curves were totally overlapped within 6 mins. However, with the further increase of mixing time, the peak around 390 nm declined gradually and a clear red-shift was observed (inset of Figure S1), which indicated the aggregation of small Au clusters. As further evidence, the broad absorption around 670 nm decreased and then disappeared after mixed for 6 mins (inset of Figure S1), which further proved that Au cluster were aggregated into large nanoparticles. Since the solution pH of the reaction system was around 2 due to the addition of H<sub>AuCl</sub><sub>4</sub>, the dopamine-quinone oxidation process was very slow and the self-polymerization of DA was difficult to happen at such acidic pH value.<sup>26</sup> And thus, only a small amount of quinone moieties would be formed, which were believed to facilitate the reduction of very small Au cluster. It was proposed that the Au cluster could be used as nucleating seeds to synthesize small AuNPs. Thus, we selected a pre-mixing time of two minutes for post-polymerization to make sure that the mixture was stopped at the level of Au clusters.



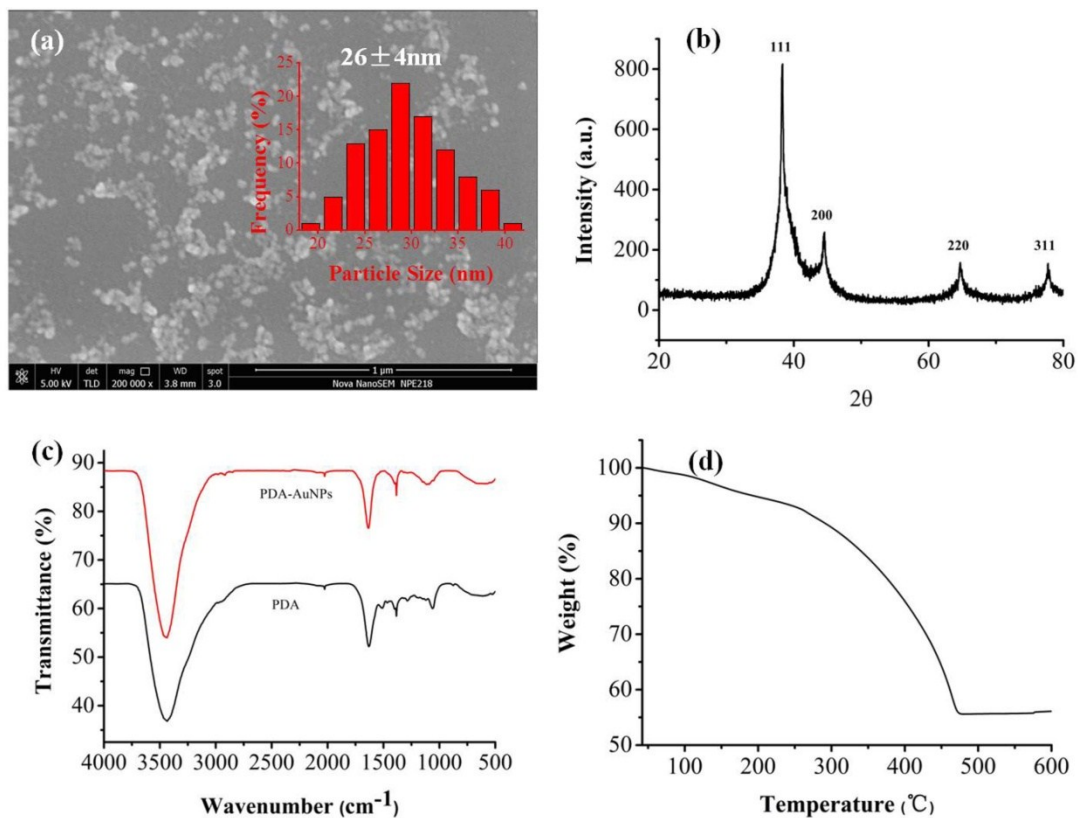
**Figure S1.** UV-vis spectra of the mixture of DA and H<sub>AuCl</sub><sub>4</sub> mixed at pH=2 for different time.



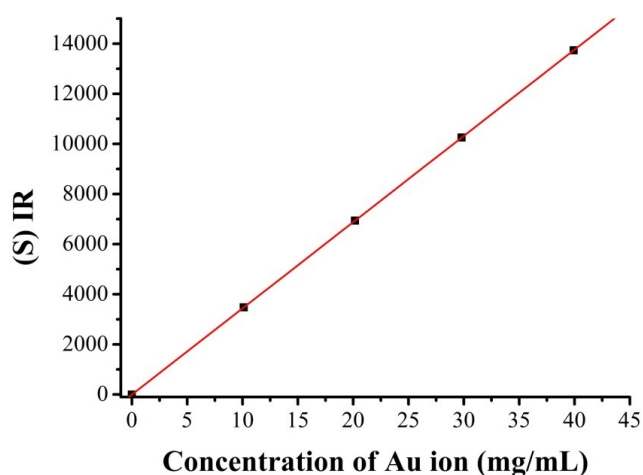
**Figure S2.** Number-averaged size distributions and the digital photos (inset) of the dispersions (pH=8) after 1 day's reaction (a) and after stored in ambient condition for 1 month (b), respectively.



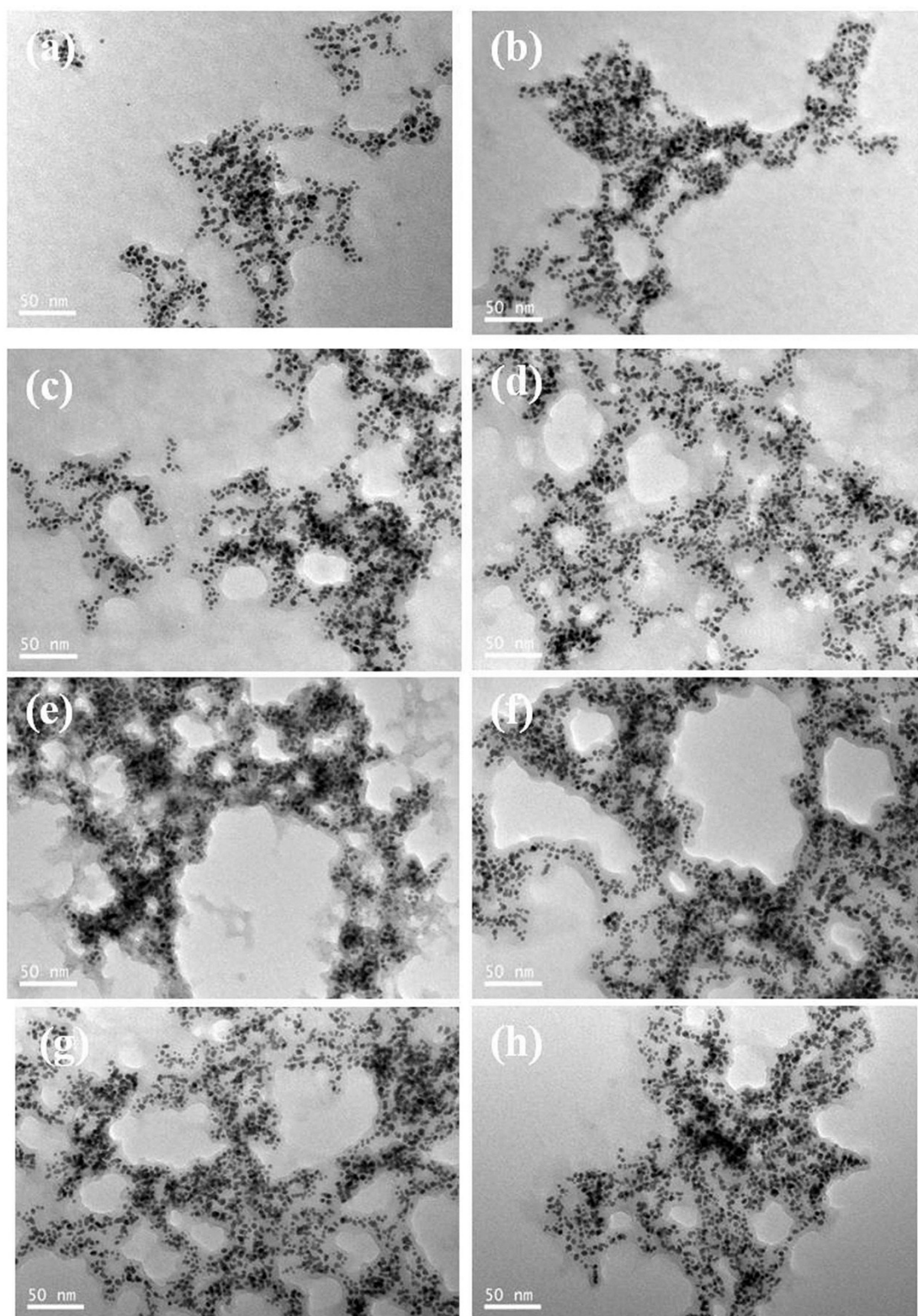
**Figure S3.** The HRTEM image of AuNPs inside the PDA-AuNP pomegranate-like nanocomposites (prepared at pH=8)



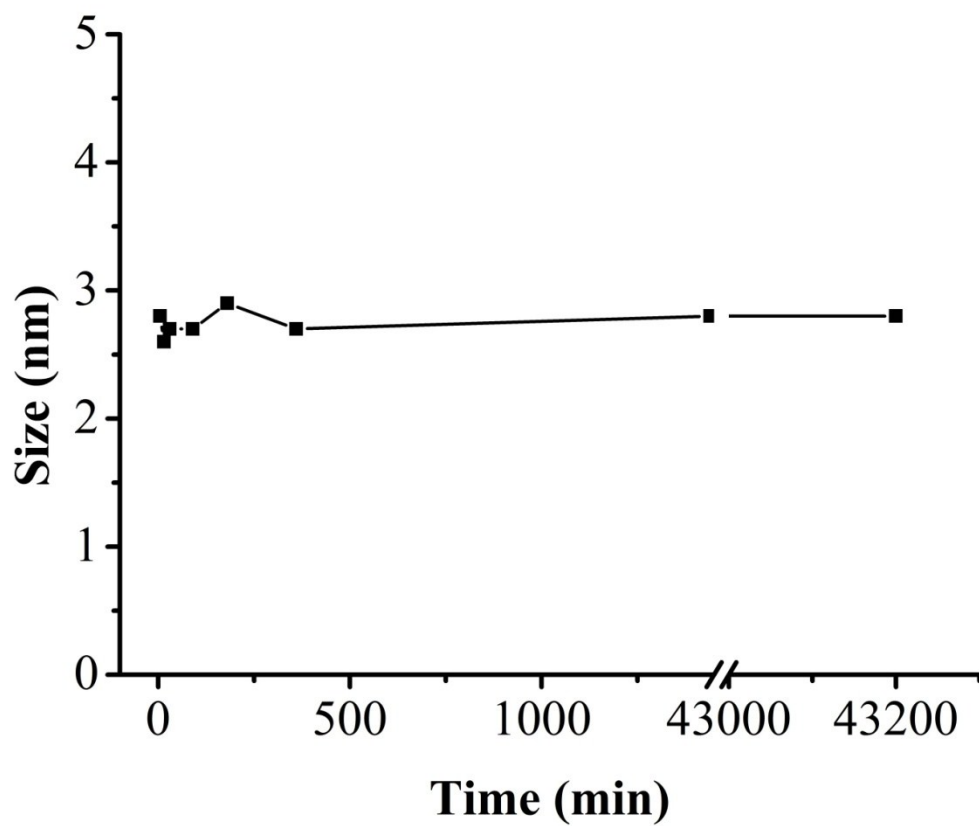
**Figure S4.** (a) SEM image PDA-AuNPs (prepared at pH=8) was stored in ambient condition for 1 month. (b) XRD pattern. (c) FTIR spectra and (d) TGA curves of PDA-AuNPs (prepared at pH=8). TGA measurement was operated under a dry air atmosphere; volatile components appeared below the temperature of about 100 °C were neglected.



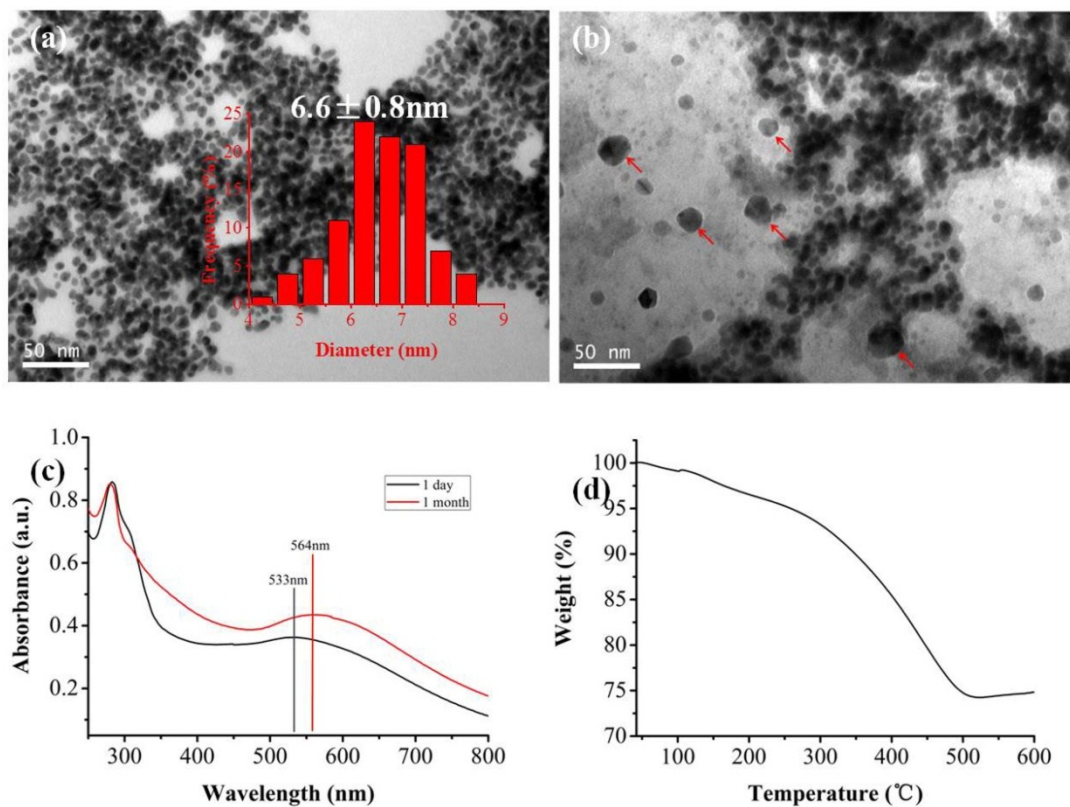
**Figure S5.** The calibration graph of ICP-OES was used for measuring Au content (The graph was linear with a correlation coefficient of 0.99998)



**Figure S6.** The TEM images of PDA-AuNPs (prepared at pH=8) at different reaction times of 5 mins (a), 15 mins (b), 30 mins (c), 1.5 hrs (d), 3 hrs (e), 6 hrs (f), 1 day (g), 1 month (h) respectively. The sample solutions reacted at above mentioned time were directly used for TEM observation without any purification.

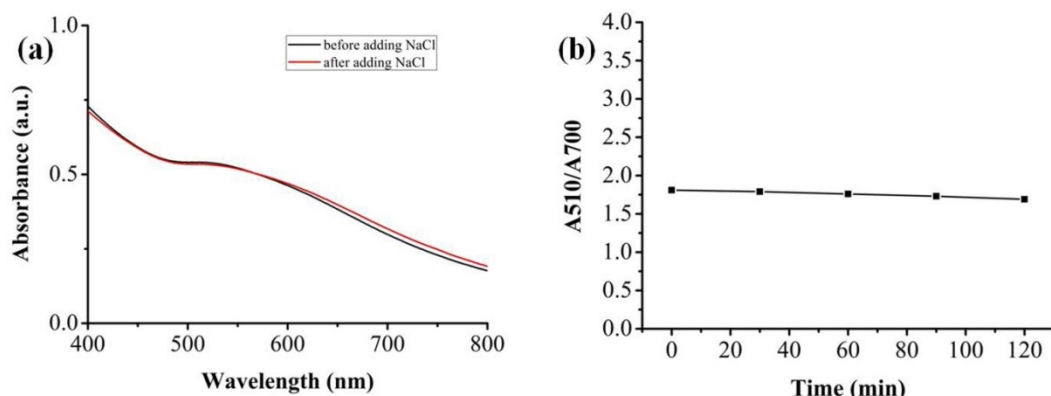


**Figure S7.** The size evolution of AuNPs versus reaction time in the PDA-AuNPs (prepared at pH=8) system.



**Figure S8.** (a) and (b) The TEM images of PDA-AuNPs (prepared at pH=4) at different reaction times of 1 day (a) and 1 month (b) respectively. (c) UV-vis spectra of PDA-AuNPs (prepared at pH=4) after reacted for 1 day (black line) and kept in ambient condition for 1 month (red line) respectively. (d) TGA curves of PDA-AuNPs (prepared at pH=4) under dry air atmosphere, volatile components disappearing until a temperature of about 100 °C were neglected.





**Figure S9.** UV-vis spectra of PDA-AuNPs (prepared at pH=8) system before and after adding NaCl to the concentration of 500 mM NaCl. (a) The spectra were taken 0.5 hr after adding NaCl to this system. Note that the SPR band of this system decreased slightly over a few hours in the investigated salt concentration. (b) A510/A700 was used to monitor the stability of this system.

**Table S1.** The list of the catalytic activity for the reduction of different concentrated 4-nitrophenol by different gold nanocatalysts.

Catalyst	Concentration of 4-NP (mM)	4-NP/Au (mol/mol)	TOF (h <sup>-1</sup> )	K (min <sup>-1</sup> )
<sup>1</sup> Au-PMMA	0.051	15/1	92	$9.0 \times 10^{-2}$
<sup>2</sup> Au/graphene hydrogel	0.093	23/1	11	$1.9 \times 10^{-1}$
<sup>3</sup> Yolk-double shell SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub> -C@Au	0.16	51/1	1044	$9.7 \times 10^{-1}$
<sup>4</sup> Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Au@mSiO <sub>2</sub>	0.24	1.5/1	6	$3.5 \times 10^{-1}$
<sup>5</sup> Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -LBL-Au	0.16	67/1	804	$3.4 \times 10^{-1}$
<sup>6</sup> graphene/PDA-Au NPs	0.03	5/1	23	$2.3 \times 10^{-1}$
This work PDA-AuNPs	50.00	6038/1	1006	$5.7 \times 10^{-2}$

**Table S2.** The list of kinetic constants K and R<sup>2</sup> for the reduction of 4-nitrophenol by PDA-AuNPs for each cycle.

Cycle entry	Kinetic constants (min <sup>-1</sup> )	R <sup>2</sup>
1	0.057	0.99841
2	0.054	0.99860
3	0.052	0.99814
4	0.049	0.99927
5	0.046	0.99892
6	0.044	0.99856
7	0.040	0.99770
8	0.037	0.99675
9	0.034	0.99625
10	0.030	0.99606

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## References

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