

Supporting Information

Mechanistic Study of Silane Alcoholysis Reaction with Self-Assembled Monolayer-Functionalized Gold Nanoparticle Catalysts

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Typical method for calculating surface Au atoms of AuNPs. The number of surface Au atoms of **10Dod-array** was calculated by the similar method which we previously reported.^[1] The similar method was applied to other AuNP-arrays.

Calculation of the number of Au atoms of AuNP. The number of Au atoms per AuNP, n , can be calculated from previously reported equation (eq 1)^[2]

$$n = 4\pi r^3 / 3 v_g \quad (\text{eq 1})$$

, where r is the radius of AuNPs and v_g is a constant volume of Au atom: $17 \text{ \AA}^3$.^[2] In the case of 10 nm AuNPs, r was determined to be 5.4 nm from SEM observations (Figure 2b), thus n value was calculated as follows.

$$n = 3.88 \times 10^4 = 6.44 \times 10^{-20} \text{ mol.}$$

Calculation of the number of surface Au atoms at the surface of AuNP. The number of Au atoms at the surface of a AuNP, n_{out} , is calculated by previously reported equation (eq 2).^[2]

$$\begin{aligned} n_{\text{out}} &= (4\pi/3v_g)\{r^3 - (r - 2.38 \text{ \AA})^3\} \quad (\text{eq 2}) \\ &= 4.90 \times 10^3 \\ &= 8.15 \times 10^{-21} \text{ mol.} \end{aligned}$$

The effective number of Au atoms at the surface of 10Dod-array. In the hexagonally packed **10Dod-array**, a single lattice (lattice axis length is 13.2 nm from SEM) contains a **10Dod-AuNP** (Figure S1). Thus, the number of AuNPs constructing the **10Dod-array** substrate ($1.0 \times 1.0 \text{ cm}^2$) with 38% coverage was calculated as follows.

$$1.0 \times 10^7 \times 1.0 \times 10^7 \times 0.38 / (13.2 \times 13.2 \times \sqrt{3}/2) = 2.52 \times 10^{11}$$

Based on the mol number of Au atoms at the surface of a AuNP ($8.15 \times 10^{-21} \text{ mol}$) and the assumption that the upper half surface of each AuNPs were exposed to reaction solution (Figure S8), the effective number of Au atoms at the surface of **10Dod-array** was obtained to be $1.02 \times 10^{-9} \text{ mol}$ as follows.

$$2.52 \times 10^{11} \times 8.15 \times 10^{-21} / 2 = 1.02 \times 10^{-9} \text{ mol}$$

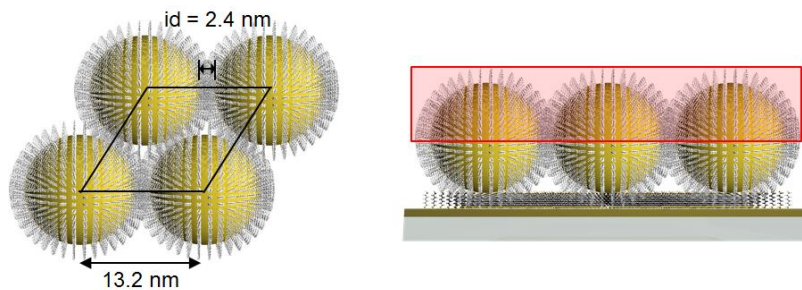


Figure S1. Schematic illustration of **10Dod-array**. Top view (left) and side view (right).

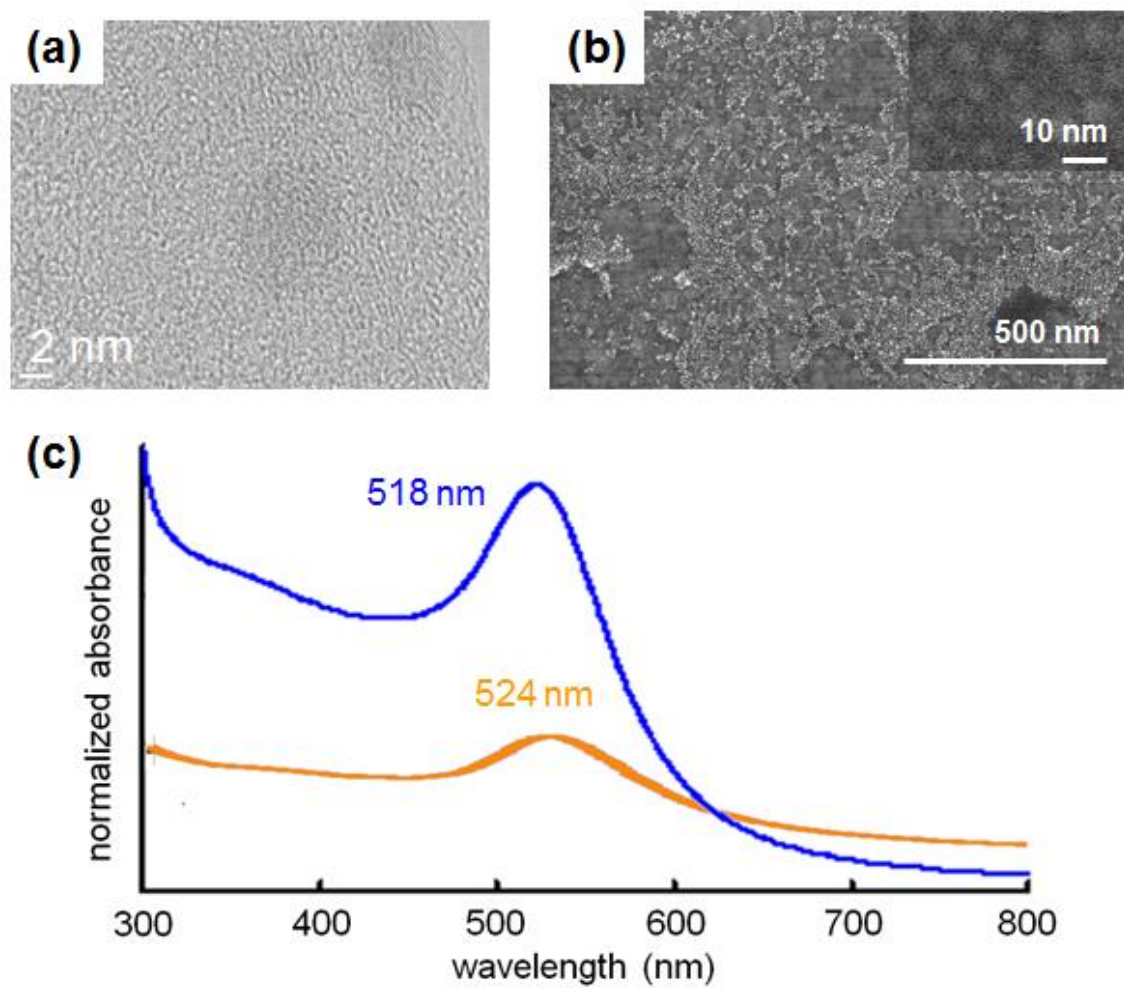


Figure S2. (a) TEM image of as-prepared 5 nm AuNPs. (b) SEM image of 5 nm AuNPs after the functionalization with dodecanethiol. (c) UV-Vis absorption spectra of the as-prepared aqueous colloidal solution of 5 nm AuNPs (blue line) and 2D-array of dodecanethiol-functionalized 5 nm AuNPs (orange line).

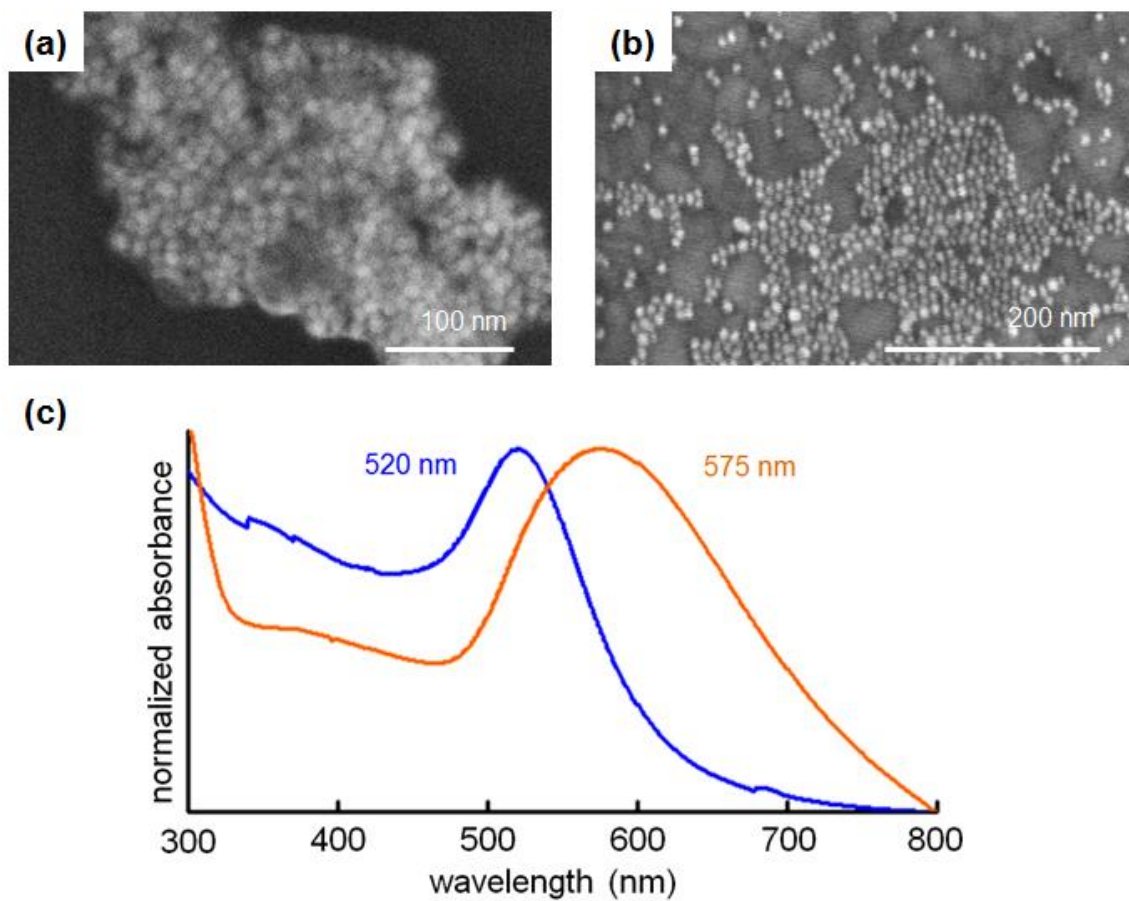


Figure S3. SEM images of (a) before and (b) after the functionalization of 10 nm AuNPs with dodecanethiol. (c) UV-Vis-NIR absorption spectra of the as-prepared aqueous colloidal solution of 10 nm AuNPs (blue line) and 2D-array of dodecanethiol-functionalized 10 nm AuNPs (orange line).

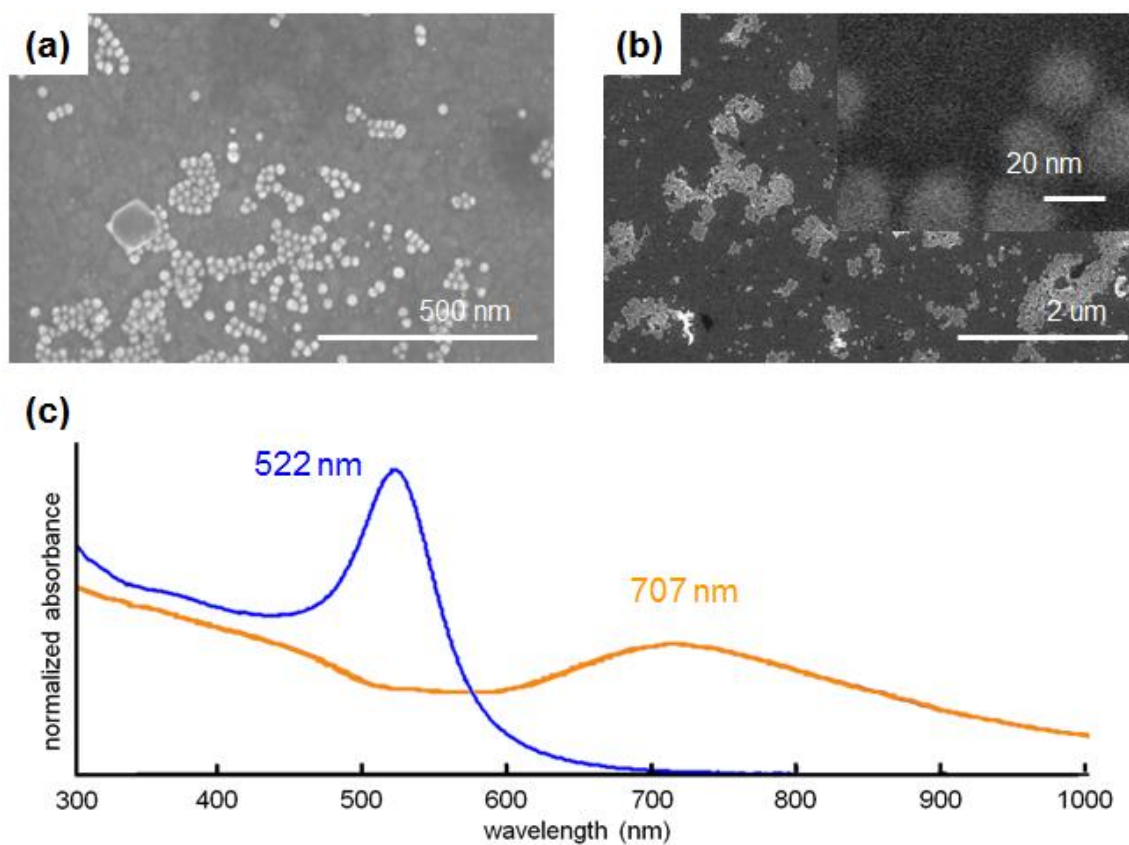


Figure S4. SEM images of (a) before and (b) after the functionalization of 20 nm AuNPs with dodecanethiol. (c) UV-Vis-NIR absorption spectra of the as-prepared aqueous colloidal solution of 20 nm AuNPs (blue line) and 2D-array of dodecanethiol-functionalized 20 nm AuNPs (orange line).

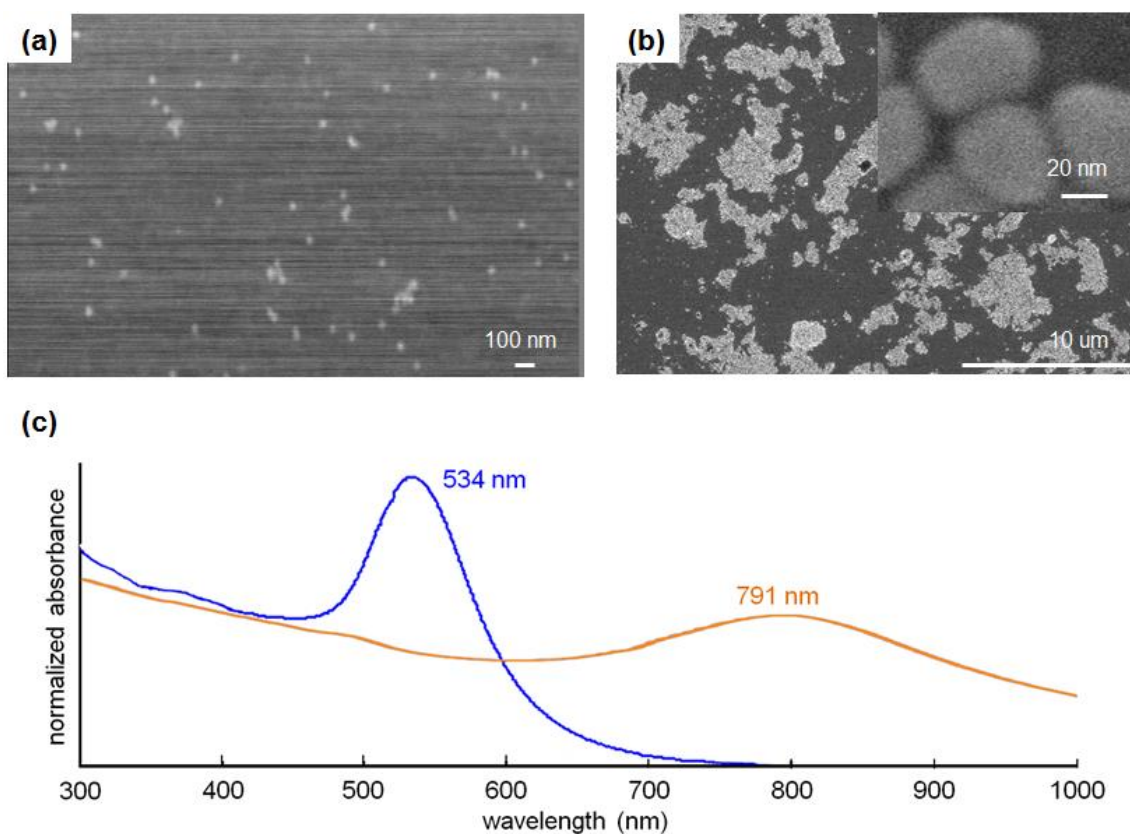


Figure S5. SEM images of (a) before and (b) after the functionalization of 40 nm AuNPs with dodecanethiol. (c) UV-Vis-NIR absorption spectra of the as-prepared aqueous colloidal solution of 40 nm AuNPs (blue line) and 2D-array of dodecanethiol-functionalized 40 nm AuNPs (orange line).

Typical method for time-course reaction trace. All time-course experiments were carried out according to the typical reaction conditions described in the experimental section. Aliquot of samples were taken at several time points at 10, 20, 30, 40, 50, and 60 min and the product yields were obtained by GC analysis. Time points of initial reaction steps were used for calculating reaction rate constants under pseudo-first order kinetics. A representative time-course reaction trace and pseudo-first order dependence of initial reaction steps are shown in Figure S2.

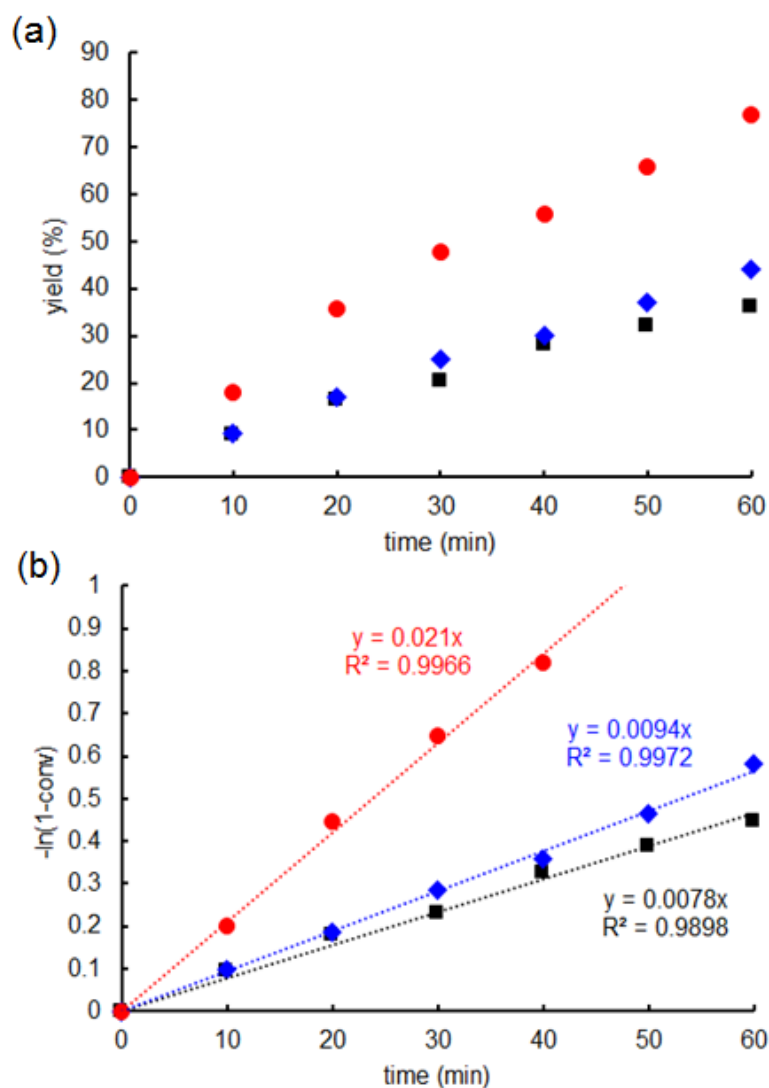


Figure S6. (a) Time-course reaction profile and (b) pseudo-first order dependence of initial steps of **10Dod-array** (black square), **10Dod-array/Cr** (blue diamond), and **10Dod-array/ITO** (red circle).

Investigation on thiol detachment during catalytic reaction. In order to investigate whether thiolate ligands are detached during the catalytic reaction ^1H NMR measurement was carried out using colloidal **10Dod-AuNP** (Figure S3). Even after 17h reaction, no detached thiol and disulfide were observed in ^1H NMR spectrum. This result suggests the negligible detachment of thiolate ligands during the catalytic reaction.

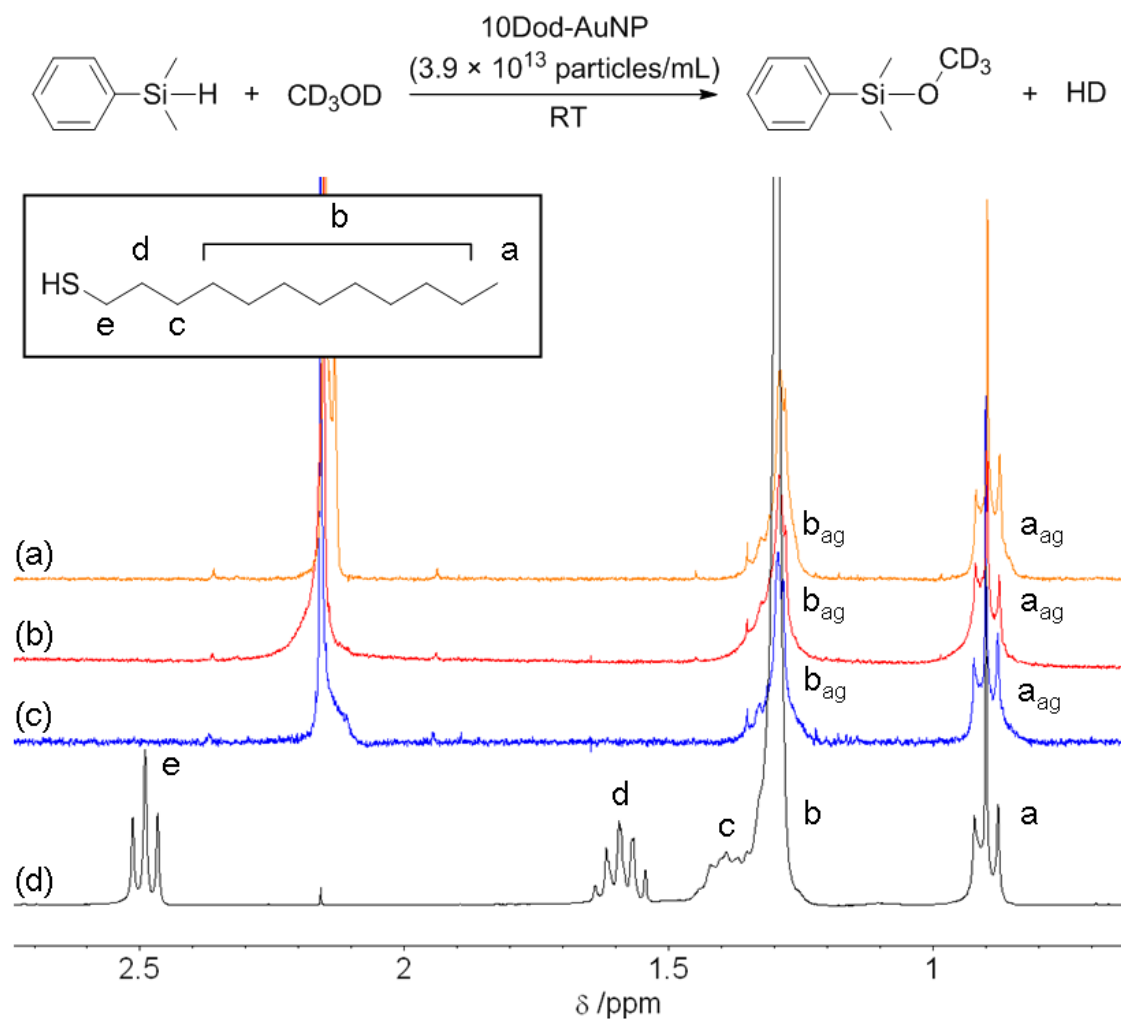


Figure S7. ^1H NMR spectra of the reaction solution with colloidal **10Dod-AuNP** in CD_3OD (a) 17 h, (b) 10 min, (c) before the addition of DMPS, and (d) dodecanethiol.

Reactivity comparison between Au₂₅ and Au₃₈ nanoclusters.

In the smaller NP size, although the reaction enhancement effect with SAM is considered to be low, the size effect of alkanthiolate SAM-functionalized AuNPs is interesting, because AuNPs have been reported to show catalytic activity maximum with the size less than 2 nm. In order to investigate the size effect below 2 nm scale, gold nanoclusters having precise molecular formula were applied for the same catalytic silane alcoholysis reaction in the homogeneous solution (Figure S1). Dodecanethiolate-functionalized Au₂₅ (Octyl₄N[Au₂₅(SDod)₁₈]), Au₃₈ (Au₃₈(SDod)₂₄), PdAu₂₄ (PdAu₂₄(SDod)₁₈),³ dodecaneselenolate-functionalized Au₂₅ (Octyl₄N[Au₂₅(SeDod)₁₈]),⁴ and glutathione-functionalized Au₂₅ (Na[Au₂₅(SG)₁₈]) nanoclusters were synthesized according to the reported methods.

Among the Au₂₅ nanoclusters, dodecanethiolate-capped Au₂₅ nanocluster showed a little catalytic activity different from almost inactive glutathione-capped and dodecaneselenolate-capped Au₂₅ nanoclusters. Although dodecaneselenolate-capped Au₂₅ nanocluster⁴ is considered to have almost the same molecular structure to dodecanethiolate-capped Au₂₅ nanocluster, it has been reported that Au–Se bonds are more covalent than those of Au–S,^{4b} which suppresses the activation of reactant molecules at the surface of selenolated Au₂₅ nanoclusters. It is noteworthy that the highest catalytic activity was observed for dodecanethiolate-capped PdAu₂₄ nanocluster, despite the little catalytic activity of Au₂₅ nanocluster. The similar enhancement of catalytic activity with Pd doping was observed for benzyl alcohol oxidation with calcined PdAu₂₄ nanoclusters immobilized on CNT,⁵ which is considered to be based on the so-called “ensemble” or “ligand” effect.⁶ It seems that the “ligand” effect, electron transfer from Pd to Au, plays an important role for the catalysis, because Toshima demonstrated the extremely high catalytic activity of “crown-jewel” nanoparticle bearing Au atoms at the vertex or corner of Pd nanoparticles towards glucose oxidation.⁷

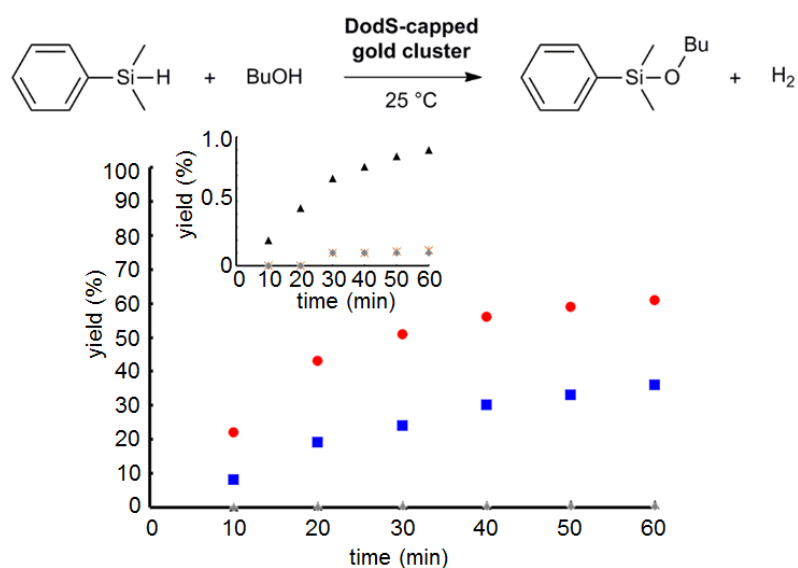


Figure S8. Time-course reaction profile of magic number gold nanoclusters (black triangle: $\text{Au}_{25}(\text{SDod})_{18}$, gray diamond: $\text{Au}_{25}(\text{SG})_{18}$, orange asterisk: $\text{Au}_{25}(\text{SeDod})_{18}$, blue square: $\text{Au}_{38}(\text{SDod})_{24}$, red circle: $\text{PdAu}_{24}(\text{SDod})_{18}$) towards silane alcoholysis. Reaction condition: DMPS (150 μmol), BuOH (3.0 mL), Au cluster (0.08 mol %) at 25 $^{\circ}\text{C}$. Inset shows the magnification of lower reaction yield range.

Table S1. Recyclable catalysis of **10Dod-array**

cycle	yield (%)
1st	86.5
2nd	96.1
3rd	94.8

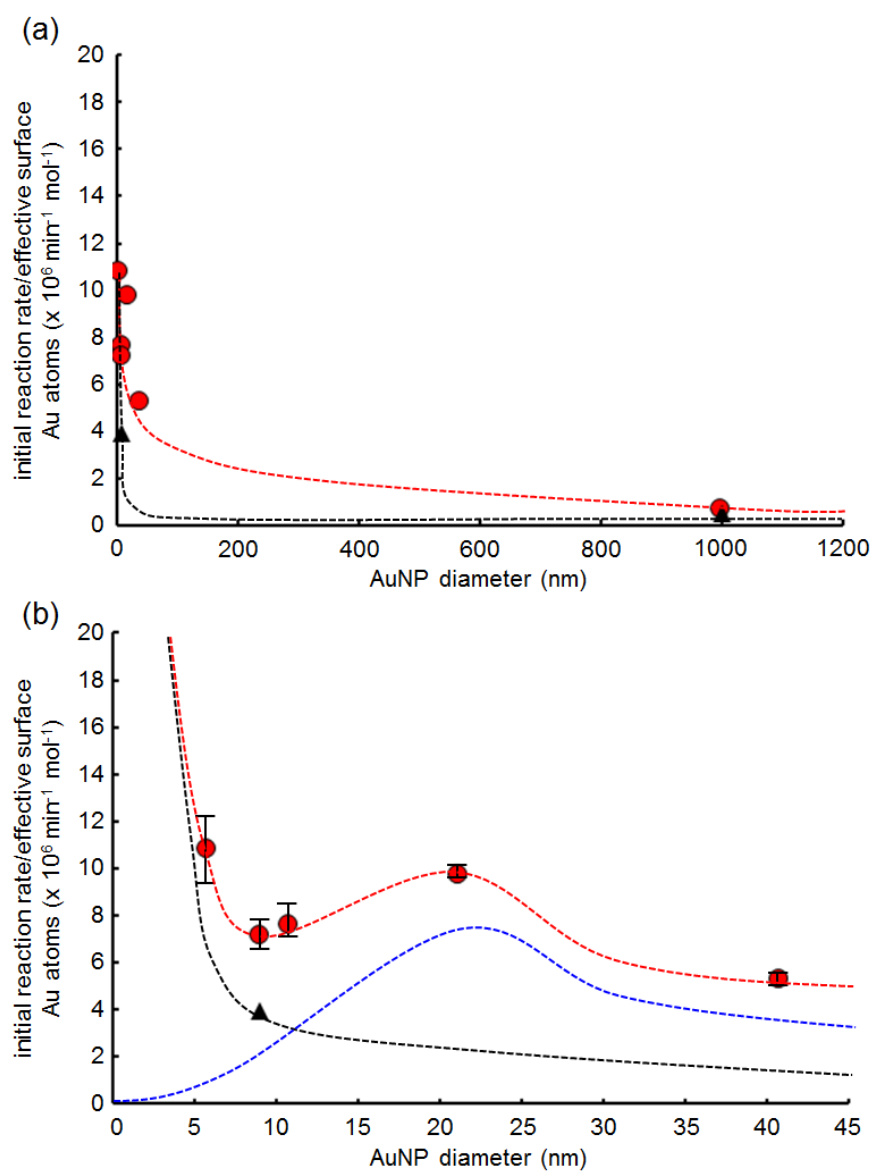


Figure S9. Size dependence of catalytic activity of AuNP-arrays and Au films with (red dotted line) or without dodecanethiolate SAM (black dotted line). The catalytic activity of 9Dod-array, immobilized 9 nm AuNPs without SAM, Au film, and Dod-Au film were taken from our previous report,¹ in which Au films are used as 1000 nm data points. Blue dotted line shows expected reaction enhancement effect with SAM.

Effect of SAM density.

In order to compare the effect of SAM density sterically hindered *tert*-dodecanethiolate (1,1-dimethyldecaneethiolate)-coated 10 nm AuNP, **10tDod-AuNP** was also prepared by Frens' method.⁸ The smaller AuNPs, **5Dod-AuNP** and **10Dod-AuNP** were synthesized by seed-mediated growth method using ascorbic acid as the reductant.⁹ The larger AuNPs, **20Dod-AuNP** and **40Dod-AuNP** were synthesized by Frens' method using citrate as the reductant.⁸ The synthesized AuNPs were characterized by IR ATR measurement (Figure S10). Although both methods use reductant containing carboxylate or ester groups which also act as original surface-capping molecules before thiolate functionalization, no signal corresponding to C=O vibration bands of reductants were observed from all dodecanethiolate SAM-coated AuNPs. In contrast, **10tDod-AuNP** shows characteristic vibrations of $\nu_{\text{asy}}(\text{COO}^-)$ at 1580, 1539 cm^{-1} and $\nu_{\text{sym}}(\text{COO}^-)$ at 1443, 1429 cm^{-1} , together with water-bending vibration at 1660 cm^{-1} , respectively, corresponding well with the feature of surface-coordinated citrates in partially thiolated AuNPs.¹⁰ These results clarify that dodecanethiol fully exchanges the original surface ligands by the formation of SAM, but *tert*-dodecanethiol resulted in covering the AuNP surface in lower density due to the steric hindrance.

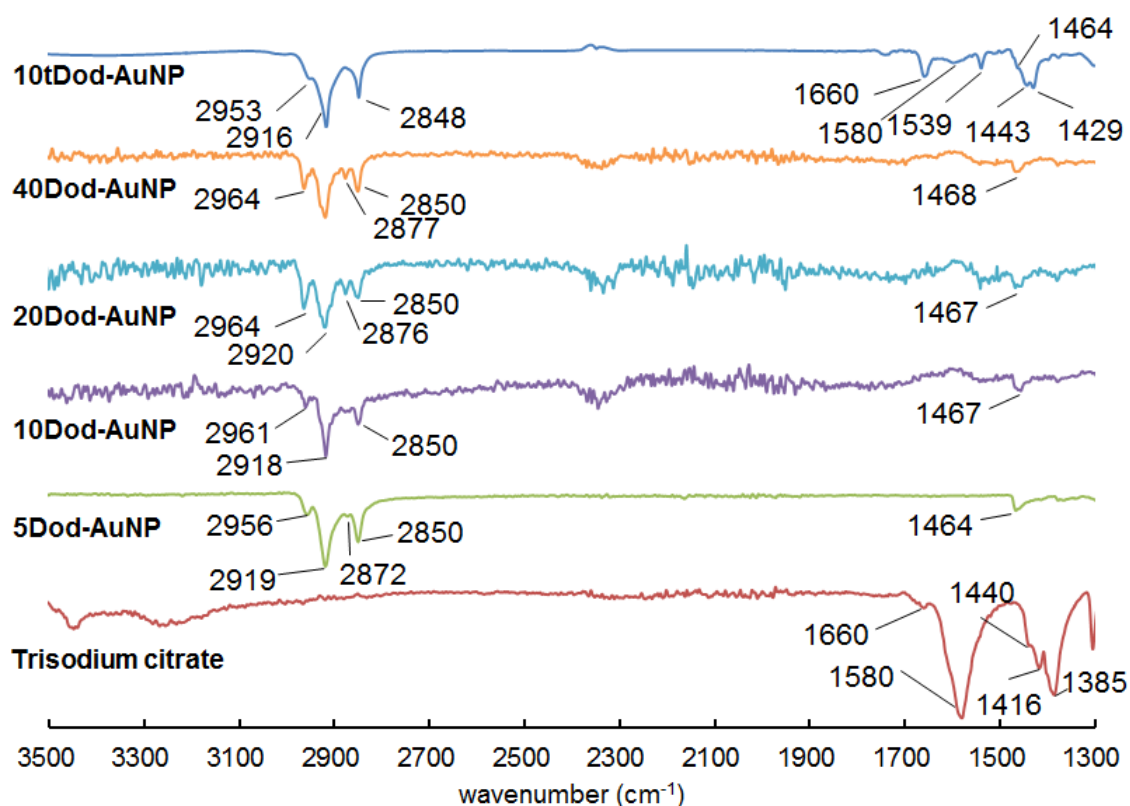
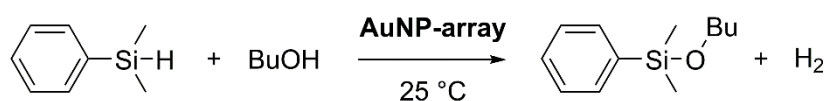


Figure S10. IR ATR spectra of dodecanethiolate or *tert*-dodecanethiolate SAM-coated AuNPs with the core size of 5, 10, 20, and 40 nm.

The effect of lower density SAM to the catalytic reaction was also investigated by preparing 2D-arrayed 10tDod-AuNPs, **10tDod-array**. The immobilized catalyst **10tDod-array** was prepared by the similar method to other 2D-array catalysts (Figure S11). The catalytic silane alcoholysis reaction with **10Dod-array** and **10tDod-array** afforded the silylether product in 82% and 41% yield, respectively (Table S2). Although the coverages of AuNPs on the substrates are almost same, the catalytic silane alcoholysis reaction gave remarkably lower yield with **10tDod-array**. This result reveals that the higher density of SAM is the key to enhance the catalytic reaction through the intermolecular interaction between SAM and reactant molecules.

Table S2. Catalytic reaction with sterically hindered thiol-capped AuNP-arrays



entry	catalyst	coverage (%)	yield (%) ^b
1	10Dod-array	95	82
2	10tDod-array	93	41

^aReaction conditions: DMPS (150 μmol) in BuOH (3.0 mL) with AuNP-array catalysts at 25 °C.

^bYield at 1 h.

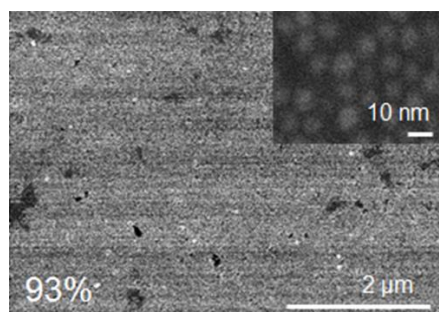
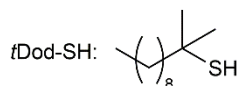


Figure S11. SEM image of **10tDod-array**.

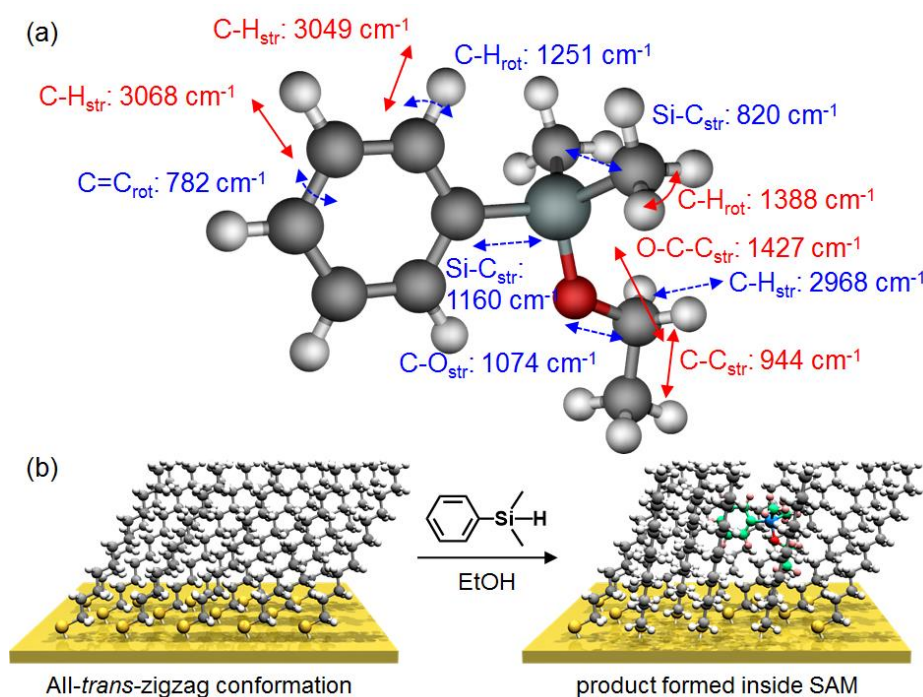


Figure S12. (a) DFT (B3LYP/6-31G**)–calculated vibration bands of DMPS–OEt. Red and blue arrows show the observed and non-observed bands by IR RA spectrum. (b) Proposed conformational change of SAM through the entrapment of substrates and silane alcoholysis reaction.

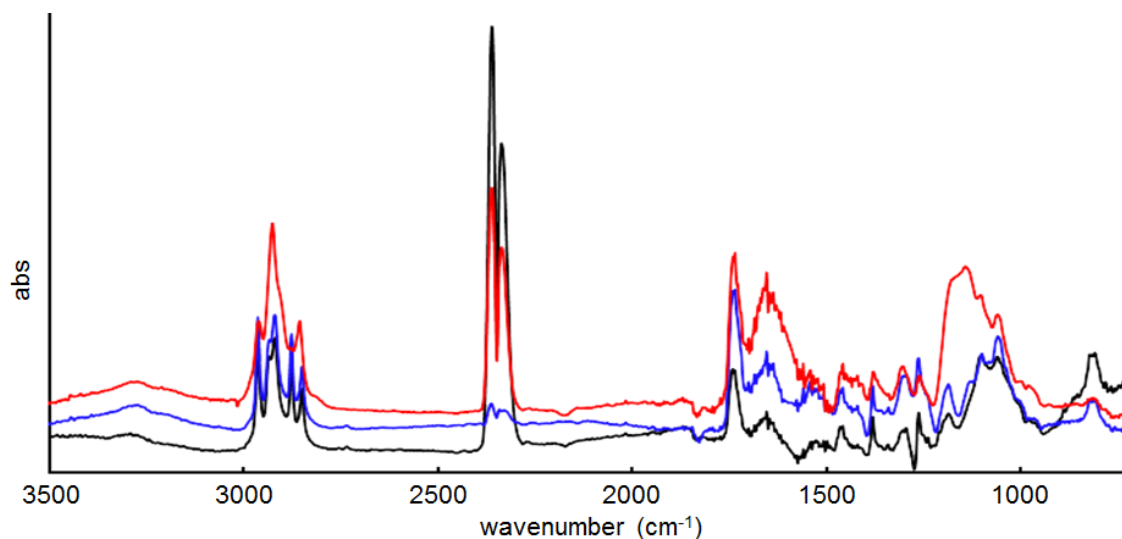


Figure S13. IR RA spectra of **Dod-Au** (black line), **Dod-Au** after immersing in HexOH for 24 h (blue line), and **Dod-Au** after immersing in HexOH with DMPS (red line).

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