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Three Dimensional Nano-assemblies of Noble Metal Nanoparticles-Infinite Coordination Polymers as A Specific Oxidase Mimetic for Degradation of Methylene Blue without Adding Cosubstrate

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Novel three-dimensional (3D) nano-assemblies of noble metal nanoparticles (NPs)-infinite coordination polymers (ICPs) are conveniently fabricated through the infiltration of HAuCl₄ into hollow Au@Ag@ICPs core-shell nanostructures and its replacement reaction with Au@Ag NPs. The present 3D nano-assemblies exhibit highly efficient and specific intrinsic oxidase-like activity even without adding any cosubstrate. Due to high substrate specificity and catalytic activity under mild conditions, natural enzymes have been attracting great interest in pharmaceutical processes, biosensing, agrochemical production, and food industry applications. However, they still bear some intrinsic drawbacks such as denaturation resulted poor stability, low sensitivity of catalytic activity owing to environmental conditions and difficulties of fabricating. Researchers therefore endeavoured to develop the artificial enzyme mimetic as a viable alternative to natural enzyme. Since the first exciting discovery of ferromagnetic nanoparticles (NPs), single-component nanomaterials with intrinsic peroxidase-like activity emerged in succession, such as noble metal NPs, metal oxide, carbon-based nanomaterials and so on. In comparison with natural enzymes, these nanoparticulate alternatives exhibit several advantages including low-price, easy preparation, high stability against denaturation, and tunability in catalytic activities. The most remarkable of these is gold NPs. For example, positively-charged gold NPs (with diameter about 34 nm) possess intrinsic peroxidase-like activity and can be used to detect H₂O₂ and glucose with colorimetric method; “naked” gold NPs are found to be able to catalytically oxidize glucose with the cosubstrate oxygen (O₂) similar to glucose oxidase. Besides, Au NPs also exhibited intrinsic superoxide dismutase-like and catalase-mimetic activity at physiological pH or under alkaline conditions, respectively. Even though, most of the single-component artificial enzyme mimetics possess relatively low catalytic activity and gold NPs are no exception. Furthermore, it is widely acceptable that two key factors including particle size and its dispersion determine the catalytic performance of gold NPs. To enhance the dispersion of the gold NPs in smaller sizes and meantime maintain their catalytic activity, they were often impregnated into or deposited onto low-cost and electronically transmitted supporting materials (such as inorganic substances and organic polymers). Therefore, a new generation of gold-bearing composite catalysts have recently been particularly impressive because they benefit from the synergistic effect and/or the electronic effect of multiplex components besides highly dispersed smaller-sized gold NPs. For example, Zhang et al. demonstrated that nano-hybrids of Au NPs and single-walled carbon nanotubes (SWCNTs) possessed remarkably enhanced peroxidase-like activity compared to the sole positively-charged Au NPs or SCWNTs; Liu et al. found the Au NPs-graphene sheets hybrids exhibit a synergetic effect in mimicking peroxidase.

In this work, a simple approach is suggested to fabricate novel noble metal NPs-infinite coordination polymers (ICPs) three-dimensional (3D) nano-assemblies based on our previous research. The obtained 3D nano-assemblies exhibit highly efficient and specific intrinsic oxidase-like activity for degradation of methylene blue (MB) even without adding any cosubstrate, e.g., H₂O₂. In this synthesis, the as-prepared Au@Ag@ICPs hollow core-shell nanostructures (Au@Ag@void@ICPs) are proposed as active precursors and 3D host frameworks for the infiltration of HAuCl₄ and its subsequent in situ replacement reaction with silver shell of Au@Ag core, because the DMcT-based ICPs shell is highly porous and beneficial for the penetration of water-soluble small molecules. Besides, DMcT is known to be one of the most promising organosulfur compounds as a cathode active material. So, the DMcT-based ICPs should be beneficial for the oxidation of 3,3′,5,5′-Tetramethylbenzidine (TMB) and MB, which is an electron transfer process.

The 3D nano-assemblies were synthesized by simply adding some volume of HAuCl₄ into the stirring solution of Au@Ag@void@ICPs (Fig. 1). In this process, the solution’s colour changes from orange to purple. Meanwhile, the silver peak belonging to Au@Ag@void@ICPs disappeared and only a wider peak at ca. 550 nm appeared (Fig. S1, ESI). It should be noted that the latter had obvious red shift in comparison with that of 30 nm Au NPs at the very beginning and meanwhile no obvious aggregation happened in this process, indicating a new nanostructure had been produced. Fig. 2A shows a typical transmission electron microscopy (TEM) image of the final
product. It can be clearly seen that some small Au NPs with diameters of approximately 14.6 nm (Fig. S2, ESI) are asymmetrically interspersed onto the shell of Au@Ag@void@ICPs (Fig. 2B) and a new highly dispersed 3D nano-assembly is prepared without additional chemical or biomolecular stabilizers. Fig. 2C and 2D further show the HRTEM lattice image of the Au NPs. The lattice spacing of 0.24 nm, marked in these two pictures, is consistent with that of Au (111) planes.27 Besides, X-ray photoelectron spectroscopy (XPS, Fig. S3, ESI) analysis indicates that such nano-assembly contains elements of Au, Ag, S, N, O and Cl. Among them, the elemental concentration of Ag is larger than that of Cl (Table S1, ESI). Factually, in our experiment, white solid AgCl precipitates were found to settle at the bottom of the container after the products placed for a period of time. Thus, the Cl element here is ascribed to AgCl and C, S, N, and the extra Ag confirmed the existence of Ag-DmCt ICPs. Additionally, the O 1s peak at 532.3 eV in the XPS spectrum shown in Fig. S3 indicated that there was chemisorbed oxygen on the surface of the 3D nano-assembly.28-29

Given that galvanic replacement reaction between Au@Ag NPs and HAuCl₄ is the key point in our synthesis, the influences of the composition of Au@Ag NPs and the amount of HAuCl₄ on the products’ nanostructure were further investigated. From Figure S4, we can see that the number of small Au NPs in the nano-assemblies gradually increases when the volume of AgNO₃ increases from 50 to 300 µL. Meanwhile, the products in these cases are highly dispersed. However, the products aggregate seriously when the volume of AgNO₃ increases to 500 µL, although the number of small Au NPs continues to increase. On the other hand, we also explored the influences of the volume of HAuCl₄ (Fig. S5, ESI). It is found that when the volume of HAuCl₄ is relatively small (5 µL), there are many small ellipsoidal Au NPs in 3D nano-assemblies with diameters less than 10 nm but they are easy to string together to form dendritic structures. When the volume of HAuCl₄ increases to 10 µL, the small Au NPs progressively grow up and are close to quasi-spheres. In this case, well-defined and mono-dispersed 3D nano-assemblies can be fabricated. Yet, when the volume of HAuCl₄ continues to increase (20 µL), the small Au NPs further grow up and reduces the distances of 3D nano-assemblies, which leads to

Fig. 3 (A) UV-vis spectra of the reaction solution containing TMB (a) in the absence of 3D nano-assemblies, (b) in the presence of 3D nano-assemblies, and (c) after quenched by H₂SO₄. Inset: photographs of different solutions corresponding to parts a-c. (B) Time-dependent absorbance changes at 652 nm in the presence of different volume of 3D nano-assemblies in BR buffer (pH 4.0) at room temperature.

As an oxidase mimic, the 3D nano-assemblies catalyze an oxidation-reduction reaction involving O₂ as the electron acceptor. It is reported that there are two kind of O₂, namely, dissolved oxygen and adsorbed oxygen in the reaction system of TMB-O₂-nanomaterials,30 due to the high specific surface area of nanomaterials. In order to determine whether the dissolved O₂
played a role in the TMB-O₂-3D nano-assemblies system, two

Fig. 4 (A) The absorbance evolution at 652 nm over time by
different catalysts: (a) 30 nm Au NPs, (b) Au@Ag NPs, (c)
Au@Ag@void@ICPs NPs, (d) Ag-DMCT ICPs, (e) Au@Ag NPs +
H₄AuCl₆, and (f) 3D nano-assemblies. The inset shows the
colour change of different samples. (B) Time-dependent UV-vis
spectra and photographs of MB solution catalyzed by 3D nano-
assemblies: (a) 0 min, (b) 1 min, (c) 3 min, (d) 6 min, (e) 10 min,
(f) 20 min, and (g) 40 min.

sets of experiments were conducted: the first one was carried out
in the presence of O₂; the other was performed under high-purity
nitrogen (N₂) and the solution was degassed before the reaction.
It is found that the reaction rate of TMB oxidation hardly
changed after saturation with N₂ (Fig. S11). This indicated that the
oxidized O₂ had no effect on the reaction, which was
different from the behaviour of some NPs-based oxidase mimics
reported. 31-32 Hence, it can be inferred that the adsorbed O₂ on
the surface of 3D nano-assemblies oxidized TMB in this system.

Besides, we investigated the electro-catalytic behaviour of a 3D
nano-assemblies modified glassy carbon electrode (GCE) toward
the electrochemical oxidation of TMB using cyclic voltammetry
(CV). The CVs of TMB at a bare GCE and the 3D
nano-assemblies-modified GCE are shown in Fig. S12. It is found that
the redox peak current of TMB increased obviously under the 3D
nano-assemblies-modified GCE, which is consistent with some
mimetic enzyme related references. 24,29 To explore the reasons
for the highly catalytic activity of 3D nano-assemblies, a series of
control experiments were conducted (Fig. 4A). It can be seen that
in our system, 30 nm Au NPs, Au@Ag NPs, Au@Ag@void@ICPs, and pure Ag-DMCT ICPs all hardly have
catalytic activity toward the oxidation of TMB. And, when some
volume of H₄AuCl₆ was introduced into the Au@Ag NPs solution
to produce small gold NPs, the products weakly catalyze the
oxidation of TMB and a light blue solution can be obtained.
However, when the 3D nano-assemblies used instead, obvious
catalysis appeared. The above results indicate that the highly
catalytic activity of 3D nano-assemblies is due to the synergistic
effect between small Au NPs and DMct-Ag ICPs rather than
small Au NPs only. In this process, much more TMB is absorbed
on the surface of the 3D nano-assemblies, due to the highly
porosity of ICPs, which results in an increase of the local
concentration of reactants in the nano-assemblies. Besides, it is
well known that DMCT is one of the most promising organosulfur
compounds as a cathode active material and the conductivity of
poly [di (2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes will
increase as temperature goes up. 33 Combined with the mechanism
described as above, the DMct-Ag ICPs here may have the ability
to accelerate the electron transfer from 3D nano-assemblies to
absorbed O₂, thus increasing the reaction rate of TMB oxidation.

Next, the oxidase-like catalytic property of the 3D nano-
assemblies was further investigated at various pH values using
steady-state kinetics and typical Michaelis-Menten curves were
obtained (Fig. S13). Results show that as the solution’s pH value
increases, larger values for the Michaelis constant (K_m) and lower
values for the reaction rate (V_{max}) are obtained (Table S2).
Specifically, the K_m of 3D nano-assemblies with TMB as the
substrate is as low as 4.31 µM at pH 4.0, which is about one or
two hundred times lower than HRP, Fe₃O₄ MNPs (magnetic
nanoparticles) and CeO₂ (Table S3), suggesting that the 3D nano-
assemblies have a higher affinity for TMB than others.

Organic dyes, as common pollutants from wastewater, were
one of the most detected targets in water analysis. Currently, the
common approaches to degrade dyes (such as MB) are usually
based on nanocatalysts with the aid of NaBH₄ or H₂O₂ or UV
irradiation and so on. Although much progress has been made,
some drawbacks need to be improved for the above methods:
NaBH₄ is easy to absorb water from the air and then deteriorates;
H₂O₂ decomposes upon prolonged storage and losses its ability;
UV irradiation needs harsh experimental conditions like light
intensity, reactor geometry, etc. As a result, more stable and
convenient methods are needed for the degradation of dyes.
Based on the excellent catalytic activity of 3D nano-assemblies to
the oxidation of TMB, they were further tested for MB
degradation without the presence of H₂O₂. MB aqueous solution
has maximum UV-vis absorption (A_max) at 663 and 614 nm. The
catalytic degradation process of MB can be monitored by the
decrease of A_max intensity. Fig. 4B shows a typical evolution
process of the UV-vis spectra of MB during the catalytic
degradation with the 3D nano-assemblies. It can be observed that
a sharp decrease in absorption with an obvious concomitant
wavelength shift of the band to shorter wavelengths happened
within 40 min, indicating that the oxidative degradation catalyzed
by the 3D nano-assemblies is superior to the reported
photocatalytic degradation without adding any cosubstrate. 35

Meantime, in this process, the solution’s colour changes from sky
blue to light blue, and then light purple, and finally almost
colourless. Noted that these phenomena are very similar to the
report by Zhang et al. 38 in which they found that N-
demethylation of MB happened before its complete degradation.
In addition, some control experiments were also conducted. It is
found that only a small amount of MB molecules were degraded
even after 40 min in the presence of pure Au NPs, Au@Ag NPs,
Au@Ag@void@ICPs NPs, or in the absence of any catalyst (Fig.
S14). Meanwhile, we also did the degradation of MB with 3D
nano-assemblies at room temperature (Fig. S15). It is found that a
small portion of MB molecules cannot be degraded even after 40
min, which indicated that the temperature (80°C) is very
significant for the degradation of MB. On the other hand, we
compared the oxidase-like activity of the 3D nano-assemblies at
room temperature and 80°C (Fig. S16). It is found that no
obvious decrease happened, which indicated that the 3D nano-
assemblies show excellent thermal stability. The above results
indicate that the 3D nano-assemblies also delivered highly
catalytic activity for the catalytic oxidation of MB even in the
absence of additional cosubstrates.

Conclusions

In summary, we present a very simple and controllable method
to prepare novel noble metal nanoparticles (NPs)-infinite
coordination polymers (ICPs) 3D nano-assemblies. These 3D
nano-assemblies are found to possess specific oxidase-like
activity and could catalyze the oxidation of TMB to produce the
typical colour reaction by the O₂ absorbed on the surface of the
3D nano-assemblies rather than H₂O₂. In addition, due to the
synergistic effect between DMCt-Ag ICPs and highly dispersed small gold NPs, the obtained 3D nano-assemblies have excellent catalytic performance with regard to the degradation of MB.

Notes and references

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2 Electronic Supplementary Information (ESI) available: Experimental details, characterization data of UV-vis, XPS, TEM and SEM, evaluation of the oxidase-like activity, studies on possible mechanism of the catalytic oxidation of TMB by cyclic voltammetry and control experiments on the degradation of MB. See DOI: 10.1039/b000000x/
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