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Supplementary Information

Tuning the Catalytic Activity of Colloidal Noble Metal Nanocrystals by Use of Differently Charged Surfactants

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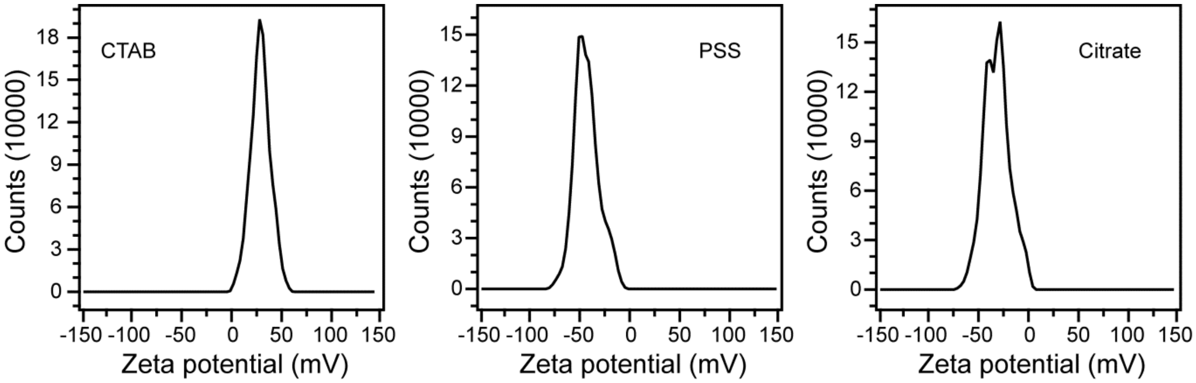


Fig. S1 Zeta potential of Au nanospheres capped with CTAB, PSS and citrate.

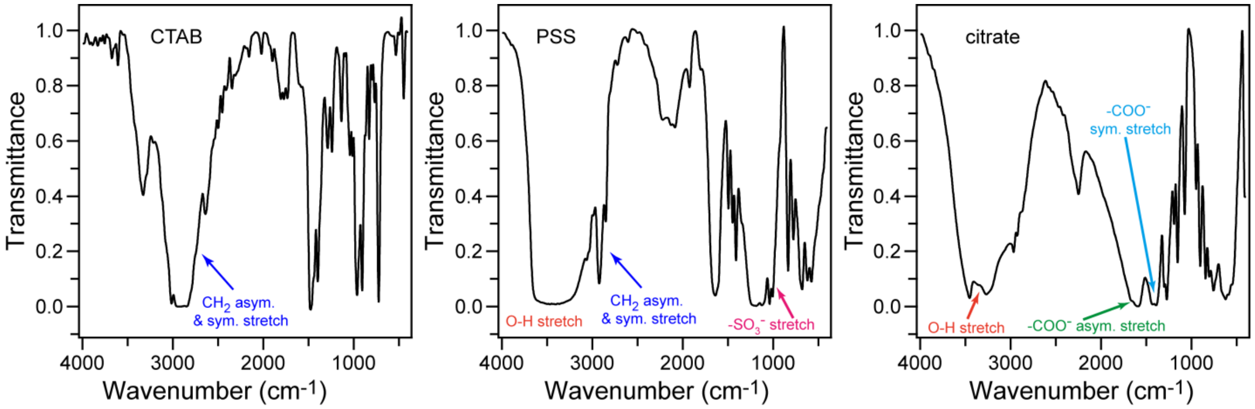


Fig. S2 FTIR spectra of free CTAB, PSS and citrate.

I: $H_2O_2 \longrightarrow 2OH\bullet$

II:

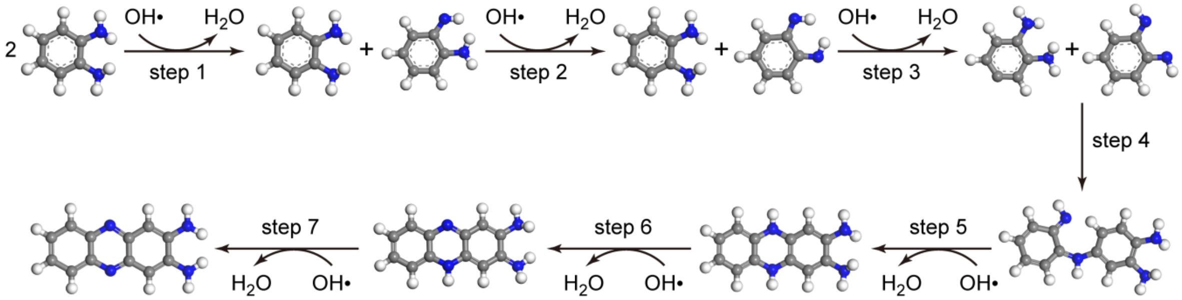
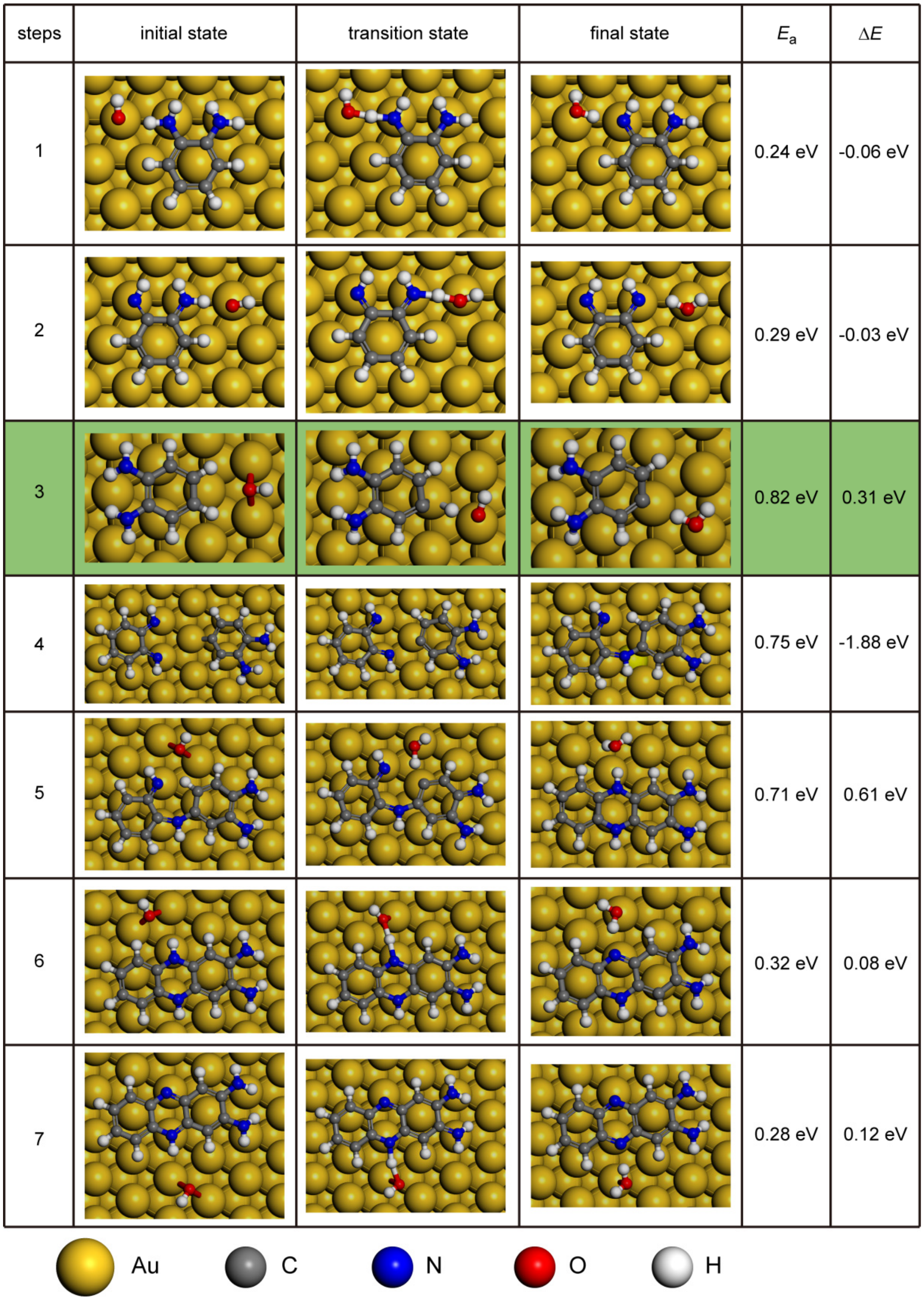


Fig. S3 Reaction process of the oxidation of OPDA to DAP by H_2O_2. The oxidation process can be divided into two large steps. The first one is the decomposition of H_2O_2 into OH radicals. The second one is the oxidation of OPDA by OH radical into DAP, which contains two reaction pathways.



steps	initial state	transition state	final state	E_a	ΔE
1				0.24 eV	-0.06 eV
2				0.29 eV	-0.03 eV
3				0.82 eV	0.31 eV
4				0.75 eV	-1.88 eV
5				0.71 eV	0.61 eV
6				0.32 eV	0.08 eV
7				0.28 eV	0.12 eV

Fig. S4 Structures and energy barriers and reaction energies of elementary steps in the second large step. The transition states searches were performed with complete LST/QST method implemented in Dmol.

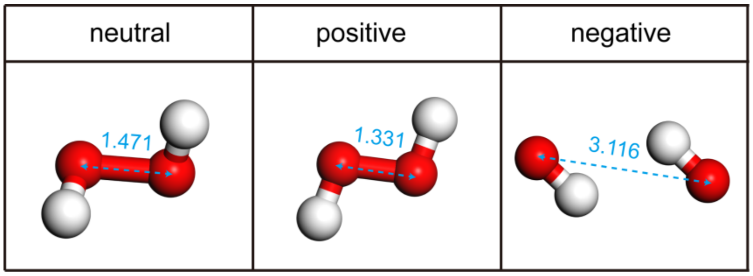


Fig. S5 Lengths of the scission bonds of H_2O_2 with different charges. Neutral charge means that the species are in neutral state. Positive and negative charge means that the species loss or get one electron. The numbers in the figures are bond lengths with unit of ångström. The red and white spheres stand for oxygen and hydrogen atoms, respectively.

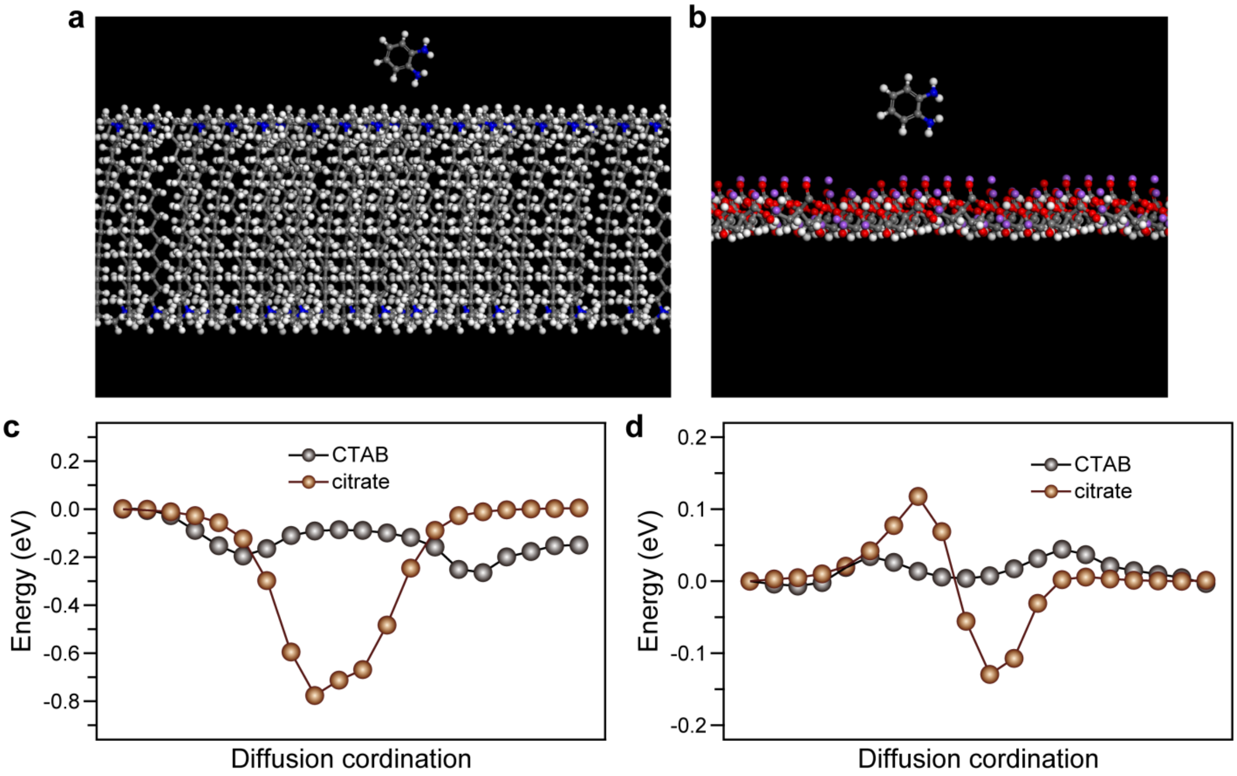


Fig. S6 (a) Model employed to study the diffusion of OPDA through CTAB layer. (b) Model employed to study the diffusion of OPDA through citrate layer. The CTAB and citrate layers used in the study of H_2O_2 diffusion are the same as those used in the study of OPDA diffusion. (c) Energy changes for OPDA diffused from top to the bottom of the CTAB and citrate layers. (d) Energy changes for H_2O_2 diffused from top to the bottom of the CTAB and citrate layers. The energy is calculated relative to that of the OPDA/H_2O_2 located above the CTAB/citrate layer. The calculation employed periodic slab. During the calculation, the CTAB and citrate molecules can move but are not relaxed. The energy barriers for OPDA and H_2O_2 diffusing through CTAB layer are smaller than 0.2 eV, indicating that the steric hindered effect of CTAB played on reactants is negligible.

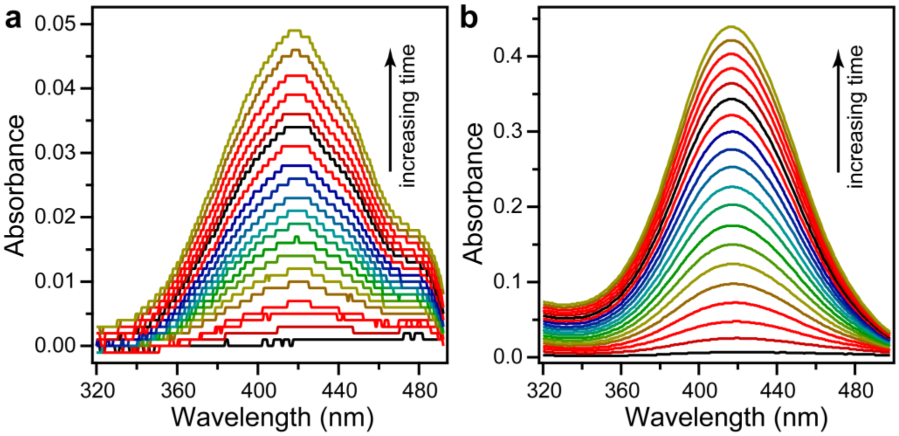


Fig. S7 Time-dependent absorption spectra of the reaction solution with the Au nanorod samples capped by CTAB (a) and citrate (b). Since the absorption of reaction solution catalyzed by CTAB-capped Au nanorods is extremely weak, the measured absorption spectra are not smooth.

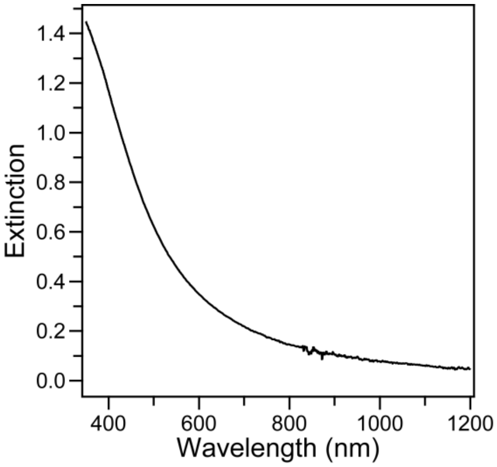


Fig. S8 Extinction spectrum of the Pd nanocubes.

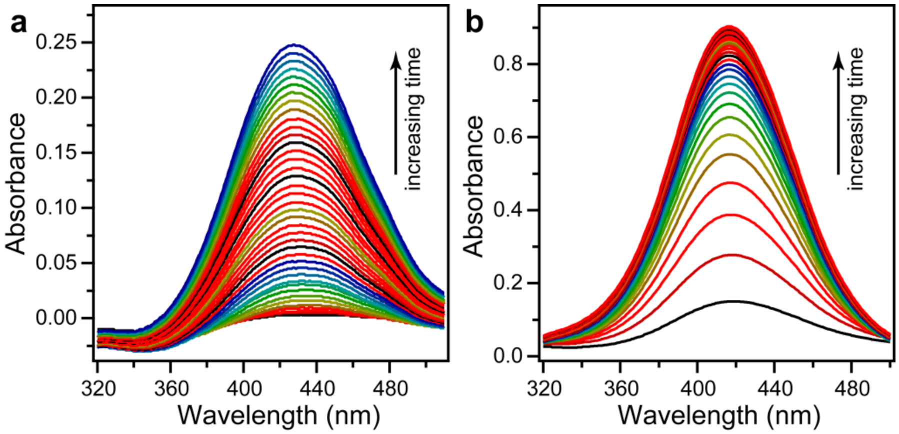


Fig. S9 Time-dependent absorption spectra of the reaction solution with the Pd nanocube samples capped by CTAB (a) and citrate (b).

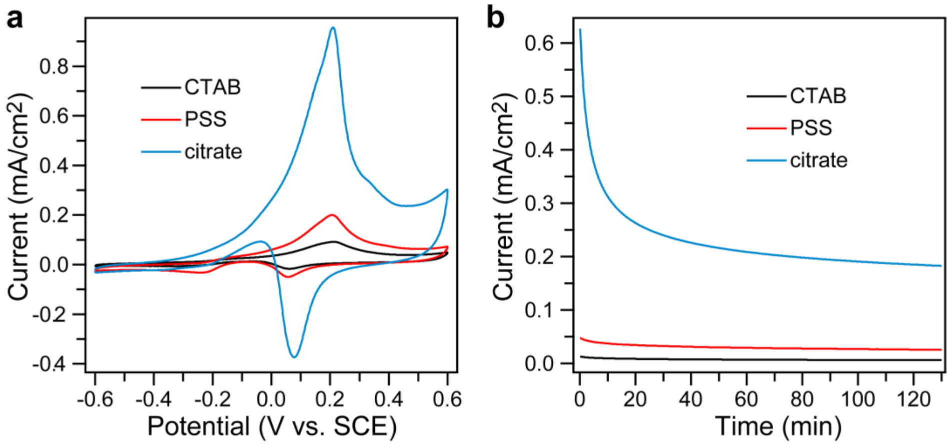


Fig. S10 Electrocatalytic oxidation of methanol by Au nanospheres capped with different surfactants. a) Cyclic voltammograms. b) Chronoamperograms at 0.21 V vs. SCE. The standard three-electrode configuration was employed. A glassy carbon electrode deposited with Au nanospheres capped with different surfactants was used as the working electrode, a saturated calomel electrode as the reference electrode and the counter electrode was a Pt wire. A KOH (0.5 M) with methanol (2 M) solution was used as the electrolyte. The working electrode was prepared by drop-casting 5 μL of the Au nanosphere suspension with the Au mass concentration of 6.2 mg mL^{-1} on the glassy carbon electrode surface. The electrode was dried in air for 1 h at room temperature before use. The citrate-capped Au nanospheres exhibit high catalytic activity for electrooxidation of methanol than CTAB- and PSS-capped Au nanospheres. Moreover, the citrate-capped Au nanospheres also show better durability for electrooxidation of methanol than the CTAB- and PSS-capped Au nanospheres.