Electronic Supplementary Material (ESI) for RSC Advances


# Functional noble metal nanostructures involving pyrene-conjugated-hyaluronan stabilised reduced graphene oxide

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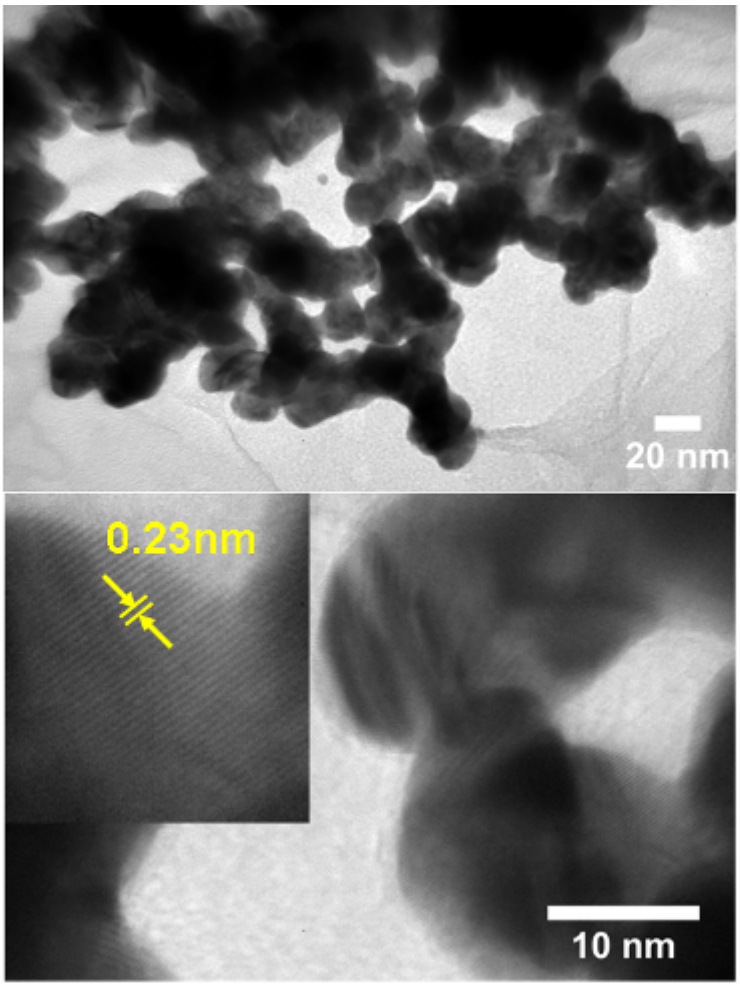


Figure S1: (A) TEM and (B) HRTEM images of Au2-Py-HA-RGO.

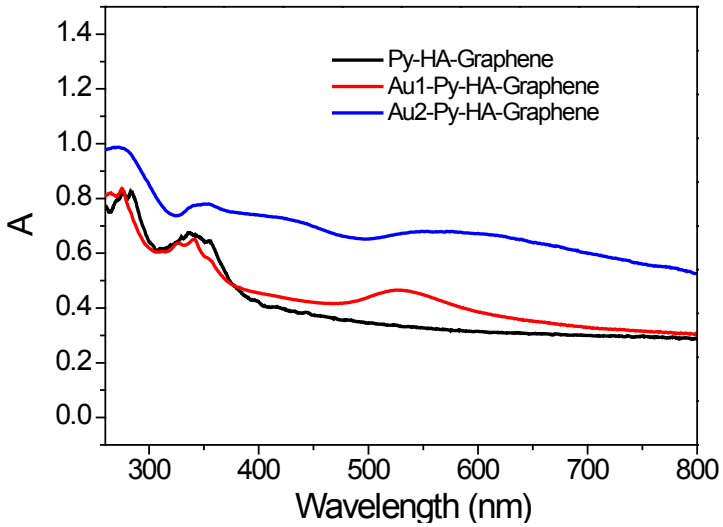


Figure S2: UV-Vis spectra for Py-HA-RGO, Au1-Py-HA-RGO, and Au2-Py-HA-RGO.

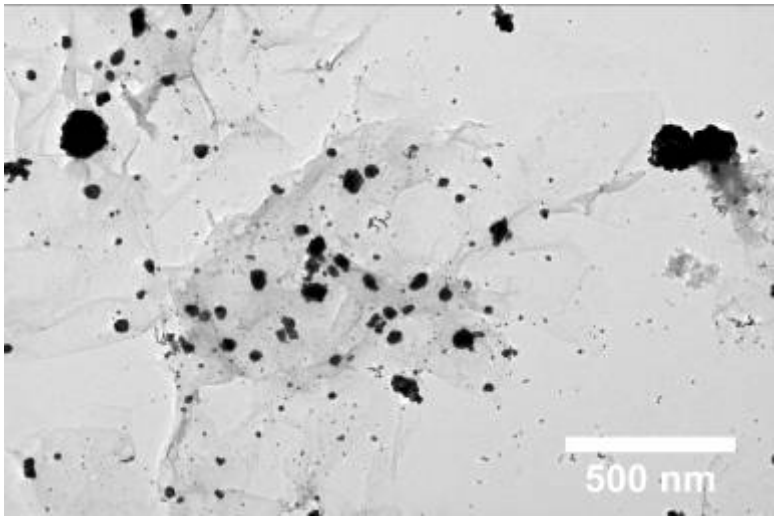


Figure S3: TEM image of the product after UV irradiation of a mixture of RGO and $HAuCl_4$ (0.02 mM) at pH 12 for 2 hours (wavelength 255 nm).

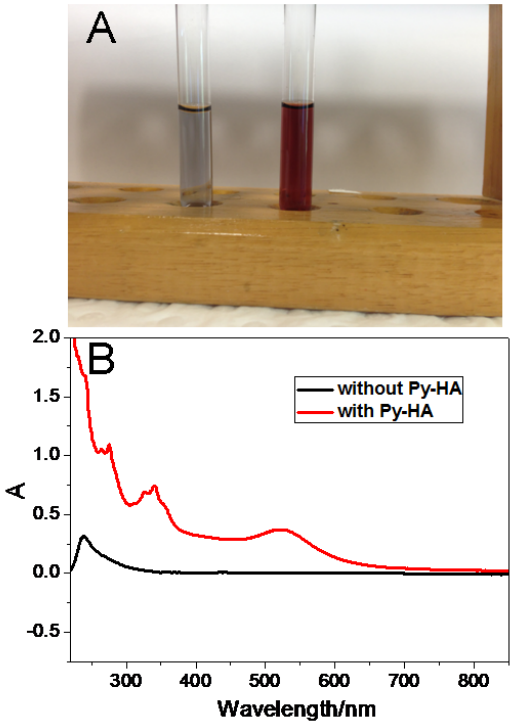


Figure S4: Samples (A) and UV-Vis spectra (B) of 0.02 mM $HAuCl_4$ solution at pH 12 in the presence or absence of Py-HA (1 mg/mL) after UV irradiation (right sample) for 2 hours (wavelength 255 nm).

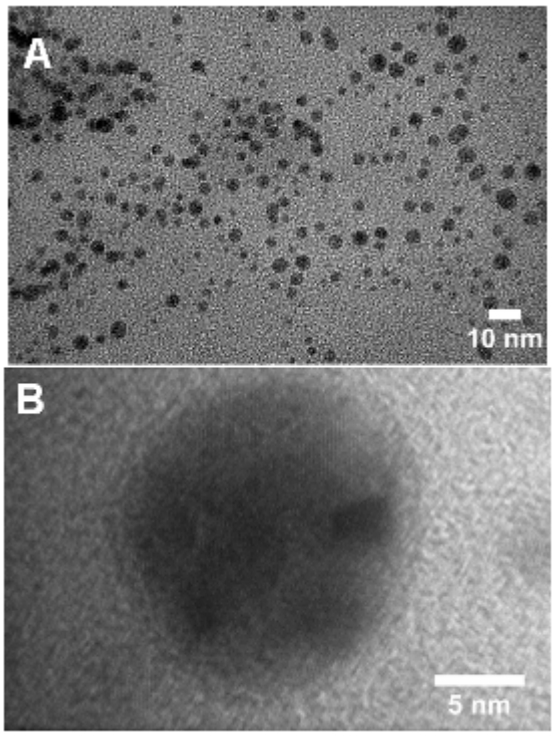


Figure S5: TEM images of the product formed using 0.02 mM $HAuCl_4$ solution at pH 12 in the presence of Py-HA (1 mg/mL) after UV irradiation for 2 hours (wavelength

255 nm).

The experiments were as follows. $HAuCl_4$ was added to the solution with or without Py-HA. The pH of the solutions (0.02 mM $HAuCl_4$ with or without 1 mg/mL Py-H) were adjusted to pH 12, and then irradiated by UV light with the wavelength at 255 nm for 2 hour. The final solutions are shown in Figure S4. The solution with Py-HA changed from colourless to pink, indicating the formation of gold nanoparticles. The solution without Py-HA became slightly darkened, which may due to small amounts of large gold particles reduced from $HAuCl_4$ under UV irradiation. In addition, the UV-Vis spectra of these solutions show dramatically different features, beyond the characteristic absorption band at around 520 nm for surface plasmon vibration for gold nanoparticles.[1] The absorption from 250 to 400 nm is attributed to the pyrene moiety of Py-HA. Without Py-HA, there was only one band at ca. 240 nm, reflecting the absorption of $Au^{3+}$ species.[2] Figure S5 shows the gold nanoparticles < 10 nm obtained from 0.02 mM HAuCl4 solution at pH 12 in the presence of Py-HA (1 mg/mL) after UV irradiation (wavelength 255 nm) for 2 hours. The shape and size of the nanoparticles is consistent with that of Au1-Py-HA-RGO. The results show the role of Py-HA in promoting the photoreduction of the Au(III) precursor, and stabilizing the resulting Au nanoparticles, as for earlier reports on the utility of HA itself.[1, 2]

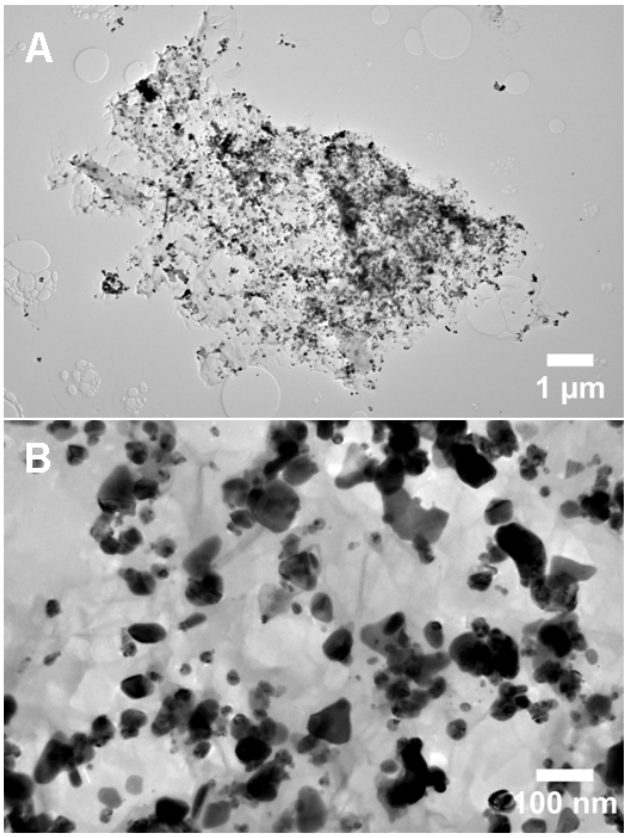


Figure S6: TEM images of Py-HA-RGO sheet decorated with Ag nanostructure (A and B)

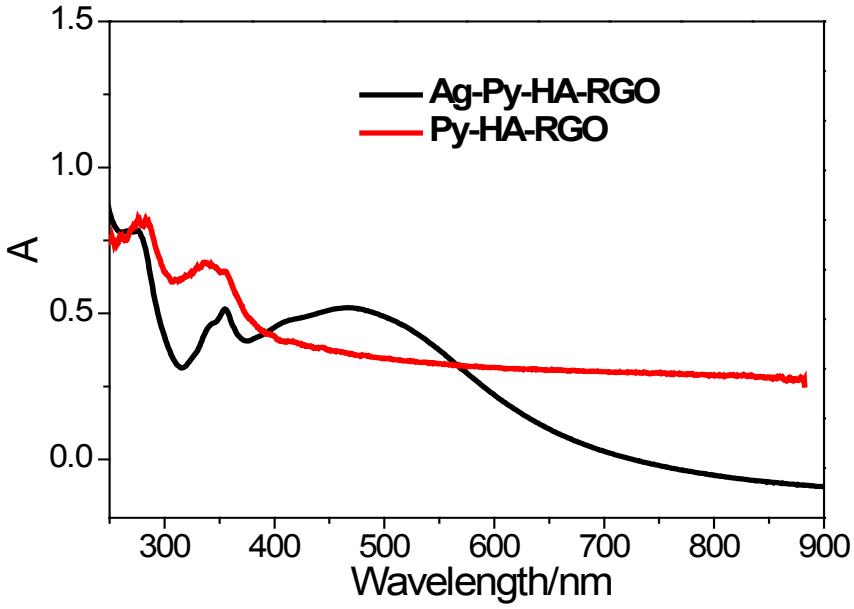

Figure S7: UV-Vis spectra for Py-HA-RGO decorated with Ag nanostructures.



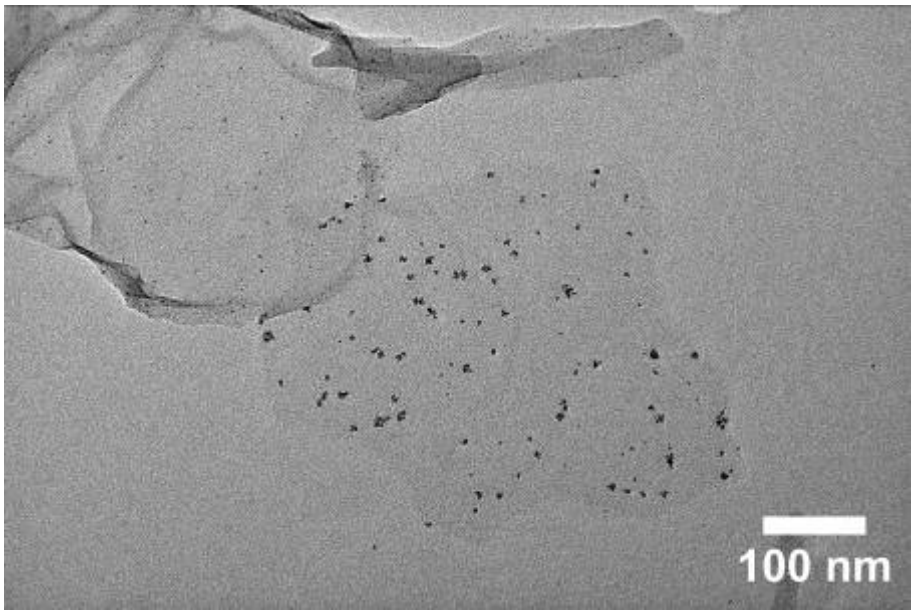


Figure S8: TEM image of the composite material formed after bubbling hydrogen gas through a mixture of RGO and $H_2PdCl_4$ (0.2 mM) for 20 minutes.

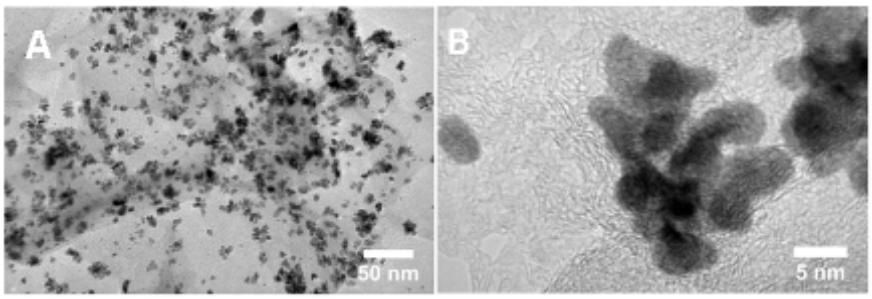


Figure S9: TEM images of Py-HA-RGO sheets decorated with Pt nanostructures.

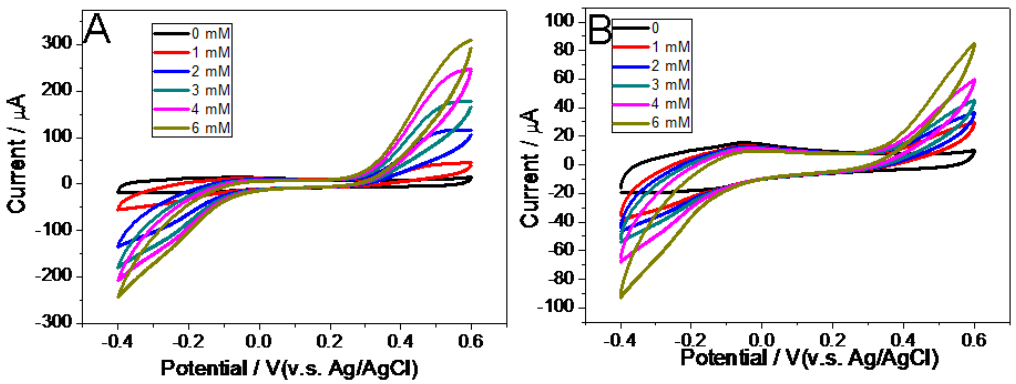


Figure S10: Cyclic voltammograms of the as-prepared Au1-Py-HA-RGO (A) and Au2-Py-HA-RGO (B)-modified GCEs in $N_2$-saturated 0.1 M PBS (pH 7.0) with different concentrations (0, 1, 2, 3, 4, 6) mM of $H_2O_2$. Scan rate: 50 mV/s.

S9 Linear regression equations of modified GCEs for amperometric response for $H_2O_2$

**Rang from 0.5 to 50 μM for $H_2O_2$ concentration**

Au1-Py-RGO/GCE:

$I(\mu A)=0.12\,C_{H_2O_2}(\mu m)+0.2$ (Correlation coefficient: 0.998)

Au2-Py-RGO/GCE:

$I(\mu A)=0.072\,C_{H_2O_2}(\mu m)+0.24$ (Correlation coefficient: 0.998)

**Rang from 50 to 50000 μM for $H_2O_2$ concentration**

Au1-Py-RGO/GCE:

$I(\mu A)=0.038\,C_{H_2O_2}(\mu m)+4.49$ (Correlation coefficient: 0.997)

Au2-Py-RGO/GCE:

$I(\mu A)=0.0078\,C_{H_2O_2}(\mu m)+3.27$ (Correlation coefficient: 0.998)

## S10 Comparison of the performance of the prototype $H_2O_2$ biosensor.

Table S1 Comparison of the performance of the prototype $H_2O_2$ biosensor relative to those of other enzymatic and non-enzymatic biosensors

| Electrode | Respond time(s) | Linear range(μM) | Stability[a] | Reference |
|---|---|---|---|---|
| Hb/Graphene-Chitosan Film/GCE | Within 5 | 6.5-230 | 80.1% for 14 days | 3 |
| Mb/GNs-Nafion/ GCE | Within 5 | 1.5-90 | 93% for 50 days | 4 |
| HRP/Polyion Cmplex Membrane /GCE | Within 15 | 0.5-10 | 80% for 30 days | 5 |
| Hb/Titania Sol–gel Film/GCE | Within 5 | 0.5-54 | 89% for 80 days | 6 |
| GNs/silicon Sol-gel/GCE | Within 5 | 2.5-45 | Stable for one week | 7 |
| GNs/GO/GCE | Within 6 | 0.5-50 | NA | 8 |
| Au1-Py-HA-RGO/GCE | Within 4 | 0.5-5000 | 95% for 30 days | This paper |

GNs: Gold nanoparticles; Mb: myoglobin; GO: graphene oxide; Hb: Hemoglobin; HRP: horseradish peroxidase

a: Stability defined as the percent of retaining the initial current response of the biosensor stored in PBS at 4℃for some days.

## References

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