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Introduction

Supported noble metals have garnered considerable attention over the past few decades due to their versatility, which has been demonstrated by their application in various catalytic protocols for the synthesis of diverse chemicals.^{1,2} Gold nanoparticles supported on high-surface-area oxides have been used in remarkable heterogeneous catalysis research,^{3,4} and supported gold nanoparticles have been applied in many areas such as chemical processing, sensors, fuel cells, and pollution control.^{5–7}

The widespread use of supported gold in catalysis is attributed to its high chemoselectivity.⁸ The catalytic properties of the heterogeneous system are quite different from those of both gold and the metal oxide support due to characteristic synergistic effects between the oxide support and the gold

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Catalytic synergy of Au@CeO2-rGO nanohybrids for the reductive transformation of antibiotics and dyes[†]

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Au@CeO₂-rGO nanohybrids (NHs) are synthesized using sucrose *via* a hydrothermal method. The interfacial interactions between gold encapsulated in CeO₂ and rGO are observed by Raman and X-ray photoelectron spectroscopy (XPS). The optical properties and crystallinity of the nanohybrids are determined by using UV-Vis and X-ray diffraction (XRD), respectively. Elemental mapping using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) clearly demonstrates the Au@CeO₂ core-shell sequence, in which the core of electron-dense Au NPs is encapsulated by the spherical CeO₂ shell; these Au@CeO₂ particles are then decorated on the reduced graphene oxide (rGO) nanosheets. As an application of the synthesized Au@CeO₂-rGO nanohybrids, the reductive transformation of organic contaminants present in wastewater is accomplished. Ampicillin (AMP) gives 6-methyl-3phenylpyrazin-2-ol and ciprofloxacin (CIP) affords 1-cyclopropyl-6-fluoro-3-(hydroxymethyl)-7-(piperazin-1-yl)-2, 3-dihydroquinolin-4(1*H*)-one. Moreover, rhodamine B (RhB) forms (2-(3,6-bis(diethylamino)-9*H*-xanthen-9yl)phenyl)methanol and Congo red (CR) produces benzidine and 3,4-diaminonaphthalene-1-sulfonic acid. The elimination of the antibacterial activities of AMP and CIP using reductive degradation and transformation shows the possibility of decreasing exposure of bacteria to antibacterial chemicals. The transformed by-product of CR is considered to be a potential anti-AIDS agent.

nanoparticles, which can enhance the catalytic activity.⁹ In addition to electronic interactions between the oxide support and the noble metal, the size, charge, and porosity of the metal nanoparticles can influence catalytic performance, as can the properties and morphology of the oxide support.¹⁰

While several inorganic oxides as catalysts have been reported, including CeO_2 ,¹¹ Fe_2O_3 ,¹² SiO_2 ,¹³ SnO_2 ,¹⁴ TiO_2 ,¹⁵ and ZrO_2 ,¹⁶ there has been significant interest in CeO_2 due to its high oxygen storage capacity, ample oxygen vacancy defects, and relative ease of transition between the oxidation states III and IV, all of which enhance the catalytic efficiency of the material. However, there have only been a few reports on the fabrication of noble metal NPs@CeO₂ core-shell nano-composites decorated on reduced graphene oxide (rGO).¹⁷⁻¹⁹

From the last couple of decades, organic pollutants are crucial to the contamination of water resources. Above all, the pollution created by antibiotics and organic dyes has become a significant threat to the environment and human health.^{20,21} Antibiotics like ampicillin (AMP) and ciprofloxacin (CIP) have been found in surface and underground water due to wastewater leakages.^{22,23} This can have undesirable consequences, such as contributing to antibiotic resistance in bacteria and endocrine disruption in the human body.^{24,25} Current methods



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Paper

Among the various water contaminants, organic dyes are toxic even at lower concentrations. Besides their prominent effect on health, organic dyes cause harmful effects, like alteration of the oxygen demand, consumption of oxygen molecules, and reduction of water transparency, and ultimately deteriorate the aquatic system.³¹ Most of the azo dyes are reported to be very toxic to both the environment and human health,³² and are considered a major contributor to environmental pollution. The presence of dyes in the wastewater generated by textile factories is of great environmental concern not only because of the release of dye molecules into the water, but also because other toxic substances can be produced through hydrolysis and oxidation reactions.33-35 Therefore, development of a facile, sensitive and fast protocol for the reductive transformations of antibiotics and dyes in aqueous media is of high interest and in demand.

Ceria has been widely used as a promising material for the elimination of organic pollutants from wastewater.^{36,37} Nanosized CeO₂ has high electronic conductivity³⁸ and is used as UV-protection material due to its strong surface plasmon resonance.³⁹ Ceria-based nanocomposites can be used as photocatalysts in visible light.⁴⁰

The water contamination caused by antibiotics and dyes is of great concern due to the significant threat for environment and human health. Therefore, it is quite necessary to transform the contaminants like antibiotics and dyes from wastewater before they get released into nature. Considering the importance and usefulness of metal NPs/oxide core–shell nanocomposites in transformation of water contaminants, we herein describe a new approach to the preparation of Au@CeO₂–rGO NHs using sucrose *via* a hydrothermal route. We further report on the catalytic synergy of these NHs for the reductive transformation of antibiotics (AMP and CIP) and dyes (RhB and CR) as a model study for removing undesirable contaminants from wastewater.

Experimental section

Synthesis of Au@CeO2

Sucrose (10 mg) was dissolved in water (20 mL), 0.2 mL of a 10 mM aqueous solution of $HAuCl_4$ was then added dropwise while stirring over 20 min. $CeCl_3$ ·7H₂O (70 mg) was added to the above mixture and stirred intensely until a clear yellow solution was formed. The solution was then kept in a stainless-steel Teflon-sealed autoclave and kept for 10 h at 180 °C. The resulting deep brown precipitate was centrifuged and washed thoroughly with water. Finally, the brown residue was calcined in a muffle furnace at 600 °C for 5 h.

Preparation of GO

GO was prepared using a slightly modified version of Hummers' method.⁴¹ Concentrated sulfuric acid (10 mL) was cooled, and graphite powder (0.4 g) was mixed and stirred vigorously for 10 min. During stirring, KMnO₄ (0.8 g) was slowly added to the suspension. The suspension was agitated for 15 min below 20 °C, and the temperature was increased to 35 °C for 30 min. After completion of the reaction, effervescence decreased and the mixture slowly thickened, changing to a brownish-gray color. Eventually, 100 mL of DI water was gradually added to the mixture and the temperature was raised to 98 °C for 15 min. The obtained suspension was centrifuged, and the residue was thoroughly washed with 5% hydrochloric acid (5 mL) until the aqueous layer no longer produced salt with barium chloride. The final GO residue was washed with acetone, and the obtained solid was dried in a vacuum oven for 5 h at 80 °C and stored.

Synthesis of Au@CeO2-rGO NHs

GO (50 mg) was diffused in water in a Teflon cup. The mixture was further sonicated to disperse the GO layers. Au@CeO₂ (50 mg) was added to the dispersed GO along with 10 mg of sucrose, and the pH was adjusted to make it alkaline. The Teflon cup was sealed and heated for 10 h at 180 °C. The Au@CeO₂-rGO NHs were collected as a black solid and dried in an oven for 12 h at 80 °C, and then processed for further use.

Reductive transformation of AMP, CIP, RhB, and CR

The reductive transformations of AMP, CIP, RhB, and CR were monitored using UV-Vis spectroscopy, ¹H, and ¹³C NMR spectroscopy, and gas chromatography-mass spectroscopy. Au@CeO₂-rGO NHs (2 mg) were added to solutions of AMP (0.025 mM in H₂O), CIP (0.025 mM in H₂O/DMSO), RhB (0.025 mM in H₂O/DMSO), or CR (0.025 mM in H₂O/DMSO) at room temperature. NaBH₄ (37.83 mg, 1.0 mmol) was added to the above mixture, which was further heated for 1 h at 100 °C. The reaction mixture was then isolated by extracting with ethyl acetate and evaporated using a reduced pressure evaporator. The residue was isolated by column chromatography using 30% ethyl acetate in hexane on silica gel to obtain the products, the structures of which were determined by spectroscopic analysis (see the ESI† for details).

Elimination of antibacterial activity of AMP and CIP

The antibacterial activity of the reduced compounds 2 and 4 was screened against Gram-positive bacteria, *Staphylococcus aureus* (KCTC-1916) and Gram-negative bacteria, *Escherichia coli* (KCTC-1924) using a modified version of the Kirby–Bauer disk diffusion method.⁴² Bacterial strains were purchased from the Korean Collection for Type Cultures (KCTC) and cultivated in 10 mL of fresh DifcoTM nutrient agar for 24 h. Then, precisely 100 μ L of a fresh batch of bacterial suspension was distributed in this DifcoTM nutrient agar. The optical density of the freshly prepared suspension of bacteria was found to be 0.7 at 595 nm. The paper discs (8 mm in diameter) were autoclaved and then

thoroughly soaked with 20 mL of the test sample (100.00 μ g mL⁻¹), transferred to the agar plate and incubated at 37 °C. The inhibition zones observed on the discs were analyzed at the end of the incubation period, with the agar depth in the plate being an evaluation factor. Filter paper discs saturated with ciprofloxacin and ampicillin were used as positive controls, whereas negative control was prepared with DMSO saturated on discs.

Results and discussion

Role of sucrose in the synthesis of Au@CeO2-rGO NHs

The Au@CeO2-rGO NHs were fabricated by using sucrose as a green protocol. Scheme 1 indicates a general approach for the synthesis of Au@CeO2-rGO NHs. While sucrose is a nonreducing sugar, chloroauric acid hydrolysis of sucrose produces fructose and glucose, which are responsible for the bioreduction of the metal salts to nanoparticles.⁴³ Thus, the Au³⁺ ions were first reduced to Au⁰ under hydrothermal conditions by glucose or fructose to form the cores. The glucose was carbonized during the hydrothermal process due to dehydration. The carbonized glucose or fructose formed carbon dioxide reacting with oxygen and diffused in the air after calcined at 600 °C for 5 h. At the same time, the CeO₂ shells formed from Ce^{3+} in two steps, with the first being the formation of cerium hydroxide during the hydrothermal treatment in the presence of NH₄OH, followed by dehydration and oxidation to form Ce⁴⁺, as confirmed by XPS.⁴⁴

Characterization of Au@CeO2-rGO NHs

Hydro-

Fructose Au³⁺ ions
 Ce³⁺ ions

Glucose

thermal

The optical properties of Au@CeO2-rGO NHs were preliminarily examined using UV-Visible spectroscopy (Fig. S1, ESI⁺). A welldefined absorption spectrum was obtained, with a distinct peak at about 300 nm being attributed to the characteristics of the CeO_2 nanoparticles,⁴⁵ while that at 210 nm was due to the rGO. Furthermore, the presence of gold in the Au@CeO2-rGO NHs was evidenced by a typical surface plasmon resonance band at about 540 nm.⁴⁶ The red shift compared to the peak of Au NPs at 525 nm indicates the presence of the surrounding medium and its morphological characteristics.47 Thus, the stable nanostructure of Au@CeO2-rGO NHs and its prominent absorption bands are due to the interactions when gold is encapsulated by CeO2 and then, decorated on rGO.48 This phenomenon demonstrates the

Scheme 1 General strategy for the fabrication of Au@CeO2-rGO NHs.



Fig. 1 (a) XRD patterns of Au (JCPDS No. 34-0394), CeO₂ (JCPDS No. 34-0394), Au@CeO2, and Au@CeO2-rGO NHs. (b) Raman spectra of Au@CeO₂ and Au@CeO₂-rGO NHs, inset: CeO₂ peaks. (c) N₂ adsorption-desorption isotherm of Au@CeO2-rGO NHs. (d) Pore size distribution of Au@CeO2-rGO NHs.

synergy between Au, CeO2, and rGO when forming Au@CeO2-rGO NHs.49

XRD was used to determine the structure of the (Fig. 1a). The XRD peaks at 2θ = 37.75°, 43.98°, 64.24°, and 77.30° were indexed as (111), (200), (220), and (311), respectively, and correspond to face-centered cubic gold reflective planes (JCPDS No. 34-0394).¹¹ In addition, the peaks at $2\theta = 28.10^{\circ}$, 32.65° , 47.10°, 55.98°, 58.73°, 69.04°, 76.35°, 78.75°, and 88.15° are attributed to the (111), (200), (220), (311), (222), (400), (331), (420), and (422) reflection planes, respectively, of the fluorite CeO₂ (JCPDS No. 34-0394).¹⁴ The XRD pattern of the Au@CeO₂rGO NHs is dominated by the CeO₂ reflections, as the CeO₂ shell wraps around the Au core.⁵⁰ The presence of a broad peak at about 25° corresponds to the (002) plane of the reduced graphene due to its reduced oxygen-rich functionality, which clearly suggests formation of Au@CeO2-rGO.51

The interfaces between the components were analyzed by comparing their Raman spectra (Fig. 1b). The Raman spectrum of CeO_2 shows a distinct peak at about 454 cm⁻¹, which is due to the F_{2g} vibrational mode of the fluorite phase, ^{52,53} while the broad peak at a 600 cm⁻¹ is correlated with the oxygen vacancies introduced into the ceria lattice.54 The shifting of the F_{2g} mode of CeO₂ in the spectrum of Au@CeO₂ was due to strain effects resulting from the core-shell interactions between Au and CeO_2 .⁵⁵ However, the Au bands were not clearly detectable in the spectrum of Au@CeO2 as their intensities were very low compared to those of the CeO₂ bands, as the Au core was shielded by the CeO₂ shell.⁵⁶ The Raman spectrum of the nanohybrid also showed the presence of rGO, with two D and G graphene bands being visible. The D-band is related to the 1st order sp³ carbons scattering, while the G-band refers to the sp²-hybridized carbons vibration. The I_D/I_G ratio for rGO in the nanohybrids was 1.02, which is associated with a rise in the

Au@CeO2

Sucrose thermal

Au@CeO2-rGO NHs

Hydro-

GO

Calcination

Au core

CeO₂ shell

extent of disorder and defects, and a diminishing the average sp² domain size.⁵⁷

The nitrogen adsorption–desorption isotherms were measured to analyze the porosities of the synthesized materials, including their specific surface areas and pore diameters. The nitrogen adsorption–desorption isotherm and the corresponding pore size distribution graph of the Au@CeO₂–rGO NHs are shown in Fig. 1c and d, respectively. The specific area of a surface offers ample active sites that are critical for enhancing catalytic activity.⁵⁸ The BET specific surface area of the Au@CeO₂–rGO NHs was found to be 47.62 m² g⁻¹, and the average pore size was estimated to be 3.80 nm.

XPS was conducted to analyze the surface chemistry of the Au@CeO2-rGO NHs, providing information about the elemental composition and oxidation states. The Ce 3d XPS spectrum was dominated by the Ce⁴⁺ state, but the two peaks at around 884.0 and 894.5 eV correspond with the Ce³⁺ valence state (Fig. 2a).⁵⁹ The unsymmetrical O 1s peak could be deconvoluted into two sections (Fig. 2b), with the peak at 529.4 eV confirming the surface lattice oxygen species from cerium oxide, while the other high binding energy peak at about 531.1 eV is known to be related to surface-absorbed oxygen species.60 The auger peak at about 533.4 eV was attributed to hydroxide or dissociated molecular oxygen.⁶¹ Likewise, the XPS spectra for the Au 4f electrons showed binding energies of 84.7 and 87.7 eV, due to $4f_{7/2}$ and $4f_{5/2}$, respectively, with a peak distance of 3.87 eV (Fig. 2c). The prominent peak at about 84.7 eV (Au $4f_{7/2}$) is due to Au⁰, although it is slightly shifted due to the core Au $4f_{7/2}$ electrons being shielded by CeO2.62,63 The XPS spectra were calibrated at 284.9 eV using the C 1s value (Fig. 2d).

The representative HAADF-STEM image of Au@CeO₂ clearly shows the core–shell pattern of the nanocomposites, in which an electron-dense core Au NP was encapsulated by a spherical CeO₂ shell (Fig. 3a). The HRTEM image clearly shows core gold nanoparticles surrounded by mesoporous CeO₂ (Fig. 3b).



Fig. 2 XPS for (a) Ce 3d electrons and (b) O 1s electrons, (c) XPS for Au 4f electrons, and (d) C 1s electrons at 284.8 eV.



Fig. 3 (a) HAADF-STEM image and (b) HRTEM image of Au@CeO₂. (c) HAADF-STEM image and (d) TEM image of CeO₂.

The morphology of CeO_2 was observed to change from a spindled shape (Fig. 3c and d) to a mesoporous form once Au was encapsulated by CeO_2 . This can be attributed to the synergistic effects of the gold on the ceria in Au@CeO₂ nanocomposites decorated over rGO. The structural changes observed by introducing multimetallic system includes the mixing of one type of metal by another one on the surfaces, electron charge transfer between metal atoms, and interfacial interactions between metal phases.⁶⁴

The size and morphology of the $Au@CeO_2-rGO$ nanohybrids were analyzed by TEM images. TEM images are shown in Fig. 4a–d, with scale bars of 50 and 20 nm. The size of Au was found to be 20 nm. EDS analysis exhibited the characteristic EDS peaks for Au, Ce, O, and C, together with Cu observed from the Lacey copper grid (Fig. S2, ESI†).

The thermal stability of Au@CeO₂-rGO NHs was confirmed by the TG–DTA analysis (Fig. S3, ESI[†]). The initial weight loss of 2.57% at around 100 °C was due to the evaporation of adsorbed moisture and other volatile matters contained in the nanohybrids. This feature was further reflected by the endothermic peak at approximately 50 °C. The second weight loss of 3.80% can be attributed to the loss of some oxygen containing functional groups present in the rGO.⁶⁵ This showed that the Au@CeO₂rGO NHs were stable at high temperature, leaving the residual mass of 93.63%. The high temperature stability of Au@CeO₂-rGO NHs leads to synergism of Au, CeO₂ and rGO.⁶⁶

Reductive transformation of AMP, CIP, RhB, and CR

The reductions of AMP, CIP, RhB, and CR (Scheme 2) were monitored by UV-Vis, FTIR, NMR, and GC-MS analyses (see the ESI† for details). A prominent absorption peak at around



Fig. 4 TEM images of Au@CeO2-rGO at 50 (a and b) and 20 nm (c and d).



 $\mbox{Scheme 2}$ Reductive transformation of AMP, CIP, RhB, and CR using Au@CeO_2-rGO NHs.

345 nm in the UV-vis spectrum indicated the transformation of AMP, as AMP itself displayed no absorption peak (Fig. S4a, ESI†). The CIP peak at about 280 nm vanished and a new peak emerged at around 225 nm, showing the transformation of CIP to its reduced product (Fig. S4c, ESI†). The peak disappearance at 550 nm confirmed the transformation of RhB (Fig. S5a, ESI†). In the presence of NaBH₄ and Au@CeO₂-rGO NHs, the absorption peak of CR at 500 nm disappeared, which supported the transformation of this material into its product (Fig. S5c, ESI†). These results show that

organic pollutants in was tewater can be sufficiently transformed using the ${\rm Au}@{\rm CeO_2-rGO}$ NHs.

Plausible mechanism for the reductive transformation of AMP

Scheme 3 shows a feasible mechanism for the reduction of AMP. Metal nanohybrids activate the carbonyl group of 1 to give complex 1'. The nucleophilic addition of water to 1' gives intermediate A through the ring opening of the β -lactam ring of AMP,⁶⁷ which undergoes C-S bond cleavage of the thiazolidine ring by a retro-Michael-type reaction to afford intermediate B. The Michael-type addition of water to B affords another intermediate C, and is followed by breaking of the C-N bond to give D and E. Intermolecular cyclization of D furnishes intermediate F, and the fragmented molecule E affords G by reduction of carboxylic acid by hydrogen on the catalyst surface. Elimination of water followed by enolization and aromatization produces intermediate H, which undergoes a reduction of the carboxylic acid moiety at the benzylic position by hydrogen on the catalyst to give the final product, 2. The compound 2 structure was confirmed by its spectral data analysis, and compound G was confirmed in the crude reaction mixture by GC-MS.

Plausible mechanism for the reductive transformation of CIP

Scheme 4 shows a feasible mechanism for the reduction of CIP. The liberated H_2 from NaBH₄ is activated through the electronically supported Au in the Au@CeO₂-rGO NHs. The hydrogenation of the double bond and subsequent reduction of the carboxylic acid moiety of CIP (3) provides the product 4, whose structure was confirmed by analyzing its spectral data.

Plausible mechanism for the reductive transformation of RhB

Scheme 5 demonstrates a plausible mechanism for the reduction of RhB. First, the hydride anion from NaBH₄ attacks 5 to afford LeucoRhB (6), which is reduced by hydrogenation on the catalyst to give product $7.^{68-70}$ The isolated compound 7 was identified by its spectral data.



Scheme 3 Plausible mechanism for the reductive transformation of AMP.



Scheme 4 Plausible mechanism for the reductive transformation of CIP.



Scheme 5 Plausible mechanism for the reductive transformation of RhB.

Plausible mechanism for the reductive transformation of CR

Scheme 6 shows a plausible mechanism for the reductive degradation of CR. The reduction of 8 by hydrogen on the catalyst gives intermediate 9, which is subjected to N–N bond cleavage to furnish 10 and 11. These two compounds were verified by the spectral data analysis. The transformed by-product, 3,4-diaminonaphthalene-1-sulfonic acid (11), is considered a potential anti-AIDS agent.⁷¹

Elimination of antibacterial activity of AMP and CIP

Antibacterial activity tests were conducted using reference species of *Escherichia coli* and *Staphylococcus aureus*. Fig. S5 (ESI[†]) shows the changes in the inhibition zones of AMP and CIP solutions after their reduction. The zone of inhibition of AMP showed that it possessed antibacterial activity; however, the transformed product 2 obtained from AMP did not show any zone of inhibition (Fig. S6a and b, ESI[†]). The CIP solution also showed antibacterial activity with a zone of inhibition, but the transformed product of CIP (4) did not show any antibacterial activity (Fig. S6c and d, ESI[†]). However, previous reports have demonstrated the elimination of the antibacterial activity of CIP



Scheme 6 Plausible mechanism for the reductive transformation of CR.

through the fragmentation of the quinolone moieties or the piperazine ring.^{72,73} These results confirmed the possibility of removing the antibacterial activities of AMP and CIP.

Synergy of Au@CeO2-rGO NHs

We have performed the control experiment. No product was detected without the use of Au@CeO2-rGO nanohybrids as the catalyst, confirming that Au@CeO2-rGO nanohybrids play a catalytic role in the reductive transformations of organic dyes and antibiotics. Moreover, the reaction rate of Au@CeO2-rGO NHs ternary catalysts was greater than that of CeO2-rGO and Au@CeO₂ nanocomposites. The significant catalytic activity of the ternary Au@CeO2-rGO NHs catalysts was due to the highly dispersed Au nanoparticles, which serve as an electron relay in the reaction mixture.⁷⁴ The integration of graphene nanosheets with metal oxide and noble metal offer massive opportunities toward potent utilities of graphene based composites.75,76 There is a strong synergistic interaction among graphene nanosheets, metal oxide and noble metal, which can significantly enhance the catalytic properties of noble metal nanostructures.77 Moreover, the synergistic interactions and support effect between ternary components play a vital role in their catalytic activity and stability.78 Thus, the synergistic effect comprising the combination of graphene, metal oxide, and noble metal is attributed to the enhanced catalytic performance.

Conclusions

Au@CeO2-rGO NHs were fabricated by using sucrose as a green hydrothermal approach. The optical and surface electronic properties of Au@CeO2-rGO NHs revealed the synergistic effects between the different materials in the catalytic active site of the Au@CeO2-rGO NHs. The synthesized nanohybrids were used as effective catalysts to reduce antibiotics and dyes using very mild NaBH₄ as a hydrogen source. The transformed by-product of CR (11) is considered to be a potential anti-AIDS agent. The elimination of the antibacterial activities of AMP and CIP using reductive degradation and transformation showed the possibility of decreasing exposure of bacteria to antibacterial chemicals, which would decrease the potential for the development of antibacterial resistance. This facile experimental protocol for the reductive transformation of antibiotics and dyes using the Au@CeO2-rGO NHs as a nanocatalyst is considered to be used in industrial application.

Conflicts of interest

There are no conflicts to declare.

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