SUPPORTING INFORMATION

Patterning of Polyoxometalate Rings on Gold Nanorods

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Experimental section

Materials

Hexadecyltrimethylammonium bromide (CTAB, ≥99%), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.99%), sodium borohydride ($NaBH_4$, ≥98%), L-ascorbic acid (AA, ≥99.0%), silver nitrate (≥$AgNO_3$, 99.0%) were purchased from Sigma-Aldrich. Deionized water (18.2 MΩ) was used in all the experiments. Polyoxometalates: $H_3PW_{12}O_{40}$ (POM3) was purchased from Sigma-Aldrich, $K_6CoW_{12}O_{40}$ (POM6), $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ (POM12) and $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ (POM14) were synthesized according to the literature.[1-6]

Synthesis of gold nanorods

The gold nanorods (GNRs) were prepared by the seed-mediated growth method reported previously. Briefly, seed solution of gold NPs were prepared by mixing $HAuCl_4$ (0.12 mL, 15 mM) with CTAB (3.5 mL, 0.14 M) and a freshly prepared, ice-cold $NaBH_4$ solution (0.50 mL, 10 mM) at 25.5 °C. The mixture was stirred for 2 min. The seeds could be used within 0.5−2 h when stored in a 25 °C bath. To prepare the growth solution, $AgNO_3$ (0.40 mL, 4.0 mM) and $HAuCl_4$ (0.50 mL, 15 mM) were added to a 1.0 mM solution of CTAB (0.3645 g in 8.86 mL of deionized water) and stirred. Following the addition of ascorbic acid (0.124 mL 0.0788 M), the dark yellow solution turned colorless. Finally, 0.10 mL of the seed solution was added to the growth solution to initiate GNR growth. The mixture was then incubated at 27 °C for more than 12 h before use.

Re-growth of gold nanorods

The curvature of the GNRs was modulated by multi-times of re-growth process. In detail,

aqueous solutions of $AgNO_3$ (0.10 mL 4.0 mM), ascorbic acid (0.031 mL 0.788 M), and $HAuCl_4$ (0.125 mL 15 mM) were added to a 2.50 mL GNR solution. The resultant solution was incubated at 27 ℃ for about 2 h. Then 0.5 mL solution was taken out each time after regrowth, after that $AgNO_3$, ascorbic acid and $HAuCl_4$ solution were added again to support the growing process. The re-growth process was totally conducted for 9 times and GNRs re-growed for 1 time (R = 5.90 ± 0.90 nm), 3 times (R = 9.00 ± 1.92 nm), 6 times (R = 10.91 ± 1.52 nm) and 9 times (R = 14.53 ± 1.49 nm) were taken for the spectra and TEM samples preparation.

Assembly of POMs on GNRs

The GNRs were purified by centrifugation at 8500 rpm for 15 min to remove the free CTAB in the solution, the final CTAB concentration was 0.01 M. After that, 0.5 mL GNRs solution was dropwise added into 0.5 mL POM solution (0.005 M) (POM3, POM6, POM9, POM12 and POM14 with the same volume and concentration) under ultrasonic condition. The mixed solution was further ultrasonic for another half an hour, then left standing overnight to make GNRs and POMs interact completely. The GNR@POM assembly needs to be further purified by centrifugation (8500 rpm, 15 min) for two times, and redispersed in 1.0 mL DI water before making TEM samples because there were still free CTAB-POM composites in the solution.

Growth of silver around GNRs mediated by POM

2 mL of GNR@POM14 assembly solution (0.29 nM) with POM14 concentration of 8.8 μM was upon UV light irradiation (CEL-M500/350 Hg lamp) for 30 min using 150 μL of isopropanol as the sacrificial reagent. As the irradiation may raise the temperature of the solution, the solution was put in an ice cold water bath to keep it cold and stable. After the photochemical reaction, 200 μL aqueous solution of $AgNO_3$ (0.4 mM) was added to the solution of GNR@POM solution, the mixture was stirred for 2 min and then stayed overnight. The $AgNO_3$ was then reduced to Ag particles which were attracted on the surface of GNRs through the adsorption of POMs.

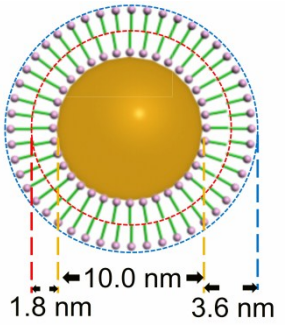
Characterization

TEM imaging was performed with a JEOL JEM-2100F transmission electron microscope and a Hitachi H-800 transmission electron microscope operating at 200 kV and 175 kV, respectively, on carbon-coated TEM grids. High-angle annular dark-field TEM (HAADF-TEM), and energy-dispersive X-ray spectrometer (EDS) were also performed with the JEOL JEM-2100F transmission electron microscope. Extinction spectra were measured with a PerkinElmer Lambda 950 UV−vis−NIR spectrometer with a data interval of 1 nm using 1 cm quartz cell. Fourier transform

infrared (IR) spectral measurement on pressed KBr pellets was performed on a Bruker IFS66v FT-IR spectrometer equipped with a DGTS detector (32 scans) with a resolution of 4 cm^{-1}.

Dynamic light scattering (DLS) measurement was performed by using a Zeta Sizer instrument (Nano ZS, Malvern Instruments Ltd., Malvern, UK) at 25℃.

Calculation of the CTAB distribution along the transverse axis of GNR



For a single GNR with the diameter D = 10.0 nm, that is, with the radius R =5.0 nm; and CTAB bilayer t = 3.6 nm, CTAB single layer r = 1.8 nm, the distribution (we use the area to present it here) of the out-layer (S_2) and the inner-layer (S_1) is calculated as below:

$S_1 = \pi (R + r)^2 - \pi R^2 = 21.24\pi$

$S_2 = \pi (R + t)^2 - \pi (R + r)^2 = 27.72\pi$

$\Delta S/S_1 = (S_2 - S_1)/S_1 = 0.305$

In this case, the volume (area) of the outer-layer is 30.5 % more than that of inner-layer.

Estimation of the number of POM14 per GNR in GNR@POM14 with the GNR radius of 4.5 ± 0.8 nm

According to TEM images in Fig. 1a and b, there were about 10 POM rings on the surface of the GNR distributed along the longitudinal direction of GNRs.

The perimeter *C* of the cross section of the GNR cylinder part is:

$C = 2\pi(R + t) = 50.9$ nm (where $R = 4.5$ nm is the radius of GNR, $t = 3.6$ nm is the thickness of CTAB bilayer)

If the POM14 in the ring were closely patterned around the GNRs, the number of POM14 per ring n_1 is about:

$n_1 = C/d = 50.9/1.8 = 28$ (where $d = 1.8$ nm is the diameter of POM14)

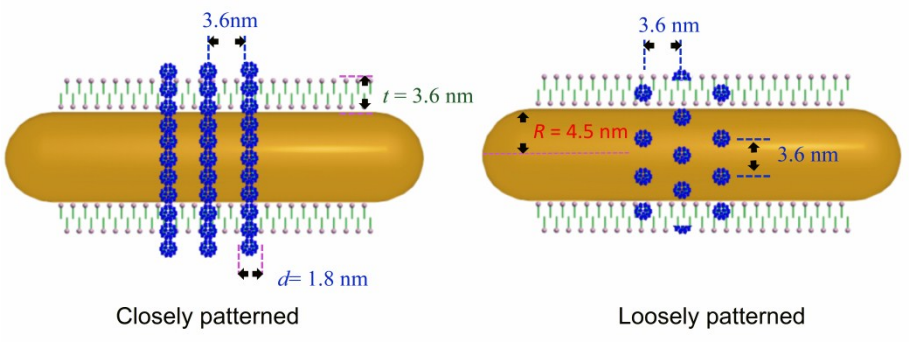
In this case, the number of POM14 per GNR is $N_1 = 10n_1 = 280$;

If the POMs in the ring were arranged with the same distance 3.6 nm in both direction, the number of POM14 per ring n_2 is about:

$n_2 = C/3.6 + 1 = 15$ (where 3.6 nm is the ring distance measured in Fig. 1a and b),

In this case, the number of POM14 per GNR is $N_2 = 10n_2 = 150$.

Therefore, there are around 150-280 POM14 per GNR in GNR@POM14 with the GNR radius of 4.5 ± 0.8 nm, estimated according to Fig. 1a and b.



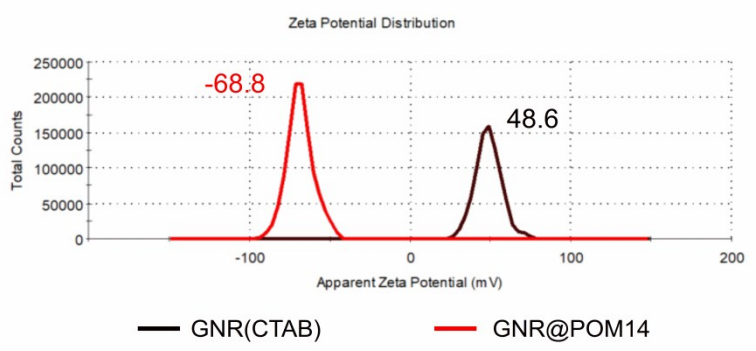


Fig. S1 Zeta potential spectra of GNR (CTAB) and GNR@POM.

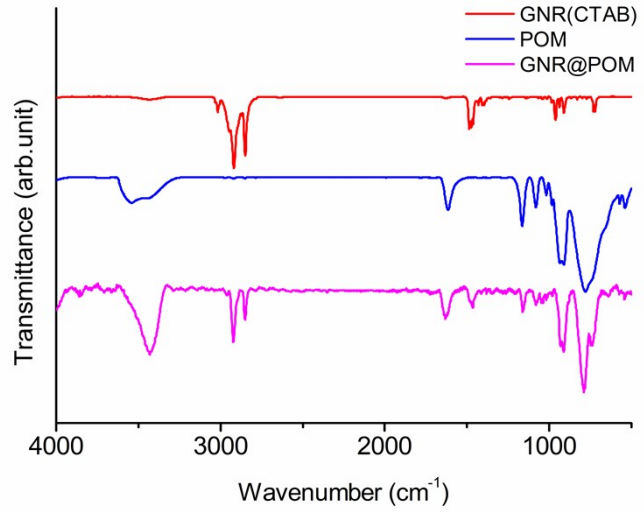


Fig. S2 IR spectra of pure POM, CTAB-capped GNR and GNR@POM assembly.

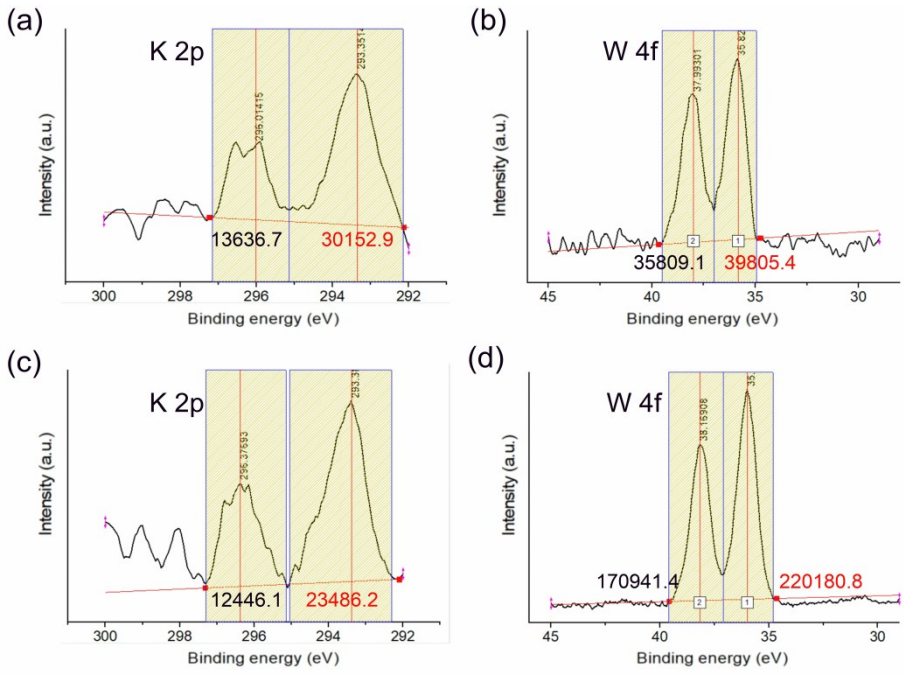


Fig. S3 XPS spectra and integral areas of K and W in pure POM14 and GNR@POM14 with the GNR radius of 4.5 ± 0.8 nm. (a) K and (b) W spectra in pure POM14, (c) K and (d) W spectra in GNR@POM14.

Calculation of the quantity of K^+ which have been removed upon grafting onto GNR in Fig. S3:

For pure POM14, the integral area of K, S_{K1} = 13636.7 + 30152.9 = 43789.6;

the integral area of W, S_{W1} = 35809.1 + 39805.4 = 75614.5.

For GNR@POM14, the integral area of K, S_{K2} = 12446.1 + 23486.2 = 35932.3;

the integral area of W, S_{W2} = 170941.4 + 220180.8 = 391122.2.

The relative sensitivity factors (ASF) of K 2p orbital, K_{ASF} = 1.466, and the ASF of W 4f orbital, W_{ASF} = 3.523.

In POM14, the ratio (R_1) of the amount of K to the amount of W is calculated as following:

$R_1 = S_{K1}/K_{ASF} : S_{W1}/W_{ASF} = 1.4$;

In GNR@POM14, the ratio (R_2) of the amount of K to the amount of W is calculated as following:

$R_2 = S_{K2}/K_{ASF} : S_{W2}/W_{ASF} = 0.2$;

Since the amount of W was not changed before and after interacting with GNR, the amount of K^+ removed (K^+_{re}) can be calculated as below:

$K^+_{re} = (R_1 - R_2)/R_1 = 85.7\%$.

Therefore, around 85.7% of K^+ have been removed upon grafting of POM14 onto GNR.

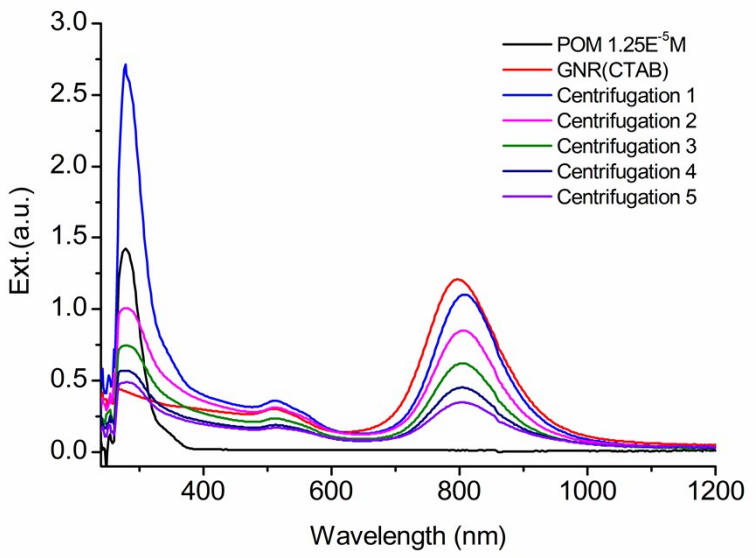


Fig. S4 UV-vis spectra of GNR, POM, and GNR@POM14 with the GNR radius of 4.5 ± 0.8 nm after different times of centrifugation. (The peak at 278 nm corresponds to the absorption peak of POM14, and the peak at 800 nm corresponds to the longitudinal localized surface plasmonic resonance of GNRs).

According to the spectra in Fig. S4, it can be seen that upon centrifugation for 2 to 5 times, the ratio of the peak intensities of POM14 and GNR remained almost the same, although the peak intensities of POM14 and GNR reduced owing to the loss caused by centrifugation. These results indicate the solution system reached the dynamic equilibrium upon centrifugation for 2 times. The POM14 concentration in GNR@POM14 upon centrifugation for 2 times is 8.8 μM according to Lambert-Beer Law (Fig. S4). The extinction coefficient of GNRs in our experiment is $3.0E^9$ $Lmol^{-1}cm^{-1}$ according to the literature by EI-Sayed,[7] and therefore the concentration of GNR is calculated to be 0.29 nM. Thus, the concentration of POMs was thirty thousand times of that of GNRs, when they were in the dynamic equilibrium, indicating that there were many free POM14 in the solution.

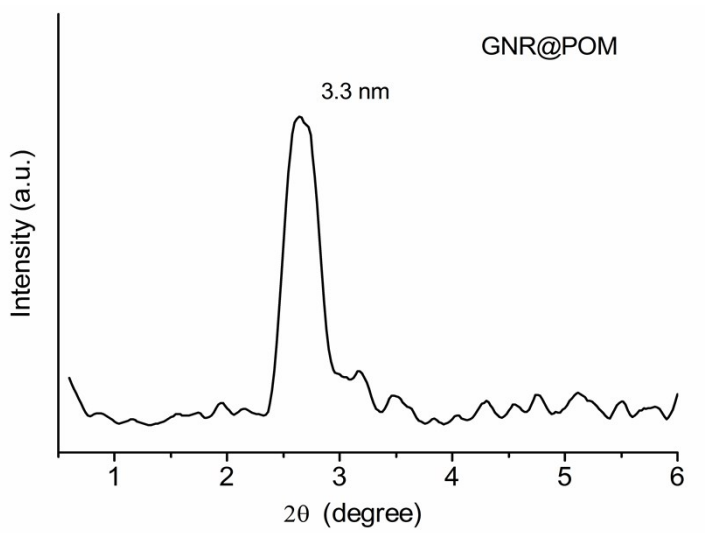


Fig. S5 XRD pattern of the GNR@POM14.

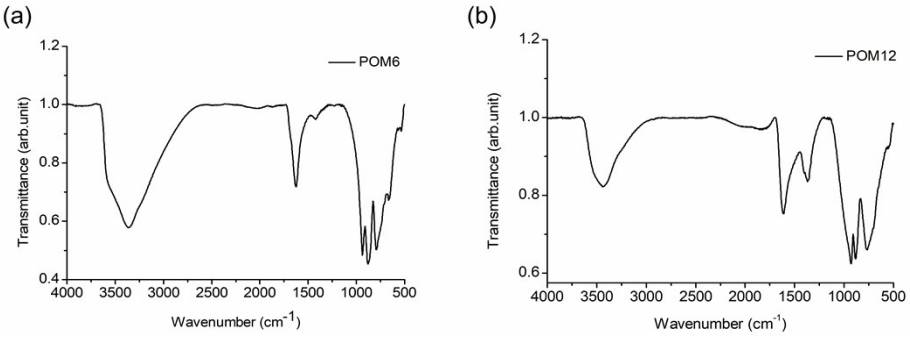


Fig. S6 IR spectra of (a) $K_6CoW_{12}O_{40}$ (POM6) and (b) $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ (POM12).

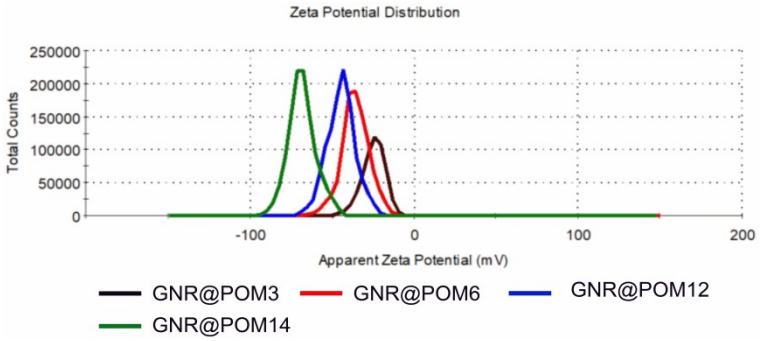


Fig. S7 Zeta potential spectra of GNRs assembled with POMs of different charges.

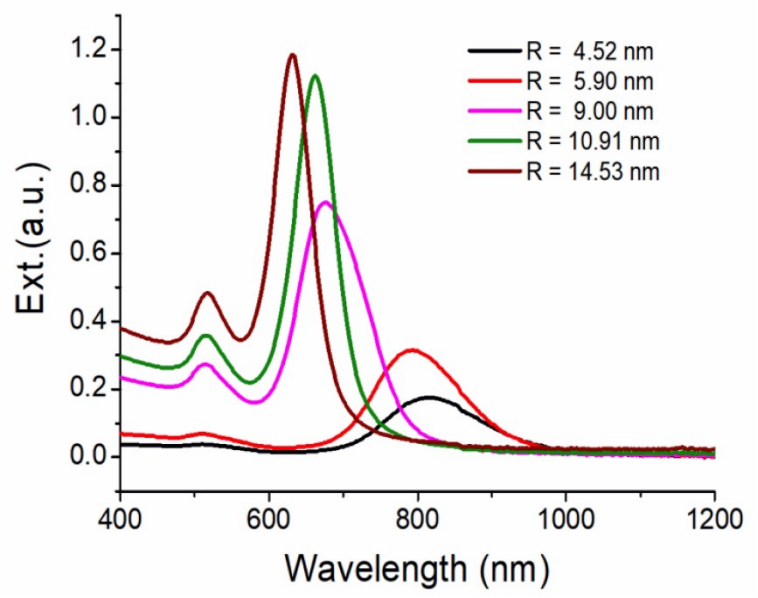


Fig. S8 UV spectra of CT AB capped GNRs with different radii. (R = 4.52 nm represents GNRs without re-growth, the others represent GNRs with different re-growth times).

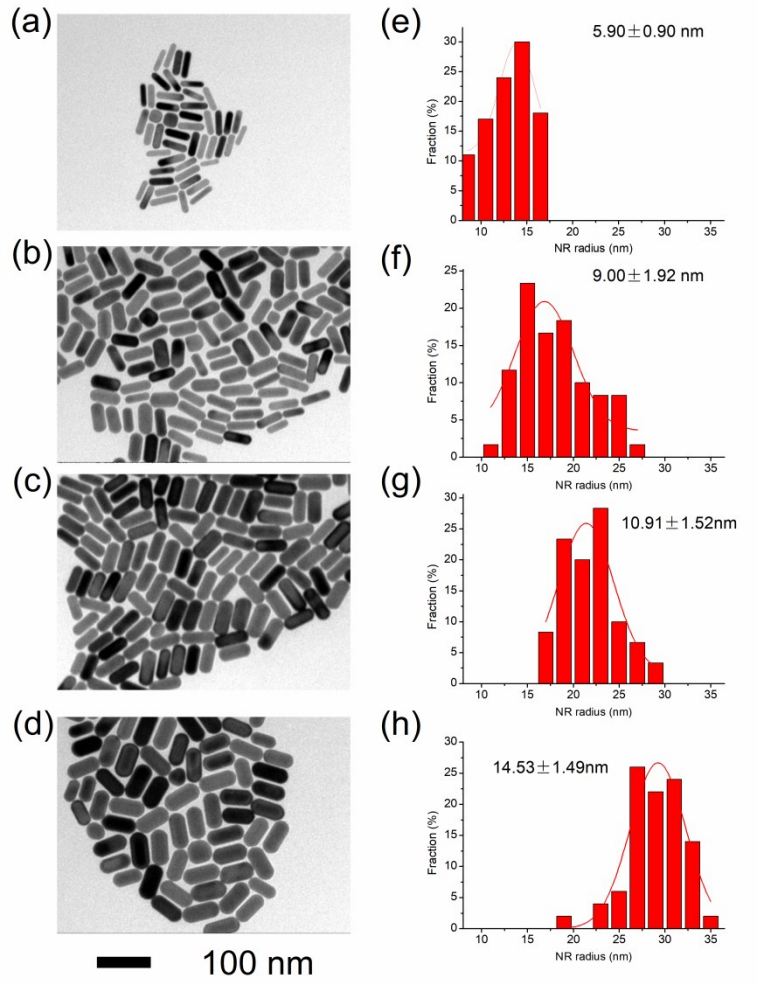


Fig. S9 (a-d) TEM images of GNRs with different radii, and (e-h) corresponding histogram of GNR

radius distribution.

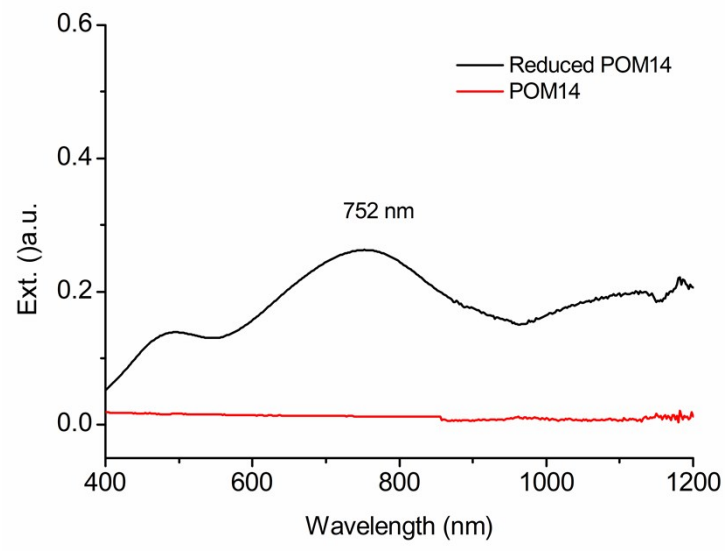


Fig. S10 UV-vis spectra of POM14 before and after UV light irradiation.

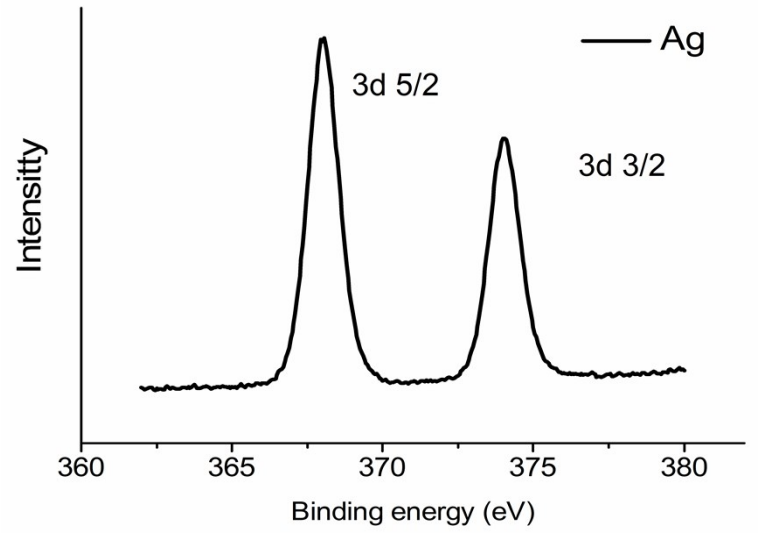


Fig. S11 XPS spectra of the Ag peak of the GNR@POM@Ag.

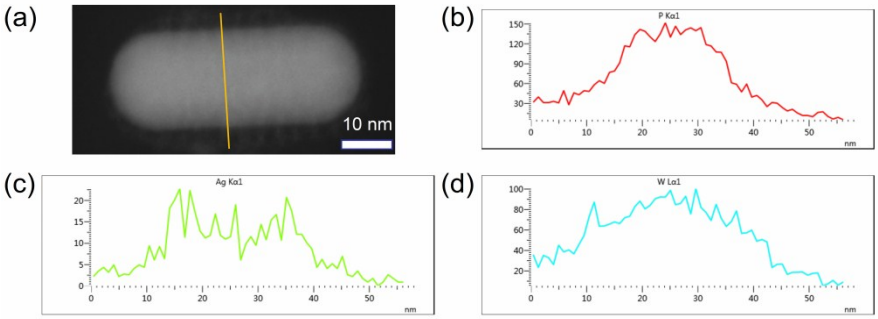


Fig. S12 (a) EDS line scan along the transverse direction of GNRs and (b) Ag peaks (c) P peaks (d) W peaks of the scan result.

Table S1 The assignments for characteristic vibrations of pure POM, CTAB capped GNRs and GNR@POM assembly.

CTAB	GNR@ POM14	POM14	POM6	POM12	Assignments
1631.76	1632.95	-			
1473.18	1465	-			CH_2N scissoring
1463.44		-			
1383	1380	-			CH_3 scissoring
-	913	911.95	874	881	W-O_b-W asym. str.
-	931	936	943	926	W-O_d-W asym. str.
-	790	780	790	770	W-O_c-W asym. str.

1 L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, 1956, **78**, 4503-4510.