

Supporting information

In situ Fabrication of Flower-Like Gold Nanoparticles in Surfactant-Polyoxometalate-Hybrid Spherical Assemblies

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1. Synthesis of Didodecylamine hydrobromide (DDAH)

Dodecylamine (2.00 g, 0.01 mol) and 1-Bromododecane (2.77 g, 0.01 mol) were dissolved in 100 mL ethanol and then heated to reflux for 24 h. After cooling, the mixture was evaporated to dryness by vacuum. The white residua was washed with diethyl ether and purified by column chromatography (silica, chloroform : methanol = 8 : 1). Finally, the product DDAH was obtained as a white powder (Yield: 50%). The ^1H NMR spectra and the assigned chemical shift of DDAH are shown as a red curve in Fig. S1.

2. Preparation of DDAH-PMo₁₂ complex (SEC-1)

50 mL chloroform solution of DDAH (0.009 mmol/mL) was added to 50 mL aqueous solution of H₃PMo₁₂O₄₀ (0.006 mmol/mL) with stirring. The molar ratio of H₃PMo₁₂O₄₀ to DDAH was controlled at 2:3, which is the double time of the actual charge ratio 1:3. This ratio can make the H₃PMo₁₂O₄₀ excessive and maintained the acidity of aqueous phase to prevent the hydrolysis of PMo₁₂O₄₀³⁻ cluster. After a further stirring of 1 h, the chloroform phase was separated and the pH value of aqueous phase was still at 1~2. Finally, the SEC was obtained as a yellow solid by evaporating the chloroform. The ^1H NMR spectra and the assigned chemical shift of SEC-1 are shown as black curve in Fig. S1.

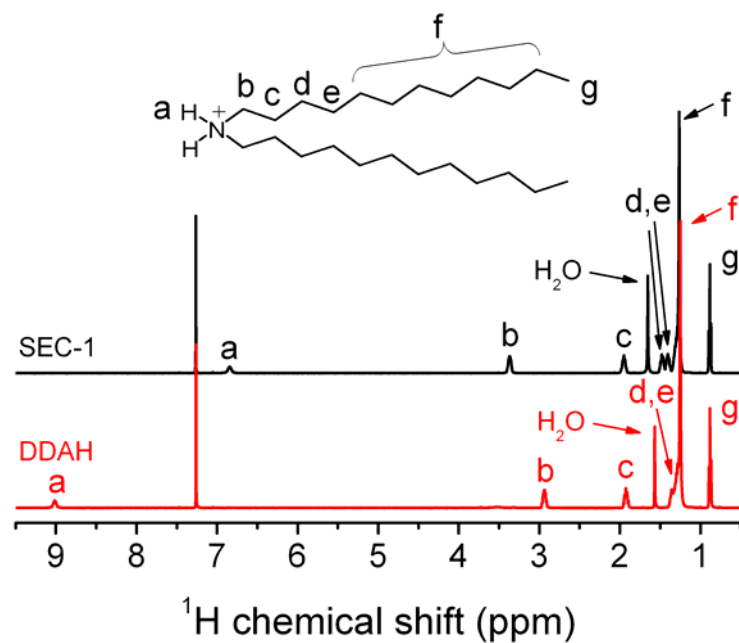


Fig. S1 ¹H NMR (500 MHz, CDCl₃) spectra of DDAH (red) and SEC-1 (black). For DDAH: δ (ppm) = 9.02 (s, 2H, a), 2.94 (m, 4H, b), 1.96-1.89 (m, 4H, c), 1.30-1.25 (m, 36H, d), 0.90-0.87 (t, 6H, e); for SEC-1: δ (ppm) = 6.85 (s, 2H, a), 3.37 (s, 4H, b), 1.95 (m, 4H, c), 1.48 (m, 4H, d), 1.40 (m, 4H, e), 1.25 (m, 28H, f), 0.90-0.87 (t, 6H, g).

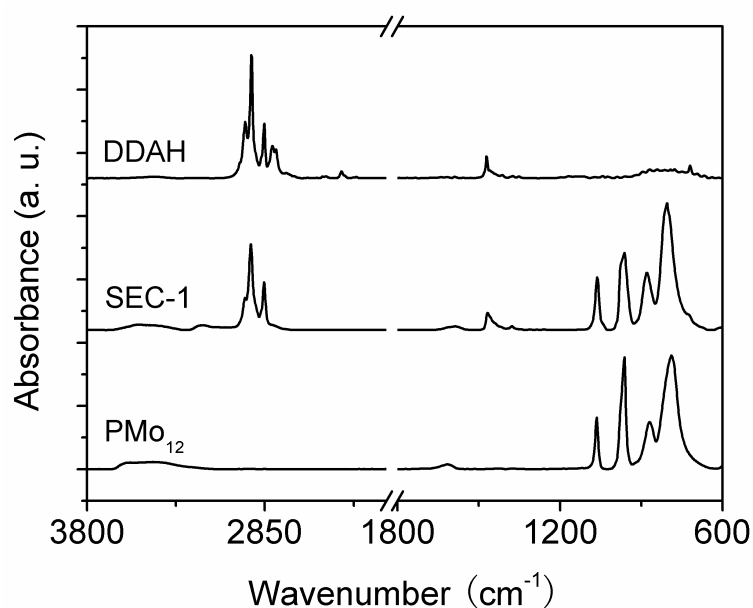


Fig. S2 FT-IR spectra of DDAH, SEC-1 and PMo₁₂, in KBr pellets.

Table S1. Assignments of the characteristic vibration bands in the FT-IR spectra of DDAH, SEC-1 and PMo₁₂.

DDAH	SEC-1	PMo ₁₂	Assignments ^a
3440	3530	3430	$\nu_{\text{as}}(\text{O-H})$
2954	2956	-	$\nu_{\text{as}}(\text{CH}_3)$
2921	2925	-	$\nu_{\text{as}}(\text{CH}_2)$
2853	2853	-	$\nu_{\text{s}}(\text{CH}_2)$
2810	-	-	$\nu_{\text{as}}(\text{NH})$
2790	-	-	$\nu_{\text{s}}(\text{NH})$
1588	1581	-	$\delta(\text{N-H})$
1470	1467	-	$\delta(\text{CH}_2)$
	1063	1065	$\nu_{\text{as}}(\text{P-O}_a)$
-	962	962	$\nu_{\text{as}}(\text{Mo-O}_d)$
-	879	868	$\nu_{\text{as}}(\text{Mo-O}_b\text{-Mo})$
-	805	788	$\nu_{\text{as}}(\text{Mo-O}_c\text{-Mo})$
720	721	-	$\rho(\text{CH}_2)$

a. ν_{as} : antisymmetrical stretching; ν_{s} : symmetrical stretching; δ : scissoring stretching; ρ : rocking stretching.

Table S2. Elemental analysis results of SEC-1.

	C (%)	H (%)	N (%)
Experimental results of SEC-1	30.33	5.19	1.71
Calculated results of (DDAH) ₃ PMo ₁₂ O ₄₀	29.96	5.54	1.46

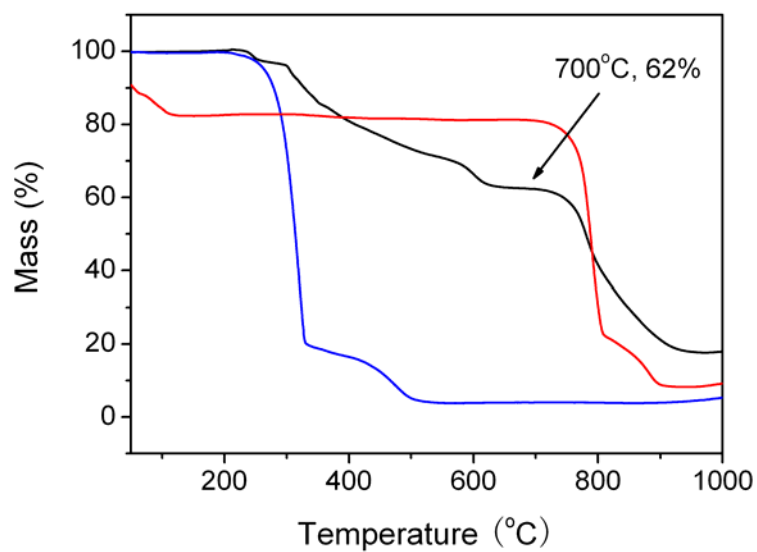


Fig. S3 TGA curves of DDAH (blue line), PMO₁₂ (red line) and SEC-1 (black line).

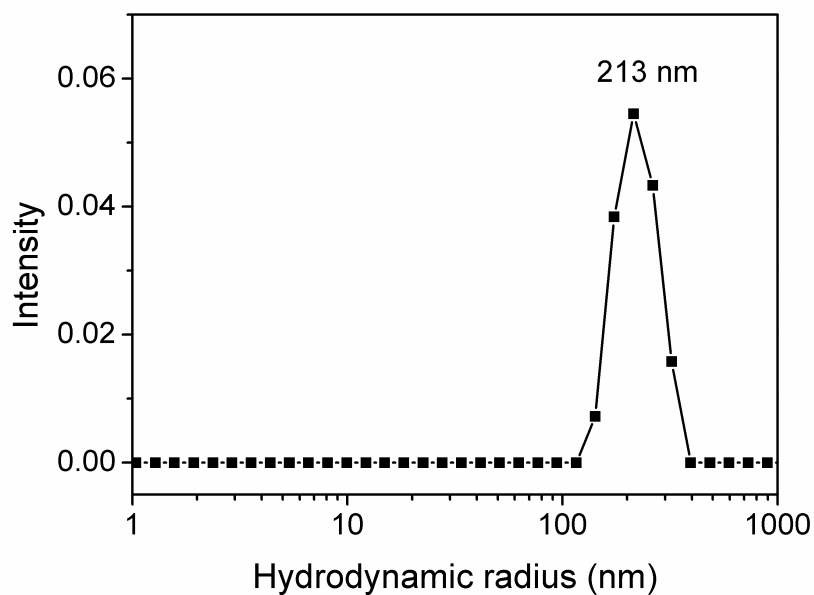


Fig. S4 CONTIN analysis of dynamic light scattering (DLS) study on SEC-1 methanol solution.

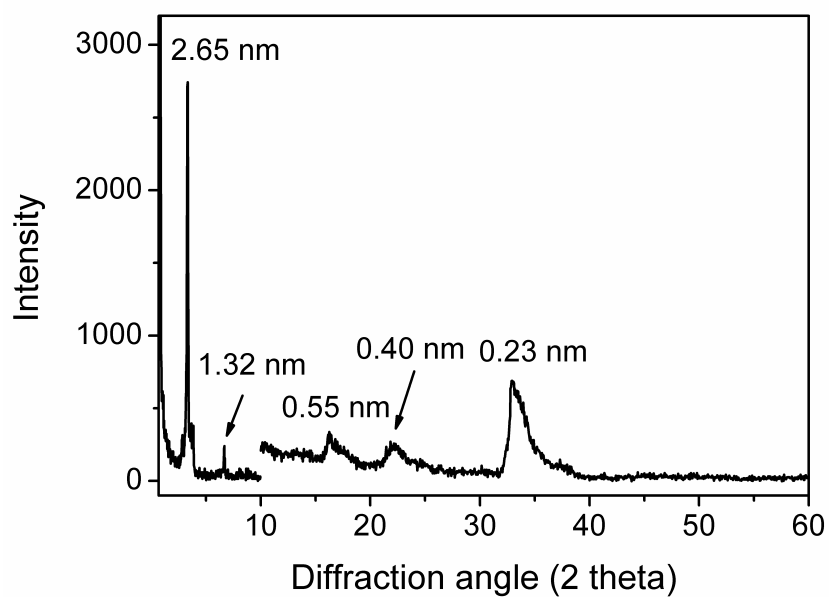


Fig. S5 X-ray diffraction pattern of the dried SEC-1 assemblies on quartz slide.

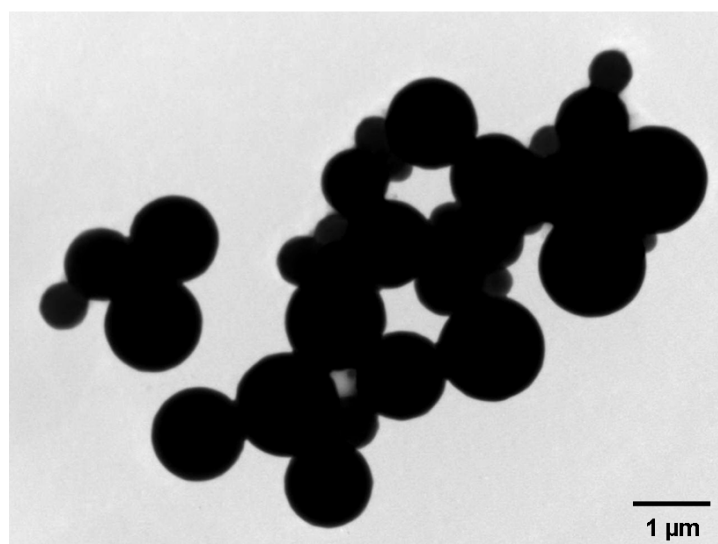


Fig. S6 TEM image of spherical SEC-1 assemblies formed in methanol (1 mg/mL).

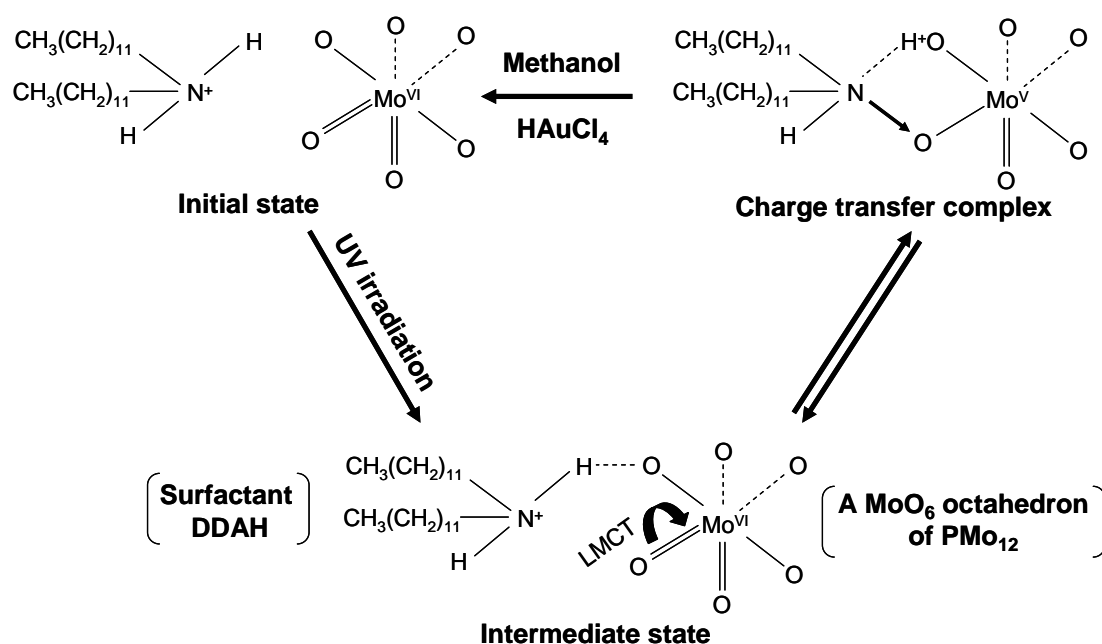


Fig. S7 Schematic drawing of the photochromism mechanism. In the photochromism process, when the solution of SEC-1 assemblies are placed under UV-irradiation, the photoexcitation of the $\text{O} \rightarrow \text{Mo}$ LMCT band of PMo_{12} will generate a transfer of the active proton at the ammonium group of DDAH to a bridging oxygen atom at the photoreducible site of MoO_6 octahedral lattice. This is followed by the interaction of the d^1 electron with the proton which was transferred to oxygen atom. Meanwhile, a hole left at the other oxygen atom due to the $\text{O} \rightarrow \text{Mo}$ LMCT transition interacts with the nonbonding electrons of nitrogen atom of amino group, forming a charge-transfer complex. Such a process implies the separation of electron and hole in SEC-1. This photochromism mechanism has been well established in the reported literatures (Please see *Chem. Rev.* **1998**, *98*, 307-325 and *ChemPhysChem* **2004**, *5*, 1020-1026).

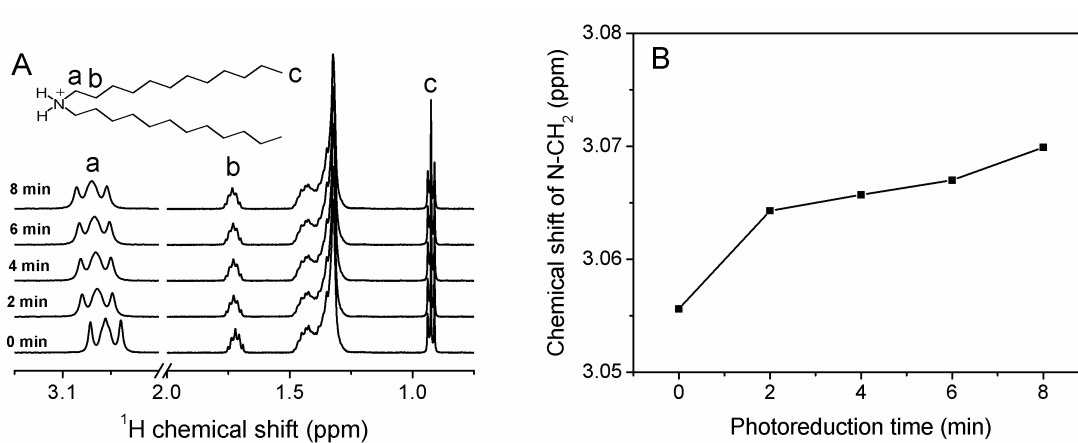


Fig. S8 (A) ^1H NMR spectrum of SEC-1 methanol solution during the photoreduction process. (B) Plot of chemical shift of N-CH₂ group in DDAH versus different photoreduction time.

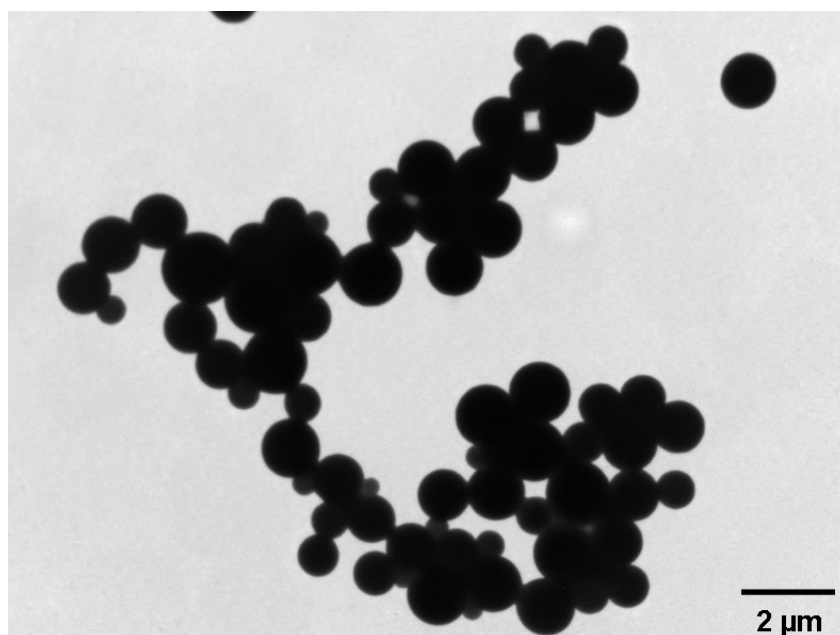


Fig. S9 TEM image of spherical SEC-1 assemblies in methanol (1 mg/mL) after the UV-irradiation for 8 min.

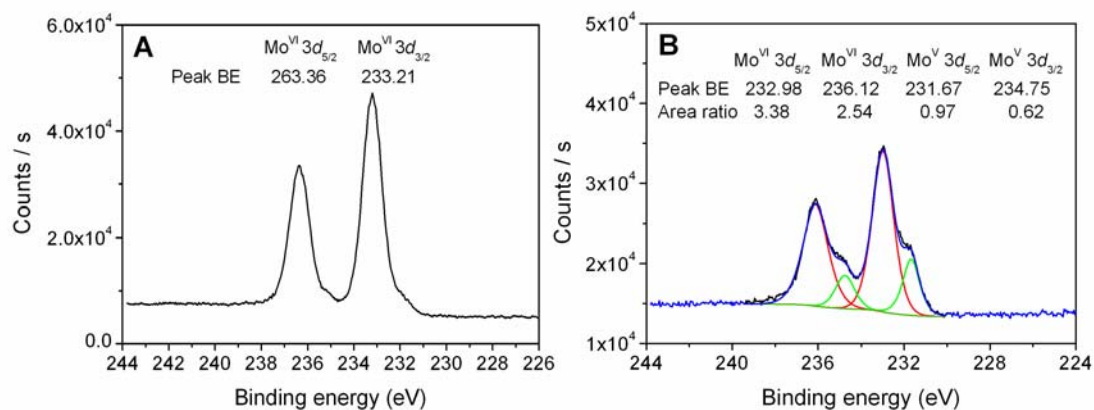


Fig. S10 XPS spectra of SEC-1 (A) before and (B) after the UV-irradiation for 8 min. The spectra were measured on a Thermo escalab 250 XPS instrument.

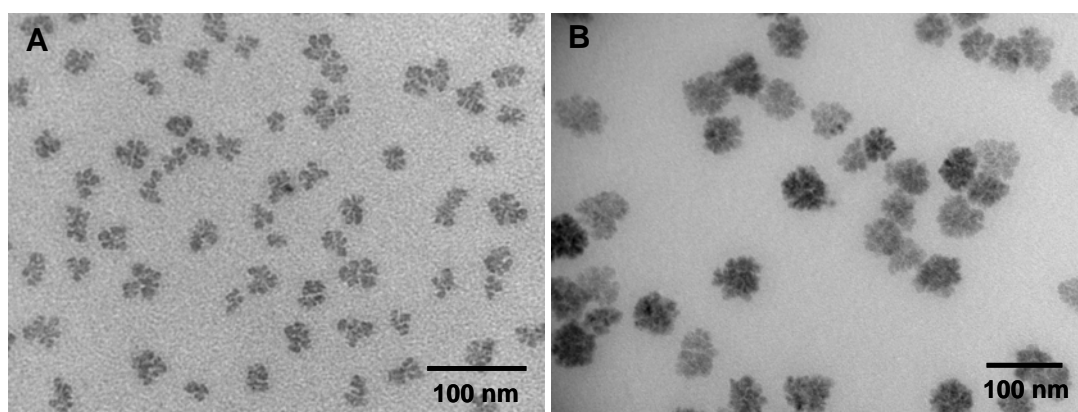


Fig. S11 TEM images of the Au-NPs formed in SEC-1 assemblies after adding H₂AuCl₄ for 5 min (A) and 10 min (B).

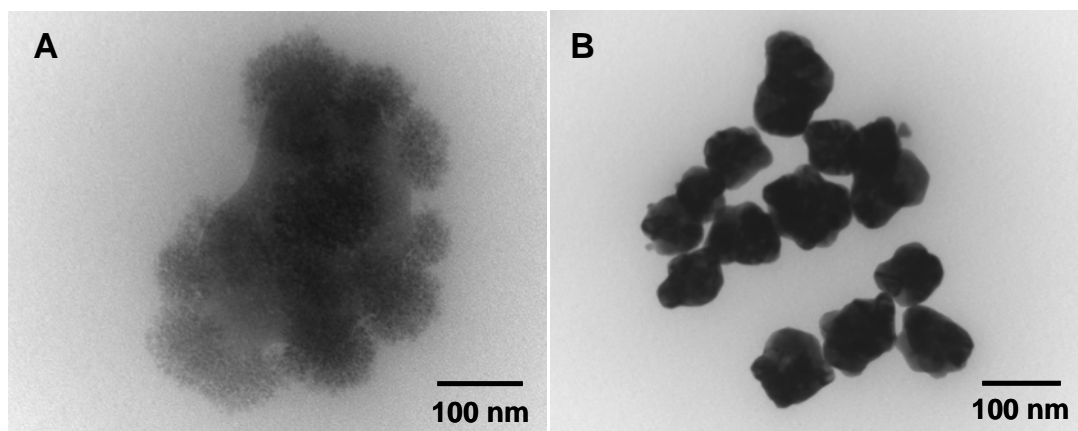


Fig. S12 (A) is the TEM image of very small Au-NPs formed on the surface of SEC-1 assemblies when the molar ratio of H₂AuCl₄ to SEC-1 is 1 : 1, and in this case the

spherical morphology of SEC-1 assemblies is partly retained; (B) is the TEM image of Au-NPs with irregular shape formed in SEC-1 assemblies when the molar ratio of HAuCl_4 : SEC-1 is 1 : 1. Based on these results, we can conclude that in the case of low concentration of HAuCl_4 , small gold nanoparticles tend to form separately and are difficult to link with each other to form large structure; while at high concentration, the formed gold nanoparticles will link so fast that the SEC-1 assemblies can not play the role of soft template to induce their growth at this moment and thus leads to the formation of large irregular gold nanoparticles. Therefore, a suitable concentration of HAuCl_4 is crucial to achieve the flower-like gold nanoparticles. The molar ratio of HAuCl_4 : SEC-1 = 3 : 1 should be in the suitable region in which the linking speed of small gold nanoparticles is just suitable for the growth of flower-like structures.

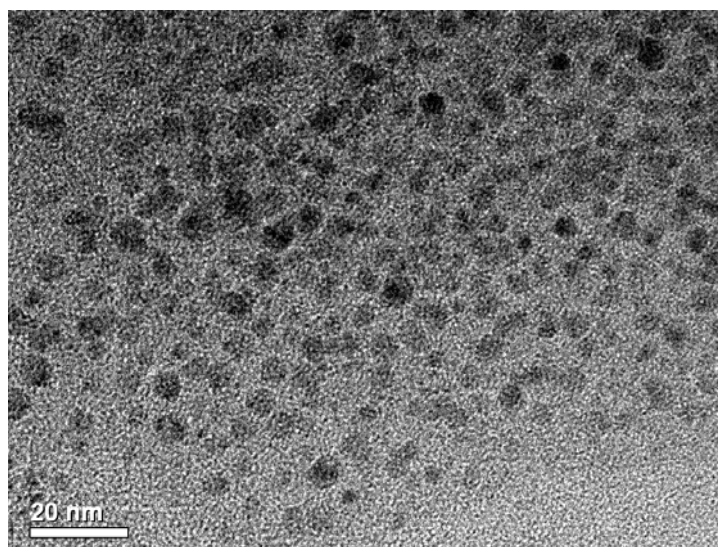


Fig. S13 TEM image of 0.4 mg/mL DDAH methanol solution containing 0.35 mg/mL HAuCl_4 after 8 min UV-irradiation. In this case, the molar ratio of DDAH to HAuCl_4 is 1:3. It is the same value to that of **Fig. 1E** in text. This image shows that only small spherical Au-NPs are formed at this condition.

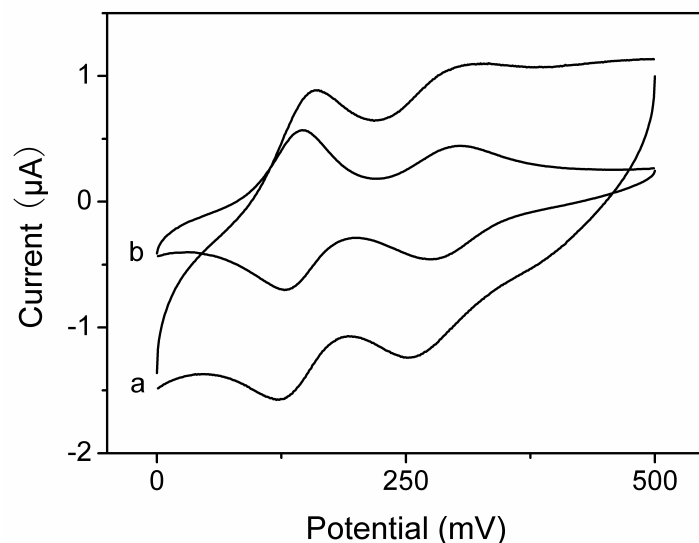


Fig. S14 Cyclic voltammograms of glassy carbon electrode modified by SEC-1/Au-NPs mixture (line a) and pure SEC-1 (line b) in 0.5 M H₂SO₄. Scan rate is 20 mV/s.

Table S3. Assignment of the cyclic voltammograms in Fig. 3. The electrode modification is performed by casting 30 mL methanol solution of SEC-1/Au-NPs or SEC-1 onto the freshly polished electrodes.

Sample	E_{pa} (V) ^a	E_{pc} (V) ^a	$E_{1/2}$ (V) ^a	ΔE_p (mV) ^a	electron number	assignments
Au-NPs	0.298	0.254	0.276	44	2	Mo ^{VI} /Mo ^V
	0.161	0.123	0.142	38	2	Mo ^{VI} /Mo ^V
SEC-1	0.299	0.277	0.288	22	2	Mo ^{VI} /Mo ^V
	0.145	0.129	0.137	16	2	Mo ^{VI} /Mo ^V

^a E_{pa} , oxidation potential; E_{pc} , reduction potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; ΔE_p , the difference between the pair of redox potentials.

Because the amount of POMs has important effect on the CV results, we designed an experiment to avoid the difference of PMo₁₂ amount. In this experiment, the methanol solution of SEC-1 were prepared and divided into two parts with the same volume. One part is used to modify the electrode as reference. The other part is used to perform the experiment of Au-reduction, and then the reaction solution containing

gold nanoparticles is directly used to modify the electrode. Because the two parts of solution contain the same amount of SEC-1, the amount of PMo_{12} on electrode should be also the same. At this condition, the enhancement of peak current should result from the existence gold nanoparticles. Moreover, the results of this experiment can be well repeated.