Biomimetic Catalysis

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Graphene supported hemin as a highly active biomimetic catalyst

*Teng Xue, Shan Jiang, Yongquan Qu, Qiao Su, Rui Cheng, Sergey Dubin, Chin-Yi Chiu, Richard Kaner, Yu Huang and Xiangfeng Duan**

Experimental Section

Synthesis of hemin-graphene conjugates.

Graphene oxide was synthesized by Hummer's method and reduced to graphene by hydrazine. The obtained graphene was dried and re-dispersed in 1.5 mM hemin methanol solution. The solution was stirred mildly for 2 hours to allow conjugation between hemin and graphene. The hemin-graphene was then centrifuged. The amount of hemin in the supernatant was measured. The hemin absorbed on graphene was quantified by subtraction of the amount of hemin left in the supernatant of the origin solution. Hemin-graphene conjugates were washed several times with methanol and then re-dispersed in pH 7.4 Tris buffer.

Morphology measurement of hemin-graphene conjugates.

Graphene was absorbed onto Si/SiO2 substrate from aqueous solution, washed by isopropanol and dried. The thickness was measured by AFM via tapping mode. The same samples were then immersed in hemin methanol solution for hemin absorption. The obtained samples were washed by methanol and isopropanol and dried by nitrogen blow. The thickness was measured at the exactly same location by AFM via tapping mode. Control studies were done following the same procedures but by immersing samples in pure methanol without hemin. To investigate whether silicon oxide (or quartz) substrate itself would absorb hemin, quartz substrate was directly immersed in hemin/methanol solution to absorbed hemin. UV-vis absorption spectrum was then used to determine that there is negligible amount of hemin absorption on quartz. In a parallel experiment, Quartz substrate was first immersed in graphene solution, dried and characterized using UV-vis absorption to determine the absorption of graphene on quartz substrate. The absorbed graphene substrate was then immersed in hemin/methanol solution and characterized by UV-vis absorption (Supporting Fig. 1), which indicate there are hemin absorbed on graphene. These studies demonstrate that hemin can be effectively absorbed on graphene but not on silicon oxide substrate, and

therefore confirming the height increase observed in AFM studies is indeed due to the absorption of hemin on graphene.

Synthesis of FeTMPyP-graphene conjugates.

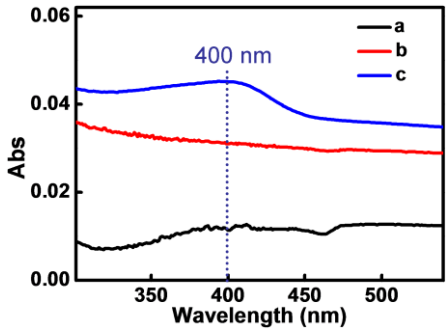
FeTMPyP was synthesized via methods described by Yamaguchi, H. et.al.[1] The obtained FeTMPyP was mixed with graphene in aqueous solution and stirred for two hours for the conjugation of FeTMPyP-graphene.

Pyrogallol oxidation kinetic studies.

The kinetic studies of pyrogallol oxidation were carried out in pH 7.4 Tirs buffer. The concentrations of pyrogallol vary from 0.1 mM to 2 mM with a fixed amount of hemin-graphene catalyst (5 μM hemin equivalent) and a hydrogen peroxide concentration of 40 mM. The oxidation product was confirmed using UI-vis spectroscopy. For kinetic studies, all the reactions were monitored in kinetic mode at 420 nm by DU800 UV-vis spectrometer. The apparent kinetic parameters were calculated based on the function $v=V_{max}\times[S]/(K_M+[S])$, where v is the initial velocity, Vmax is the maximal reaction velocity, [S] is the concentration of the substrate and KM is the Michaelis constant.

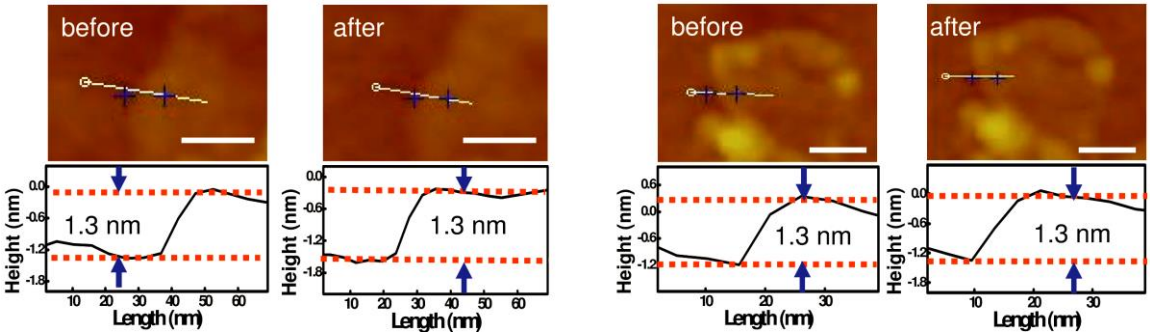
Supporting Figures

1. UV-vis inspection of hemin on substrate.



Supporting Figure 1. UV-vis inspection of hemin on substrate. (a) Hemin absorbed directly on quartz substrate. No obvious Soret band was observed, suggesting little hemin was absorbed on substrate. (b) Graphene absorbed on quartz substrate. (c) Hemin absorbed on quartz substrate with pre-absorbed graphene. Hemin Soret band can be clearly seen at 400 nm, demonstrating the effective absorption of hemin on graphene.

2. AFM morphology of hemin before and after immersed in methanol.



Supporting Figure 2. AFM morphology of hemin before and after immersed in methanol. The thickness doesn't change. The scale bars are 50nm.

Reference:

[1] H. Yamaguchi, K. Tsubouchi, K. Kawaguchi, E. Horita, A. Harada, *Chemistry-a European Journal* **2004**, *10*, 6179-6186