Supporting information

Au nanoparticles on citrate-functionalized graphene nanosheets with high peroxidase-like performance

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In the experiment, we compared the color changes of TMB-H_2O_2 solution with the addition of GNs, Cit-GNs and AuNPs/Cit-GNs, respectively. The amount of GNs for each test was 1 μg mL^{-1}. As shown in Fig. S1, it is clear that TMB-H_2O_2 solution in the presence of GNs exhibits no color change, indicating the oxidation reaction is slowly in the presence of GNs. In contrast, with the addition of AuNPs/Cit-GNs and Cit-GNs, the solutions showed obvious blue colored change, and the blue color of the solution containing AuNPs/Cit-GNs is much deeper than that of Cit-GNs. This result indicated that the AuNPs played an importance role in the catalytic reaction and suitable amount of citrate with many carboxyl groups is beneficial for the improvement of peroxidase-like activity.

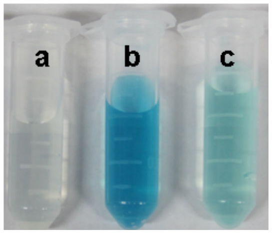
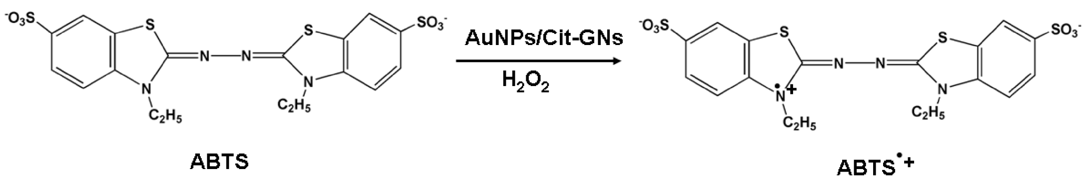


Fig. S1 Color evolution of TMB in different reaction systems: (a) TMB + H_2O_2 + GNs; (b) TMB + H_2O_2 + AuNPs/Cit-GNs; (c) TMB + H_2O_2 + Cit-GNs. TMB: 200 μM; H_2O_2: 100 mM; NaAc-HAc buffer: pH=3.8; Time: 10 min.

Moreover, to further study the charge characteristics of the catalyst and the substrate in the reaction system, we test the peroxidase-like catalytic activity of these enzyme mimics with 2, 2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) in the presence of H_2O_2. In contrast to TMB, ABTS is a negatively charged chromogenic substrate which has two sulfo groups per molecule. Therefore, the electrostatic interaction between the carboxyl groups on the enzyme mimics and the ABTS will be different from that of TMB. As shown in Scheme S1, ABTS can also be catalytically oxidized by H_2O_2, and an oxidized colored product ($ABTS^{\cdot+}$) is formed with an absorbance maximum at 415 nm.



Scheme S1 Corresponding reaction scheme for the AuNPs/Cit-GNs catalysis H_2O_2 reduction with ABTS.

Fig. S2A shows the UV-vis absorption spectra of enzyme mimics catalytic reaction systems upon reaction for 15 min. The absorption peak at 415 nm suggests the formation of ABTS$^{\cdot+}$. Different from the results of TMB, according to these curves, AuNPs/GNs showed the highest absorbance at 415 nm. Moreover, from the time-dependent absorbance changes at 415 nm (Fig. S2B), AuNPs/GNs also exhibited the fast reaction rate of these composites, suggesting that AuNPs/GNs revealed the highest catalytic activity towards ABTS. In this system, as ABTS is a negatively charged chromogenic substrate, the same negatively charged capping agent-citrate on the surface of AuNPs is unfavorable for the attracting of ABTS, which means that the affinity of AuNPs/Cit-GNs with ABTS is weaker than that of AuNPs/GNs. Moreover, this conclusion can also supported by comparison with the results of the two simply mixture: Cit-AuNPs+GNs and Cit-AuNPs+GO (GO surface owns many negatively charged carboxyl groups), in the ABTS system, the former revealed better peroxidase-like catalytic ability, however, in the TMB system, the later express better peroxidase-like catalytic ability (Fig. 5). These observations indicate that the charge characteristics of the catalyst and the substrate also play an important role in the catalytic reactions.

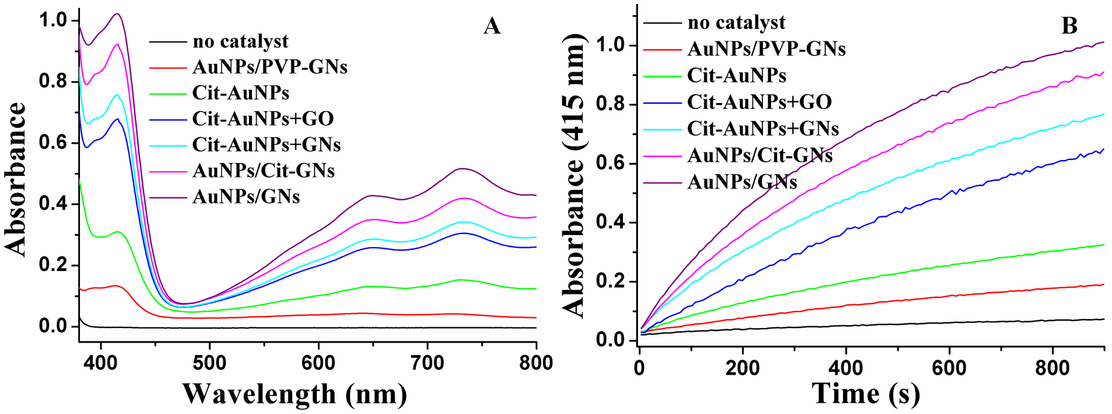


Fig. S2 (A) UV-vis absorption spectra of various enzyme mimics catalytic reaction systems upon reaction for 15 min. (B) Time-dependent absorbance changes at 415 nm of ABTS reaction solutions catalyzed by these enzyme mimics.