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COMMUNICATION

Significant impact of polydopamine on catalytic performance of the carried Au nanoparticles

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Mussel-inspired polydopamine catalyst carriers dramatically enhance the catalytic performance (~450%) of Au nanoparticles in methylene blue reduction, which is attributed to the local enrichment mechanism caused by the favourable attractive interaction between the polydopamine and reactants.

Recently, inspired by marine mussel, polydopamine (PDA) has attracted intense research interests.¹ The universal adhesive ability and excellent biocompatibility of PDA leads to prominent applications in many fields.¹⁻⁶ PDA films can grow and adhere on a wide spectrum of organic and inorganic substrates that allows further modification, resulting in multi-functional surfaces.² Due to its excellent biocompatibility, PDA hollow capsules, particles and films were synthesized and utilized in biomedical science, such as drug delivery, bioimaging, photothermal therapy and anti-microbial applications etc.³ In colloid and interface sciences, PDA has been used to manifest the interfacial basicity,⁴ prepare PDA-Au Janus particles and the specific Janus-like Pickering emulsions.⁵ In water treatment, PDA-functionalized hybrid materials were developed and utilized as efficient adsorbents to remove heavy metal and organic pollutants.⁶

Very recently, PDA has been applied in various catalytic systems and served as a catalyst carrier due to its unique merits.^{6c, d, 7} PDA is reactive to noble metal ions which allows facile and in-situ deposition of metallic catalyst nanoparticles (NPs) such as Ag, Au, and Pt.^{2a, 5a, 7b, 8} Concurrently, PDA film can be deposited on virtually all substrates.^{2a} Combining these two unique features, in principle, the catalytic metal NPs can be loaded onto any core particles or substrates with the assistance of PDA interlayer. One typical model catalytic particle is

composed of magnetic core particle, PDA interlayer coated on the core, and the metal NPs deposited on the PDA layer.^{6c, d, 8a} The utilization of PDA carriers brings hybrid catalyst particles with diverse functions that significantly widen their applications. It is expected that, as a catalyst carrier, PDA has no significant effect on the catalytic performance of the loaded catalysts. In this work, we for the first time quantitatively study the effect of PDA carrier on the catalytic activity of Au NPs. Surprisingly it is found that the PDA carriers can dramatically enhance the catalytic performance (~450%) of Au NPs in methylene blue (MB) reduction.

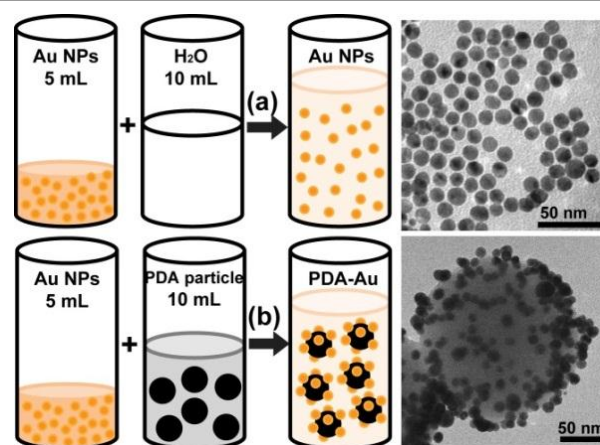


Fig. 1 Preparation of model catalytic particles. (a) Au NPs dispersed in water, (b) Au NPs loaded on PDA particles that dispersed in water. The amount and the surface properties of Au catalyst NPs in these two cases are identical.

To quantify the effect of the PDA carriers, the catalytic activity of the same amount of freely dispersed Au NPs and PDA carried Au NPs were studied and compared. First, Au NPs

were synthesized by a modified Turkevich method.⁹ The mean size of the obtained Au NPs is about 9.5 nm. In the first case (Fig. 1a), 5 mL of the prepared Au NP suspension (~0.05 mg/mL) was diluted with 10 mL water, and then used for catalytic reactions. In the second case (Fig. 1b), the same amount of Au NP suspension (5 mL) was first mixed with 10 mL of PDA particle suspension (~0.1 mg/mL, the mean size of PDA particle is ~230 nm). The mixed solution was stirred for 24 h to allow the adsorption of Au NPs onto the surface of PDA particles. The amount of loaded Au NP was monitored via the change of UV-vis spectra of the Au suspension. The surface plasmon resonance (SPR) band of Au NPs in the suspension vanished after 24 h (Fig. S1), indicating that almost all the Au NPs were adsorbed onto the PDA particle surfaces. The estimated load amount of Au NPs for each PDA particle is about 220. After adsorption, the PDA carried Au NPs were used for the same catalytic reactions. In these two parallel tests: (1) the amount of catalyst Au NPs is identical; (2) the volume of the solution is the same (viz. the concentration of catalyst and reactant are the same); (3) the surface properties of Au NPs are identical because the load of Au NPs is an adsorption process. The only difference is that in the first case (Fig. 1a), the Au NPs are freely dispersed while in the second case, Au NPs are loaded on the surface of PDA carriers (Fig. 1b). Therefore, if there is any discrepancy in the catalytic performance of Au NPs between the two sets of test, it should be attributed to the effect of PDA carriers.

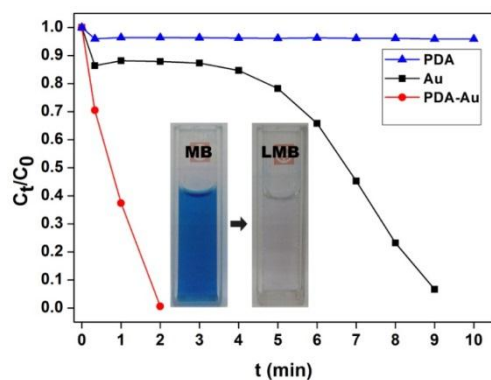


Fig. 2 The reduction of MB as a function of time catalysed by Au NPs and PDA carried Au NPs; the adsorption of MB by PDA particles. Inset: photographs of MB and LMB solution.

Surprisingly, it is found that via loading the Au NPs onto PDA surfaces, the catalytic performance of the Au NPs can be dramatically improved in the catalytic reduction of MB. As shown in Fig. 2, after the catalytic reduction, the blue colour of MB faded. The maximum adsorption peak ($\lambda_{\max}=664$ nm) of MB decreased, while a new adsorption peak ($\lambda=257$ nm) appeared, indicating the formation of leuco MB (LMB) by catalytic reduction (Fig. S2). When the freely dispersed Au NPs were used as catalyst, the MB reduction was finished in 9 min, the colour of the MB solution thoroughly faded (Fig. 2 and S2a). For comparison, the PDA carried Au NPs show much higher catalytic activity (Fig. 2 and S2b). The maximum

adsorption peak ($\lambda_{\max}=664$ nm) of MB decreased quickly. The catalytic reduction completed in 2 min. The catalytic performance of PDA carried Au NPs is about 450% higher than that of freely dispersed Au NPs. The effect of pure PDA particles on MB bleaching was also investigated. PDA can't catalyse the MB reduction since no new adsorption peak ($\lambda=257$ nm) for LMB appeared (Fig. S2c). However, an instant adsorption of MB by PDA particles was observed. About 4.5% of MB was adsorbed by PDA particles within 20 s. Then the adsorption reached equilibrium. All these results confirm that when the Au NPs are loaded on PDA carriers, their catalytic performance is significantly improved.

Because of the identical surface properties and amount of the Au NPs used in the two catalytic reactions, it is evident that the PDA carrier causes the discrepancy in catalytic performance of Au NPs. A synergistic effect between PDA carriers, MB molecules and the carried Au NPs is proposed. The catalytic reaction is a surface process involving diffusion of reactants to the surface of catalyst, catalytic reaction and mass exchange. Rapid local enrichment of reactants at the surface of catalyst can definitely enhance the reaction kinetics. It has been well demonstrated that in the layer-by-layer process, the electrostatic attraction between oppositely charged particles and organic molecules can be applied to enrich and build inorganic-polymer multilayers.¹⁰ Herein, the PDA carriers could enrich the reactant MB for the carried catalysts (Au NPs) due to the electrostatic attraction. The PDA particles are negatively charged in a wide pH range (Fig. S3). While the MB molecule is positively charged (Fig. S4a). In our experiments, the pH of the reaction solution is ~9.5, the zeta potential of PDA is measured to be about -43 ± 9 mV (Fig. S3). Electrostatic attraction between PDA particles (-) and MB molecules (+) induces the adsorption of MB toward PDA surface. A fast enrichment of MB at PDA surface is realized, manifested by the instant adsorption of 4.5% MB within 20 s (Fig. S2c). As a result, the local concentration of MB at PDA surfaces is much higher than that in bulk solution (Fig. S5a). When the Au NPs are loaded on the PDA surface, they benefit from the MB enrichment (Fig. S5a). Therefore, the rate of the catalytic reaction and the performance of the catalysts are significantly improved. The concentration of the MB (c) at the PDA surface can be estimated according to the Boltzmann law:¹¹

$$c = c_0 \exp \frac{ze\psi}{k_B T} \quad (1)$$

where c_0 is the concentration of MB in bulk solution, z is the ion valence (for MB, $z=1$), e is the charge of an electron ($e = 1.6 \times 10^{-19}$ C), ψ is the local electrical potential, k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K) and T is the temperature in Kelvin. Approximating the surface potential of PDA as the zeta potential measured ~-45 mV, the c/c_0 is estimated to be about 600%. It is believed that the adsorbed MB molecules in the stern layer are immobile and not reactive, therefore the real enchantment of reaction kinetics is expected to be <600%, which could explain the experimental results of ~450%. In contrast, the freely dispersed Au NPs catalyse the

reaction at a relatively lower MB concentration (Fig. S5b), leading to a lower reaction rate.

It is noted that the electrostatic interactions, van der Waals and π - π interactions all contribute to the interaction between PDA and MB. However, it is believed that the long-range electrostatic interactions favour the efficient enrichment of the reactant molecules to the PDA surfaces, which in turn affect the rate of the catalytic reaction. To further demonstrate this effect, we investigated another model catalytic reaction, catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). Typically, before conducting the catalytic reaction, NaBH_4 was first added into 4-NP solution to produce 4-nitrophenolate. Different from the positively charged MB molecule, the 4-nitrophenolate molecule is negatively charged (Fig. S4b). Therefore, electrostatic repulsion between PDA carriers (-) and 4-nitrophenolate (-) exists, which is unfavourable for the local enrichment of 4-nitrophenolate at PDA surfaces. As shown in Fig. S6a, no adsorption of 4-nitrophenolate by PDA particles is observed. Therefore, it is expected that the PDA carriers have no positive effect on the catalytic performance of the carried Au NPs.

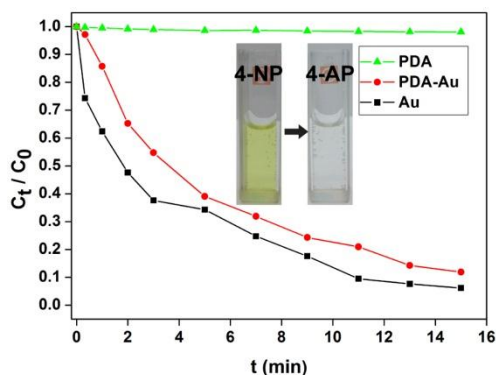


Fig. 3 The reduction of 4-NP as a function of time catalysed by freely dispersed Au NPs and PDA carried Au NPs; the adsorption of 4-NP by PDA particles. Inset: photographs of the 4-NP and 4-AP solution.

The catalytic reduction of 4-nitrophenolate (yellow colour) to 4-AP (colourless) by Au NPs was investigated via monitoring the change of the adsorption peak at 400 nm (Fig. 3 and S6). When the catalytic particles were added into the 4-nitrophenolate solution, the adsorption peak of the solution (400 nm) began to decrease. As shown in Fig. 3 and S6b, the reduction of 4-nitrophenolate is about 94% after 15 min reaction catalysed by the freely dispersed Au NPs. When the reaction was catalysed by the PDA carried Au NPs, the reduction of 4-nitrophenolate is 88% after 15 min (Fig. 3 and S6c). These results demonstrate that the PDA carrier has no positive effect on the catalytic performance of the carried Au NPs. It is noticed that the reaction rate in the first 20 s catalysed by PDA carried Au NPs is much lower than that catalysed by freely dispersed Au NPs (Fig. 3 and S6). This should be ascribed to the electrostatic repulsion between the PDA carriers and 4-nitrophenolate, which leads to a temporarily lower reactant concentration at PDA surfaces in initial stage of the

process as compared to its bulk concentration. As a result, the rate of reaction catalysed by the Au NPs located on PDA surfaces is lower than that of the freely Au NPs in bulk phase.

In summary, we have investigated the effects of the PDA carrier on the catalytic performance of Au NPs loaded on its surface. It is found that the PDA carried Au NPs has much higher (~450%) catalytic activity than the freely dispersed ones in the catalytic reduction of MB. The electrostatic attraction between PDA carriers and MB gives rise to rapid enrichment of MB toward PDA surfaces, creating a locally concentrated layer of MB. These factors significantly accelerate reduction reaction and enhance the catalytic performance of the Au NPs loaded on the PDA surfaces. In contrast, the PDA carrier shows a slightly negative effect on the catalytic performance of carried Au NPs in the catalytic reduction of 4-nitrophenolate because the electrostatic repulsion between PDA and 4-nitrophenolate hinders the localized enrichment of 4-nitrophenolate at PDA surfaces. The interactions between the PDA carriers and reactants remarkably affect the catalytic performance of the loaded catalysts. It is believed that this mechanism can be extended to other catalyst carriers in liquid phase catalysis. Deliberate design and control of the surface properties of the carriers to rapid enrich reactants would significantly boost the reaction rate and enhance the performance of the loaded catalysts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure, UV-vis spectra of the reaction solutions, Zeta potential of PDA particles etc. See DOI: 10.1039/c000000x/

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