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Enhanced Catalytic Activity of Self-Assembled-Monolayer-Capped Gold Nanoparticles

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Natural metalloenzymes mediate highly selective and efficient catalytic reactions on the basis of molecular recognition (i.e., highly ordered and selective non-covalent encapsulation of a substrate molecule within the enzyme's active reaction space and subsequent transformation of the substrate to the target product by metal-complex-based catalysis).^[1] Much effort has been devoted to mimic molecular-encapsulation-based catalysis since the mechanism of this catalytic reaction provides an ideal and promising model to develop highly active catalysts. In this sense, semiartificial approaches based on the use of natural proteins (e.g., apoenzyme), wherein a metal-complex catalyst is incorporated into the reaction sites as a cofactor,^[2,3] and artificial approaches, in which large molecules such as polymers,^[4–6] dendrimers,^[7] supramolecular hosts,^[8,9] and mesoporous materials^[10] provide the protein-like reaction space required for enhancing the catalytic activity of the metal complex, have been adopted.

As a result of the growing interest in metallic nanoparticle (MNP) catalysts,^[11,12] there are numerous reports on the incorporation of MNPs into a reaction space constructed within different architectures such as polymers,^[13] dendrimers,^[14] micelles,^[15] and mesoporous materials.^[16,17] One key feature of MNPs is their surface-functionalizing property, which has allowed for the design of recyclable catalyst supports,^[18] sensors,^[19] and drug-delivery materials.^[20] Among the different surface functionalization strategies developed for MNPs, creation of self-assembled monolayers (SAMs) offers the possibility of mimicking biological structures such as micelles and lipid bilayers,^[21] thereby affording a molecular recognition field to encapsulate molecules. However, with a few exceptions,^[22] SAM functionalization has not been used in catalysis since capping of the catalyst surface generally degrades the catalytic activity. Recently, it has been reported that alkanethiol-SAMs improve

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the reaction selectivity at the Pd(111) surface, although thiols are generally known to act as catalyst poisons; nevertheless, the catalytic activity in this case decreased to 40% of that observed when using unmodified Pd(111).^[23] Consequently, the simultaneous realization of improved catalytic activity and molecular recognition via surface functionalization of MNPs remains a challenge.

Herein, we report an unprecedented catalytic-activity enhancement effect of alkanethiol-SAMs on Au nanoparticles (AuNPs). In this system, the alkanethiol-SAM acts as a soft interface that shows molecular-recognition properties based on intermolecular hydrophobic interactions. This arrangement allows for the encapsulation of substrate molecules inside the alkanethiol-SAM space, thereby facilitating interactions with the AuNPs and accelerating catalytic reactions at the AuNP surface (Figure 1). The activity of the SAM-capped AuNP catalytic system is maximized (turnover frequency, $TOF = 55\ 000\ h^{-1}$; turnover number, $TON = 200\ 000$, on the basis of the surface Au atoms) when the SAM-capped AuNPs are immobilized on Au-thin-film-coated quartz substrates to form dense two-dimensional arrays (Figure 1a,b).^[24] On the other hand, the activity enhancement is only moderate in the colloidal state because of self-aggregation issues. These results are valuable in that they indicate the possibility of developing highly active catalysts with excellent enantio-, stereo-, or substrate selectivities by designing SAM interfaces on MNPs.

Various Au materials were investigated to study the catalytic enhancement effect of the alkanethiol-SAM system in a probe reaction, *n*-butanolysis of dimethylphenylsilane (DMPS). A homogeneous Au catalyst such as tetrachloroauric acid (HAuCl₄·3H₂O) showed very low alcoholysis activity (2.8% yield, Table 1, entry 2), while a blank experiment (Table 1, entry 1) confirmed the catalytic nature of the selected reaction. A Authin-film-coated quartz substrate showed higher catalytic activity than the homogeneous Au salt catalyst (6.7%, Table 1, entry 3). A commercial citrate-capped 10 nm AuNP catalyst (10Cit-AuNP, Funakoshi Corp.) and a mercaptotetraethyleneglycol-SAM-capped 10 nm AuNP catalyst (10TEG-AuNP) could be efficiently dispersed in the reaction solution, and the silvlether products were obtained in 14.7% and 12.8% yields, respectively (Table 1, entry 6 and 7). Dodecanethiol-SAM-capped 10 nm AuNPs (10Dod-AuNP) displaying noticeable self-aggregation properties in the reaction solution showed unexpectedly higher activity (12.5% yield, entry 8) as compared with the well-dispersed 10Cit-AuNP.

The specific catalytic activity (TOF) of the Au-based materials was calculated on the basis of the surface area of the AuNPs.^[25] In the case of the 10Dod-AuNP, the effective surface area was calculated from the mean diameter of the self-aggregated

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Figure 1. a) Schematic illustration of a AuNP array. b) SEM image of a 10Dod-array. c) Schematic illustration of the metalloenzyme-like catalytic-enhancement mechanism based on molecular encapsulation in the alkanethiol-SAM interface around the AuNPs.

particles (ca. 60 nm) determined by dynamic light scattering (DLS) measurements (Supporting Information, Figure S14). Interestingly, the specific activities of the well-dispersed 10Cit-AuNP and 10TEG-AuNP catalysts were consistent with that of a flat Au thin-film material (4900 and 4300 vs. 4350 h^{-1} , Table 1, entries 3, 6, and 7). These results are consistent with those of previous studies, which state that the size effect is not observed when AuNPs larger than 10 nm are used.^[26] Surprisingly, when the number of surface metal atoms was taken into consideration, the self-aggregated 10Dod-AuNP catalyst showed approximately three times higher activity (TOF = 13 900 h^{-1} ,

Table	1.	Heterogeneously	catalyzed	<i>n</i> -butanolysis	of DMPS. ^a
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10Dod-AuNP

10Dod-array

n-BuOH Entry Catalyst Yield surface area Surface Au atoms TOF of surface Au [× 10⁻⁹ mol] [h⁻¹] [%] [cm²] 1 no catalyst 0 _ 29 8^{b)} 2 HAUCI4•3H₂O 28 Au thin film 6.7 4350 3 1.0 2.31 Dod-Au thin film 4 87 1.0 2.31 5650 Dod-quartz 10 5 18 6 10Cit-AuNP 14.7 2.04 4900 4.49 7 10TEG-AUNP 128 2 04 4 4 9 4300

125

82.8

n-Bu

a)Reaction conditions: DMPS (150 μmol) in n-BuOH (3.0 mL) with Au catalysts (10Cit-AuNP, 10TEG-AuNP, 10Dod-AuNP, 10Dod-array: 2.67 × 10¹¹ mL⁻¹, 2.98 × 10⁻⁸ mol for Au atom) at 25 °C for 1 h; ^{b)}Homogeneous solution.

0.93

1.02

SAM. Unlike a previous study that reported a noticeable decrease (to 40%) in the activity of an alkanethiol-capped Pd(111) catalyst at high temperatures, the results herein revealed a rate enhancement even under roomtemperature conditions.^[23] An SAM-coated Au film (Dod-Au thin film) exhibited higher catalytic activity than the parent bare Au thin film (8.7% vield vs. 6.7% yield, TOF = 5650 vs. 4350 h^{-1} , Table 1, entries 3 and 4), despite the low accessibility of the catalyst surface by the substrate molecules. These results suggest that the alkanethiol-SAM either: 1) acts as an enzyme-like reaction space showing catalytic activity similar to porous co-

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Table 1, entry 8) than did the

well-dispersed 10Cit-AuNP and 10TEG-AuNP catalysts. This unprecedented catalytic enhancement was presumably due to the surface-capping alkanethiol-

ordination compounds,^[8,27-30] or 2) favors the encapsulation and subsequent access of substrate molecules via co-operative intermolecular interactions, as in the case of metalloenzymes (Figure 1c).^[1] To investigate the intrinsic catalytic activity of dodecanethiol-SAM, we developed a dodecanethiol-SAM-coated quartz substrate (Dod-quartz) by means of the self-assembly and a silane-coupling reaction^[31] of dodecyltrimethoxysilane with a piranha-cleaned quartz substrate. Even though the Dod-quartz showed measurable catalytic activity (1.8%, Table 1, entry 5), the catalytic activity of the Dod-Au thin film was confirmed to originate mainly from the Au surface. Furthermore, because of

1 3 5

2.24

8

8

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140

13 900

55 000

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their spherical shape, the AuNPs seemed to favor effective the encapsulation of the substrates, in contrast to the comparatively rigid SAMs on flat surfaces, as suggested by the drastic catalytic enhancement observed for the AuNP-containing materials after alkanethiol-SAM capping (Table 1, entries 3, 4, 6, 8).

Most interestingly, the 10Dod-array showed a remarkably high catalytic activity, affording the product in an 82.8% yield (Table 1, entry 9). In order to calculate the effective number of Au atoms in the 10Dod-array, we assumed that the upper half surface of each AuNP was exposed to the reaction solution (Supporting Information, Figure S8). Following this assumption, the TOF of the 10Dod-array was calculated to be 55 000 h⁻¹, which was nearly four times that of the 10Dod-AuNP (Table 1, entries 8, 9). Although the origin of this catalytic enhancement remains unknown, a similar effect has been reported for AuNP catalysts supported on porous metallic oxides or polymer supports.^[32-41] From these results, the high activity of the 10Dod-array could be attributed to a synergistic combination of the positive effect of the support and the catalytic enhancement effect of the alkanethiol-SAMs. Moreover, the 10Dod-array was highly stable as it could be reused thrice without appreciable loss of catalytic activity (96.1% and 94.8% yields after two and three reuses, respectively, Table S2). The TON was calculated under the same reaction conditions using a smaller 10Dod-array substrate catalyst (substrate size: 0.23×1.00 cm², AuNPs: 1.84×10^{11} particles, Au atoms: 6.85×10^{-8} mol). The calculated TON values were 15 000 (total Au basis) and 200 000 (surface Au basis), indicating that the 10Dod-array showed a much more stable catalytic activity than the homogeneous HAuCl₄ 3H₂O catalyst (TON: 19 000).

In order to investigate the catalytic activity of alkanethiol-SAMcapped AuNPs for a variety of substrates, a series of silanes, alcohols, and AuNP catalysts such as the 10Cit-AuNP, the 10Dod-AuNP, and the 10Dod-array were tested in the silane alcoholysis reaction at room temperature (**Table 2**). In the reactions with the aliphatic silanes (Table 2, entries 1–4), both the 10Cit-AuNP and

Table 2. Alcoholysis of trialkylsilanes catalyzed by AuNP catalysts.^{a)}

R² ∕ R¹−Sį́−H	+	R ³ -OH	AuNP-cat	R ² R ³ R ¹ -Si-O	+	H ₂	
R ²	Ŧ		25 °C	R ²	Ŧ	112	

the 10Dod-AuNP showed poor catalytic activity, especially in the case of the bulkier triisopropylsilane and tris(trimethylsiloxy) silane substrates, thereby suggesting steric-hindrance effects.
The 10Dod-array showed a similar trend, although the activity
values were far higher for this sample. These results strongly
suggest that the alkanethiol-SAM interface around the AuNPs
acts as a hydrophobic encapsulating nanospace in which linear
and long-alkyl-chain-substituted molecules are better accommo-
dated, resulting in higher reactivity for these substrates. The aro-
matic silanes showed a higher reactivity than the aliphatic silanes
for all the AuNP catalysts (Table 2, entries 5, 6, 8), with DMPS
being the most reactive within 1 h of the reaction (lable 2, entry
8). when using IOCIT-AUNP, primary alcohols such as ethanol,
tivities (Table 2: 13 5% 14 7% 14 1% and 13 2% vields entries
7, 8, 11, and 12, respectively), in contrast to sterically bulky sec-
ondary (s-butanol: 1.9% yield) and tertiary alcohols (t-butanol:
0% yield) (Table 2, entries 9, 10). The 10Dod-AuNP and the
10Dod-array showed comparatively higher catalytic activities for
s-butanol (7.1% and 50.3% yields, respectively), although exces-
sive steric hindrance led to poor activities for t-butanol. Interest-
ingly, the 10Dod-AuNP and the 10Dod-array afforded reactivities
different from those afforded by the 10Cit-AuNP for primary
alcohols, depending on their alkyl chain lengths. In this sense,
the 10Dod-AuNP and the 10Dod-array showed the highest reac-
tivities for <i>n</i> -dutanoi (12.5% and 82.8% yields, respectively),
and 37.6% vields), and benzyl alcohol (1.1% and 31.2% vields).
This trend suggests that the hydrophobic nanospace in the
alkanethiol-SAM allows for molecular recognition on the basis
of the relative affinity between the alkanethiol-SAM and the
substrate molecules, which ultimately determines the catalytic

Further insight into the molecular-recognition properties of alkanethiol-SAM was obtained from the relationship between

activity of the SAM-capped AuNPs.

Entry	R1	R ²	R ³	Time [h]	Yield [%]			
					10Cit-AuNP	10Dod-AuNP	10Dod-array	
1	Et	Et	<i>n</i> -Bu	10	1.2	0.2	24.9	
2	<i>i</i> -Pr	<i>i</i> -Pr	<i>n</i> -Bu	10	0.3	0.1	0.9	
3	<i>n</i> -Hex	<i>n</i> -Hex	<i>n</i> -Bu	10	0	0.7	63.6	
4	Me ₃ SiO	Me ₃ SiO	<i>n</i> -Bu	10	0	0	0	
5	Ph	Ph	<i>n</i> -Bu	10	0.9	0.7	95.5	
6	Me	Ph	<i>n</i> -Bu	10	0.6	0.5	91.4	
7	Ph	Me	Et	1	13.5	9.4	65.2	
8	Ph	Me	<i>n</i> -Bu	1	14.7	12.5	82.8	
9	Ph	Me	s-Bu	1	1.9	7.1	50.3	
10	Ph	Me	<i>t</i> -Bu	1	0	0.1	2.3	
11	Ph	Me	<i>n</i> -Hex	1	14.1	5.9	37.6	
12	Ph	Me	Bzl	1	13.2	1.1	31.2	

^{a)}Reaction conditions: Silane (150 μmol) in alcohol (3.0 mL) with 10Cit-AuNP, 10Dod-AuNP (2.67 × 10¹¹ mL⁻¹), or 10Dod-array at 25 °C.





Figure 2. a) Alcoholysis activity for different substrates with varying alkyl chain lengths. b) Alcoholysis yield when using the 10Dod-array (blue plot) and LSPR absorption shift of colloidal 10Dod-AuNP solution (in *n*-BuOH, $2.67 \times 10^{11} \text{ mL}^{-1}$) as a function of temperature.

the reactivities and alkyl chain lengths of the alkanethiols and alcohol substrates. Thus, catalytic alcoholysis reactions of DMPS were carried out at room temperature (RT) for 1 h using three different alcohols (ethanol, *n*-butanol, and *n*-hexanol) and AuNP-array catalysts capped with three different alkanethiols such as *n*-hexanethiol, *n*-dodecanethiol, and *n*-hexadecanethiol (**Figure** 2a). When ethanol was used, the reactivity decreased with an increase in the alkyl chain length of the alkanethiol-SAM, in the following order: *n*-hexanethiol > *n*-dodecanethiol > *n*-hexadecanethiol. Since ethanol is a short-alkyl-chain alcohol, it shows much lower hydrophobic affinity for the alkanethiol-SAM, and therefore, the reaction proceeds with kinetic control. This trend was confirmed for the rest of the alcohol substrates. Owing to steric repulsion, longer-alkyl-chain-substituted substrates



showed lower reaction rates as compared with ethanol derivatives. The activity of the long-chain molecules increased with the chain length of the alkanethiol-SAM. These results clearly showed that in the case of the long-alkyl-chain-substituted alkanethiol-SAM, thermodynamic control prevails as the hydrophobic interaction between the SAM and the substrate molecules contributes to an increase in the reactivity. Interestingly, in the case of the n-dodecanethiol- and n-hexadecanethiol-capped AuNP array catalysts, the moderately long-alkyl-chain-substituted n-butanol gave the highest reactivity (85.9% and 78.8% yields, respectively) because of the competing kinetic control and thermodynamic control. The important role of hydrophobic affinity was further supported by a catalytic alcoholysis reaction in a mixed alcohol solvent (EtOH:n-BuOH:n-HexOH = 1:1:1) with the 10Dod-array, where the catalytic reaction proceeded slowly to afford silvlether products in the following yield: *n*-hexyloxysilylether > *n*-butoxysilylether > n-ethoxysilylether (Supporting Information, Figure S10). These results clearly indicate that the alkanethiol-SAM acts as a reaction field showing molecular-recognition properties.

The behavior of alkanethiol-SAM as a soft-interface was identified from the temperature dependence of the catalytic activity of the 10Dod-array and the self-aggregation property of the 10Dod-AuNP colloid. Catalytic alcoholysis reactions of DMPS were carried out at various temperatures in n-BuOH using the 10Dod-array as the catalyst. The yield vs. temperature plot showed a characteristic nonlinear profile, with the maximum catalytic activity at around 25 °C (Figure 2b). A similar temperature dependence was observed with the Dod-Au film and the 10Dod-AuNP. but not with the 10Cit-AuNP (Supporting Information, Figure S15). Remarkably, this temperature dependence resembled that of

natural enzymes with specific optimum temperatures originating from their soft structures based on non-covalent bonding interactions.^[1] In order to examine the origin of this temperature dependence, the self-aggregation property of the parent 10Dod-AuNP colloids in *n*-BuOH was investigated by localized surface plasmon resonance (LSPR), ¹H NMR spectroscopy, and DLS measurements. The LSPR band of the 10Dod-AuNP redshifted gradually from 550 nm with increasing concentration, saturating at 557 nm over 6.0×10^{11} mL⁻¹ (Supporting Information, Figure S12). In contrast, the hydrophilic 10Cit-AuNP and 10TEG-AuNP did not show such a concentration dependency (Supporting Information, Figure S16). This concentration dependency revealed the self-aggregation property of the 10Dod-AuNP, as the above-mentioned red-shift was caused



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by the close packing of the AuNPs (Supporting Information, Figure S4).^[42] The DLS measurements also showed a similar concentration dependency for the formation of larger aggregated particles of the 10Dod-AuNP (diameter: ca. 130 nm) over $6.0 \times 10^{11} \text{ mL}^{-1}$ (Supporting Information, Figure S14). In the ¹H NMR spectra, a new triplet signal due to the terminal methyl proton of the dodecanethiols bound to AuNPs appeared in the up-field region, and the peaks due to the internal methylene protons broadened with increasing concentration (Supporting Information, Figure S17), clearly indicating the formation of self-aggregated polymer-like particles with a bilayer structure of interdigitated alkanethiol-SAMs.^[43] This concentration dependence is typical of self-aggregation behavior based on non-covalent bonding interactions, which is evidence for the molecular encapsulation property of the alkanethiol-SAM around the AuNPs through intermolecular hydrophobic interactions. Most importantly, the temperature-dependent UV-vis extinction spectra of the 10Dod-AuNP dispersed in *n*-BuOH (2.7 \times 10¹¹ mL⁻¹) indicated that dissociation of the self-aggregated particles started at around 25°C (Figure 2b and Supporting Information, Figure S13), which is close to the temperature at which the 10Dod-array shows a high non-linear catalytic activity. This coincidence strongly suggests that the observed temperature dependence of the catalytic activity for the 10Dod-array is due to the thermal stability of the dodecanethiol-SAM around the AuNPs. This relationship between catalytic activity and thermal stability is similar to the origin of the optimal temperature in the case of enzymes and results from the competition between two opposite effects: the kinetic effect, which increases the reaction rate with increasing temperature, and the thermodynamic effect, which decreases the catalytic activity by thermal denaturation of the protein backbone.^[1] Therefore, the non-linear high catalytic activity of the 10Dod-array probably resulted from the competition between the kinetic and thermodynamic driving forces affecting the molecular encapsulation property of the alkanethiol-SAM. The combination of such a catalytic enhancement effect of the alkanethiol-SAM at room temperature and the linear temperature dependence of the background catalytic activity of the AuNPs affords the characteristic temperaturedependent catalytic activity of the 10Dod-array, as depicted in Figure 2b.

In conclusion, we found an unprecedented catalyticenhancement effect of alkanethiol-SAMs on AuNP systems. The product yields observed in a series of catalytic silane alcoholysis reactions strongly suggested that the alkanethiol-SAMs around the AuNPs act as a reaction space for encapsulating substrate molecules. This behavior was based on molecular recognition through intermolecular hydrophobic interactions, because of which catalytic reactions between the encapsulated molecules and the AuNPs were highly accelerated. Because of the synergistic combination of the catalytic enhancement effect of the alkanethiol-SAM and the NP immobilization effect, the 10Dod-array exhibited an excellent catalytic activity for a variety of silane alcoholysis reactions, with a maximum TOF of 55 000 h⁻¹ and TON of 200 000. The effect of temperature and concentration on the self-aggregation of the colloidal 10Dod-AuNP revealed significant thermal instability of the hydrophobic reaction space constructed of the alkanethiol-SAM. As a result, the 10Dod-array showed a high catalytic activity at low temperatures

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(even at room temperature), in contrast with the other AuNP catalysts, which required higher temperatures.^[35,40] This paper is the first to report on the catalytic-rate-enhancement effect of alkanethiol-SAMs through hydrophobic-interaction-based molecular encapsulation, which is opposite to the conventional effect (i.e., decrease in the catalytic activity after complete capping of the catalyst surface). This new concept enables us to design highly active and selective nanoparticle catalysts based on the molecular-recognition properties of SAM interfaces.

Experimental Section

Fabrication of Alkanethiol-SAM-Capped AuNP-Arrays: AuNP arrays such as 10Hex-array, 10Dod-array, and 10Hexd-array were fabricated by our previously reported hybrid method: electrophoresis under solventevaporation conditions and chemical immobilization of AuNPs on the thiol-terminated flat surface of Au-thin-film-coated quartz substrates ($10 \times 10 \times 0.6 \text{ mm}^3$) (Supporting Information, Figure S1).^[24] The synergistic combination of electrophoresis and solvent evaporation gave almost complete coverage (90%) of the AuNP arrays on the substrates. Annealing enhanced the substitution of thiols between the substrates and the AuNPs in the first layer. After sonication cleaning for 1 min in *n*-hexane, the upper AuNP layers were removed, and chemically immobilized monolayer AuNP arrays were obtained. Scanning electron microscopy (SEM) measurements and small-angle X-ray scattering (SAXS) analysis revealed the formation of regular-hexagonal AuNP arrays on the entire substrate (Supporting Information, Figure S2–S4).

Reaction Procedures for Immobilized AuNP Catalysts: A AuNP-array substrate ($1.0 \times 1.0 \text{ cm}^2$) was suspended from a poly(tetrafluoroethylene) (Teflon)-coated wire in a reaction vessel to immerse the substrate completely inside solution. Alcohol (3.0 mL) and silane ($150 \mu \text{mol}$) were added, and the reaction mixture was stirred in a temperature-fixed water bath. The yield was determined by gas chromatography (GC) analysis. All of the reaction yields reported were averaged values from 3 time experiments.

Reaction Procedures for Colloidal AuNP Catalysts: A colloidal solution of AuNPs dispersed in *n*-hexane (10Dod-AuNP) or water (10Cit-AuNP) was prepared to have a concentration of 2.7 × 10¹¹ mL⁻¹, with the same number of particles immobilized on the 10Dod-array, by checking the concentration by UV-vis extinction spectroscopy. The concentration-fixed colloidal AuNP solution was centrifuged and dried under vacuum to remove solvent. The dried AuNP was dispersed into alcohol (3.0 mL) by sonication and silane (150 µmol) was added into the solution. The colloidal solution was stirred in a temperature-fixed water bath. The yield was determined by GC analysis. All of the reaction yields reported were averaged values from 3 time experiments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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