

Supplementary Information *for*

Au Nanoparticles-Loaded PDMAEMA Brushes Grafted Graphene Oxide Hybrid Systems for Thermally Smart Catalysis

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For example, the peaks at 3444 cm⁻¹ (–OH), 1735 cm⁻¹ (C=O), 1098 cm⁻¹ (C–O) can be found in pure GO. In the spectrum of neat PDMAEMA, an intense increase of the absorption peak appears at 1730 cm⁻¹ corresponding to the stretching vibration of ester carbonyl group in the PDMAEMA. By comparing the FTIR spectra of GO and pure PDMAEMA in **Fig. S1**, in the spectrum of GO@PDMAEMA, the peaks at 2772cm⁻¹ and 2948cm⁻¹ (C–H), and stronger peak at 1730cm⁻¹ (C=O) and 1152cm⁻¹ (C–N) can be detected. These peaks are the characteristic absorptions of PDMAEMA chains.

As seen in **Fig. S1**, the spectrum of GO@PDMAEMA/Au was similar to that of the GO@PDMAEMA. The obvious difference between the two IR spectra was the disappearance of the peak at 2772 cm⁻¹, which was in assignment of C-H stretching vibrations of the N-CH₃ groups of PDMAEMA brushes. Moreover, this disappeared absorption further implied that the N-CH₃ group was reduced to quaternary amine salts or other coordination compounds. Therefore, the end tertiary amine groups of PDMAEMA were thought to be the primary role in the reductive reaction between PDMAEMA and HAuCl₄.

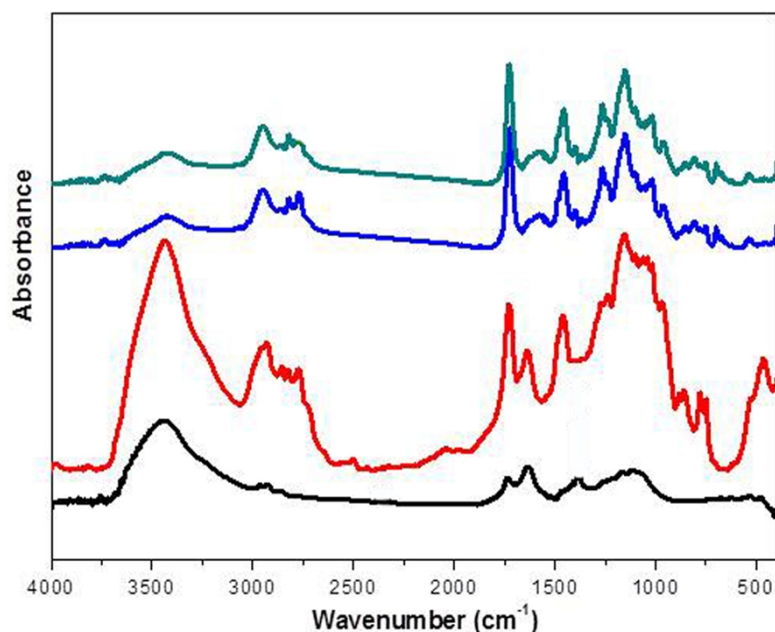


Fig. S1 FT-IR spectra of (black) GO, (red) pure PDMAEMA, (blue) GO@PDMAEMA and (green) GO@PDMAEMA/Au.

Dynamic light scattering (DLS) results indicated the thermosensitivity of the prepared GO@PDMAEMA. It was shown that the average size (around 2.0 μm) due to remarkable aggregation was firstly obtained below 30 $^{\circ}\text{C}$, but that the size decreases to 400 nm near 42 $^{\circ}\text{C}$. The decrease of composites size can be ascribed to the collapse of PDMAEMA upon its LCST.

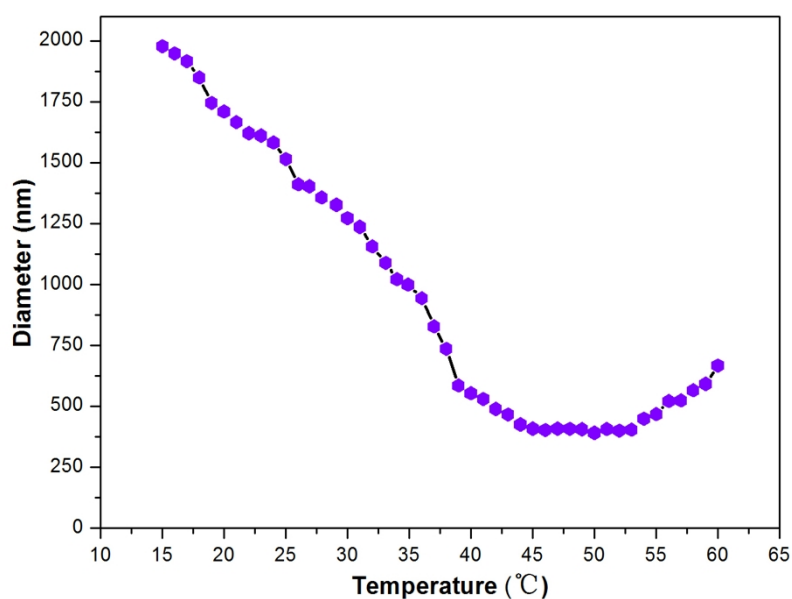


Fig. S2 Variation in particle size as a function of temperature value for GO@PDMAEMA.

These two distinct weight loss stages of GO@PDMAEMA and GO@PDMAEMA/Au between 200 and 500 °C are very similar, as shown in **Fig. S3**, which illustrates that GO@PDMAEMA/Au hybrid system remained high thermostability.

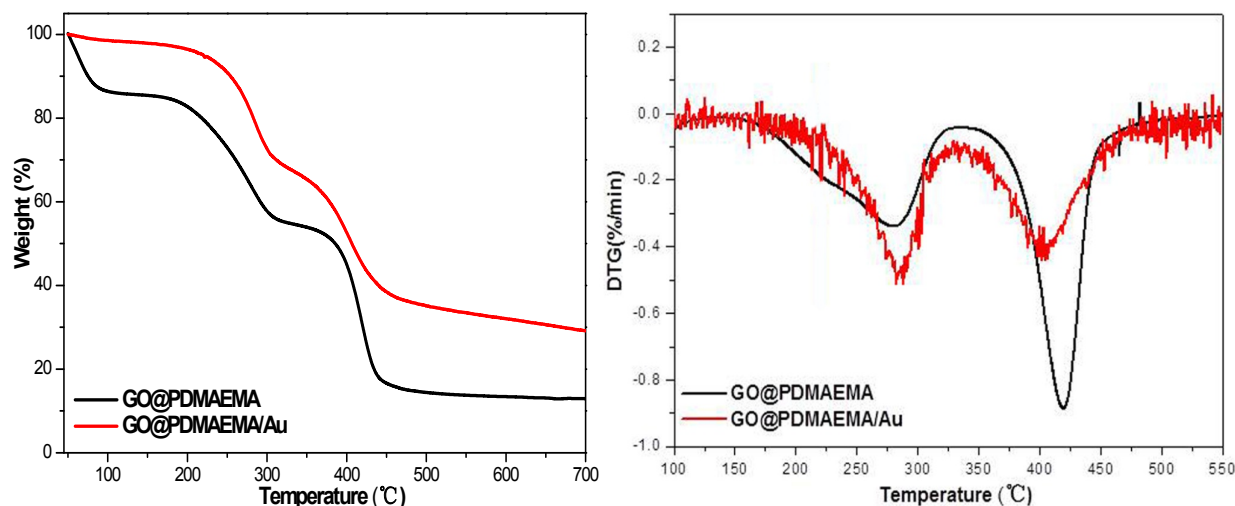


Fig. S3 TGA and DTG spectra of GO@PDMAEMA and GO@PDMAEMA/Au.

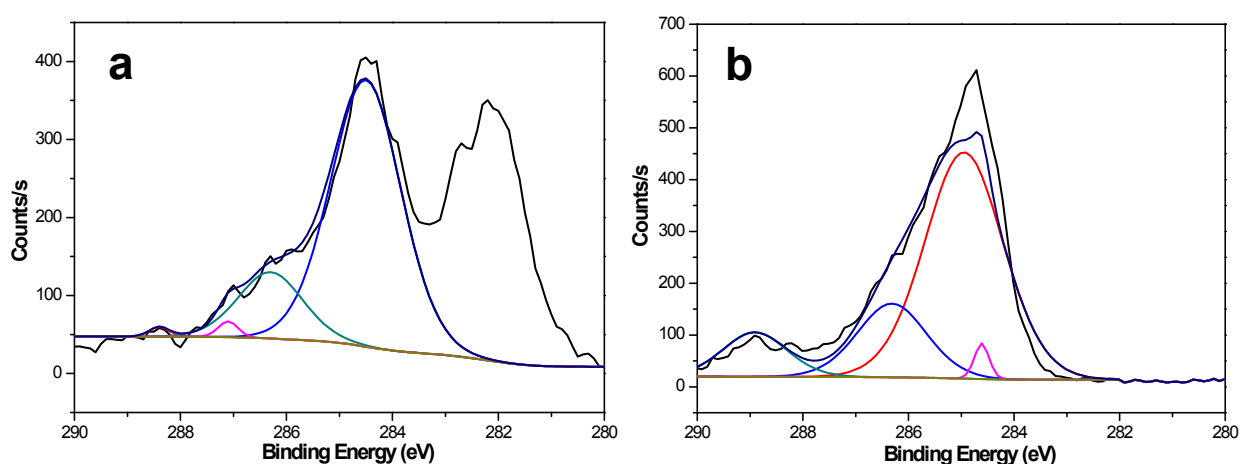


Fig. S4 C1s XPS spectra of (a) GO and (b) GO@PDMAEMA nanocomposite.

The details of loading the gold NPs were as following: 50mg of GO@PDMAEMA were first dispersed in 10 mL of deionized water and then 0.25 mL of 8 mM or 2 mM HAuCl_4 aqueous solution was added. The reaction lasted for 1 h after adding 1 mL of 0.05 M NaBH_4 aqueous solution dropwise under the ice water bath with shaking. The final product was purified through washing with water three times and dried under vacuum oven until constant weight. **Fig. S5** displayed the TEM images of the synthesized GO@PDMAEMA/Au nanocomposites. In **Fig. S5 (a)**, it can be seen that

the GO@PDMAEMA surface was decorated with a few Au nanoparticles with irregular distributions. As the Au^{3+} concentration increased from 2 mM to 8 mM, we can also identify some relatively large Au particles with obvious aggregation on the GO@PDMAEMA surface. The particle sizes of the aggregated Au particles are larger than 100 nm as shown in **Fig. S5 (b)**. So we can conclude that the optimal concentration of Au^{3+} is 4mM, just used in our hybrid system.

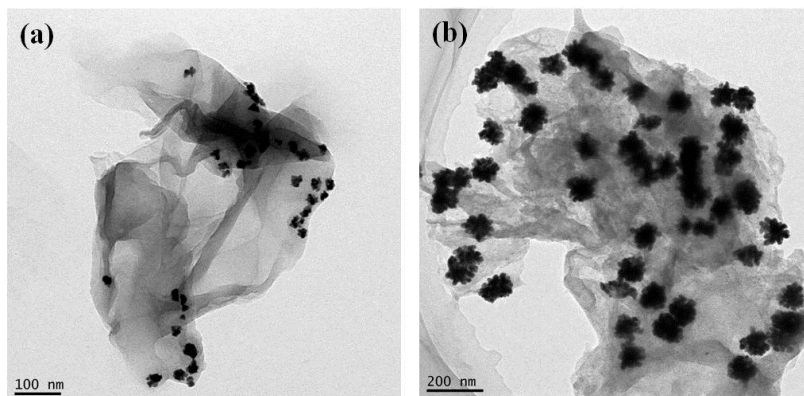


Fig. S5 TEM images of Au NPs in GO@PDMAEMA/Au nanocomposites prepared with (a) 2 mM Au^{3+} and (b) 8 mM Au^{3+} .

In the UV-Vis absorption spectrum (**Fig. S6**), the red line was the characteristic peak of the GO in the PDMAEMA. After formation of GO@PDMAEMA through the SIPGP, the peak of GO@PDMAEMA (black line) was observed at 260 nm. The red shifts from 230 to 260 nm suggests that the electronic conjugation within GO sheets has been restored after the SIPGP. The absorption peaks for GO@PDMAEMA/Au (blue line) appeared separately at 260 nm and 522 nm. The peak at 522 nm corresponded to the surface plasmon band of gold NPs in the GO@PDMAEMA.

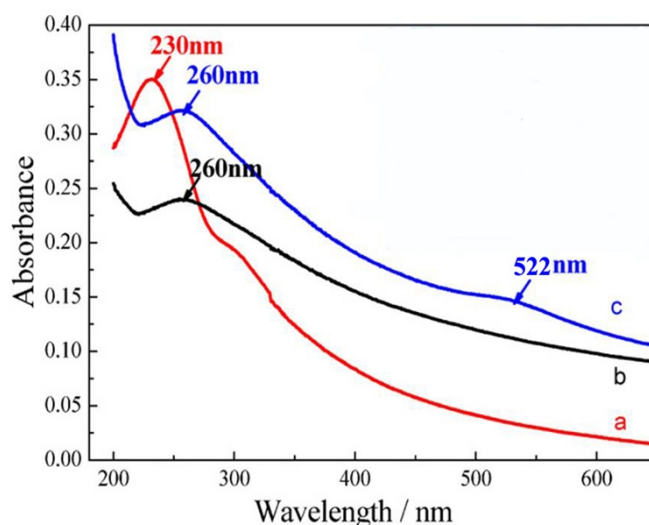


Fig. S6 UV-vis spectra for aqueous dispersions of (a) GO, (b) GO@PDMAEMA and (c) GO@PDMAEMA/Au .

For example, UV/Vis detection of the reduction process (**Fig.S7**) clearly showed that the peak at 400 nm, which is due to the 4-nitrophenolate ions, decreases gradually with reaction time, and a new peak appears at 300 nm, which results from product of 4-aminophenol. Here, the generation of 4-nitrophenolate ions takes place immediately after addition of BH_4^- to the system. The difference in the absorption length between 4-NP and 4-AP can be ascribed to their functional groups such as $-\text{NO}_2$ and $-\text{NH}_2$ corresponding to electron acceptor and donor, respectively. Meanwhile, we found that GO@PDMAEMA/Au catalyst took 12min to finish the catalytic reaction at 35°C.

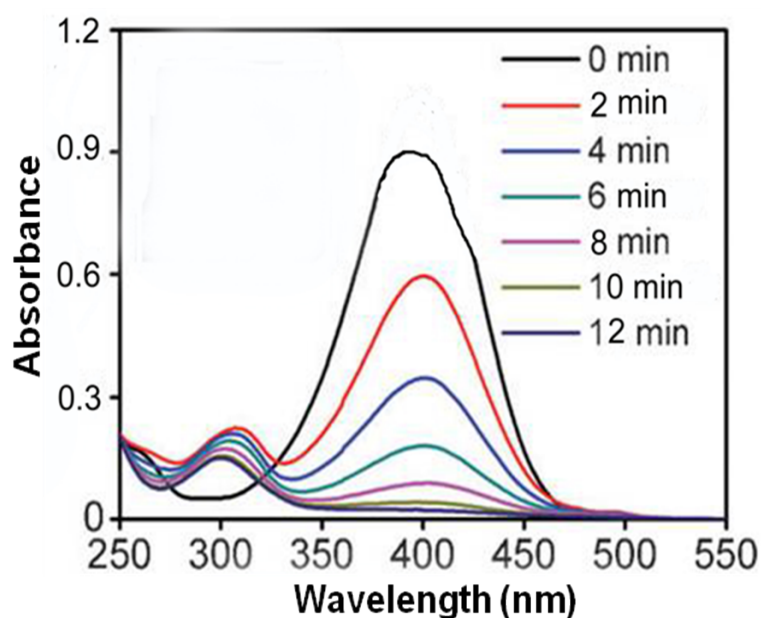


Fig. S7 UV-vis absorption spectra for the successive reduction of 4-NP in the presence of GO@PDMAEMA/Au at 35°C with different time.

Fig. S8 shows A_t/A_0 versus reaction time, where A_t/A_0 was obtained from the relative intensity ratio of the absorbance (A_t/A_0) at 400 nm. The A_t/A_0 ratio hardly changed even after 20 min in the absence of catalyst, while the addition of a trace amount of GO@PDMAEMA/Au catalyst resulted in a high reaction rate, implying the high catalytic activity of the as-synthesized nanocatalyst.

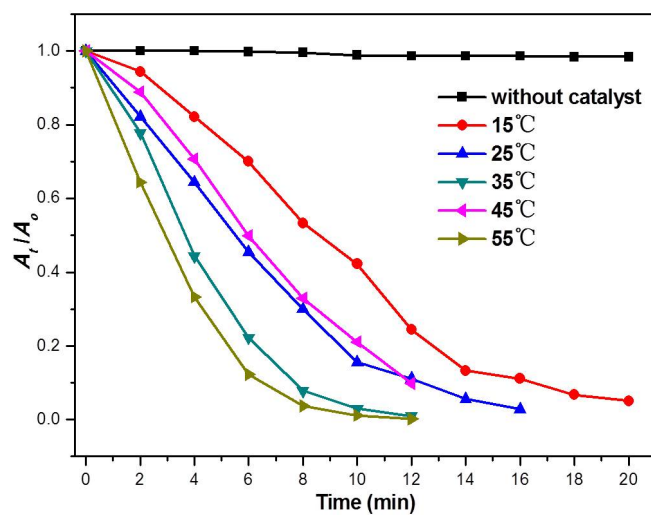


Fig. S8 A_t/A_0 versus reaction time for the reduction of 4-NP over no catalyst and GO@PDMAEMA/Au at different temperatures. A_0 and A_t are the absorption peak at 400 nm initially and at time t .