Synthesis and Characterization of Pd@M$_{x}$Cu$_{1-x}$ (M = Au, Pd, and Pt) Nanocages with Porous Walls and a Yolk–Shell Structure through Galvanic Replacement Reactions


Abstract: This paper describes the synthesis of Pd@M$_{x}$Cu$_{1-x}$ nanocages with a yolk–shell structure through galvanic replacement reactions that involve Pd@Cu core–shell nanocubes as sacrificial templates and ethylene glycol as the solvent. Compared with the most commonly used templates based on Ag, Cu offers a much lower reduction potential (0.34 versus 0.80 V), making the galvanic reaction more easily to conduct, even at room temperature. Our structural and compositional characterizations indicated that the products were hollow inside, and each one of them contained porous M–Cu alloy walls and a Pd cube in the interior. For the Pd@Au$_{x}$Cu$_{1-x}$ yolk–shell nanocages, they displayed broad extinction peaks extending from the visible to the near-IR region. Our mechanistic study revealed that the dissolution of the Cu shell preferred to start from the slightly truncated corners and then progressed toward the interior, because the Cu {100} side faces were protected by a surface capping layer of hexadecylamine. This galvanic approach can also be extended to generating other hollow metal nanostructures by using different combinations of Cu nanostructures and salt precursors.

Keywords: copper · galvanic replacement · gold · nanocages · yolk–shell structure

Introduction

Nanostructures with hollow interiors and porous walls have many interesting properties, such as enlarged surface areas, reduced densities, and tunable compositions in comparison with their solid counterparts. Considerable efforts have been made in the preparation of a wide variety of hollow nanostructures as well as exploration of their applications in a number of areas, including catalysis, energy conversion, and site-specific drug delivery.[1–6] In particular, nanocages made of noble metals are of great interest because of their tunable localized surface plasmon resonance (LSPR) peaks from the visible to the near-IR region,[7,8] and the enhanced electrochemical catalytic activity.[2,9] Up to now, methods based on chemical etching,[10,11] self-templating,[12,13] Kirkendall effect,[14,15] and galvanic replacement[16–21] have been developed to prepare various hollow structures. Among them, galvanic replacement seems to be the most versatile one. The driving force of galvanic replacement is the difference of electrical potential between two metals. In the past decade, because of its relative low standard reduction potential, various Ag nanostructures have been explored as the sacrificial templates for various noble-metal salt precursors such as HAuCl$_4$, Na$_2$PdCl$_4$, and Na$_2$PtCl$_4$ to generate Au–Ag, Pd–Ag, and Pt–Ag alloy hollow/porous nanostructures.[18–21] To this end, our group has studied the Au–Ag nanocages prepared through galvanic replacement between Ag nanocubes and HAuCl$_4$, as well as their fantastic LSPR properties for biomedical applications.[7,8,22] Similar approaches have also been reported by other groups using Ag nanocrystals with various morphologies for the preparation of hollow metal nanostructures.[23–26] However, during the replacing process, the Ag $^+$ ions generated from a Ag template could precipitate out with Cl$^-$ to generate insoluble AgCl as a byproduct, which might coat on the targeted nanostructures at room temperature, and negatively affect the galvanic reaction.[16,20] Meanwhile, using Ag nanostructures as sacrificial templates can possibly introduce cost concerns for a
potential of Cu
preparing noble-metal nanocages. The standard reduction
date to substitute Ag nanocubes as sacrificial templates for
practical and large-scale application. Hence, seeking a less-
expensive template for synthesizing noble-metal hollow
nanostructures through galvanic replacement is significant and
desirable.

In principle, Cu nanocubes could be an appropriate candi-
date to substitute Ag nanocubes as sacrificial templates for
preparing noble-metal nanocages. The standard reduction
potential of Cu+/Cu pair (0.34 V versus the standard hydro-
gen electrode, SHE) is much lower than that of Ag+/Ag
pair (0.8 V versus SHE), which could provide a stronger
driving force for galvanic replacement with a broader range
of salt precursors. In this respect, the conditions for galvanic
replacement with Cu nanocubes can be relatively mild, com-
pared to what is typically involved in Ag nanocubes.[37]

Meanwhile, the generated Cu** ions during the replacement
process would remain in the solution in an ionic state with-
out forming an insoluble byproduct, eliminating the need to
purify the products. Significantly, the abundance of Cu is
1000 times more than Ag in nature, while the cost is only
one percent of that of Ag, making Cu nanostructures a per-
fected candidate as the sacrificial templates.[38] Till now, very
few galvanic processes involving Cu-based nanostructures
have been reported. Liu and Walker demonstrated the diffu-
sion of Cu during an unconventional galvanic replacement
between Cu–Cu S hetero-oligomers and HAuCl4 in an or-
ganic environment.[39] They found that the controlled addi-
tion of HAuCl4 led to the preferential outward diffusion of
Cu, forming Au–Cu alloy nanowires. In another example,
Sen and co-workers reported that Ag nanostructures, includ-
ing nanodisks, nanobelts, and dendrites, can be formed by
galvanic replacement between Cu nanoparticles and
AgNO3.[40] In our previous work, noble-metal nanotubes
were also obtained by using galvanic replacement reaction
that involved Cu nanowires.[37]

One of the major obstacles for using well-defined Cu
nanostructures as templates in galvanic replacement is the
absence of an ability to control their synthesis. Although
several publications in the literature have reported the syn-
thesis of Cu nanocubes,[31–33] their repeatability is pretty
poor: even later studies suggest that some of the products
likely consisted of Cu2O rather than Cu. Most recently, our
group has successfully developed an effective route to the
synthesis of Cu nanostructures by using glucose as a reduc-
tant and hexadecylamine (HDA) as a capping agent. The
morphologies of Cu nanostructures can be controlled from
nanowires to nanocubes by simply reducing the amount of
HDA.[34] Subsequently, by introducing Pd nanocubes as
seeds into the reacting system, the resultant Cu atoms could
be directed to epitaxially grow on the Pd seeds to generate
Pd@Cu core–shell nanocubes with tunable sizes.[35]

In this work, we studied the use of Pd@Cu core–shell
nanocubes as sacrificial templates to galvanize with HAuCl4
in ethylene glycol at room temperature. The final products
were Pd@Au,Cu nanocubes with porous walls and a yolk–
shell structure. Electron microscopy and energy-dispersive
X-ray (EDX) analysis were applied to characterize both the
morphology and composition of the yolk–shell nanocages.

The evolution of both the structures and extinction spectra
from Pd@Cu core–shell nanocubes to Pd@Au,Cu, yolk–
shell nanocages at different stages were monitored and ana-
yzed in detail. We also investigated the influence of the sur-
fase capping HDA layer on the galvanic replacement pro-
cess, which plays a role similar to poly(vinyl pyrrolidone)
(PVP) in the galvanic replacement involving Ag nano-
cubes.[36] By simply varying the size/shape of the Cu-based
nanostructures and the noble-metal salts involving in the
galvanic replacement, we obtained hollow nanostructures in
many different sizes, compositions, and morphologies.

Results and Discussion

In the first step, well-defined Pd nanocubes of 18 nm in
diameter and 25 nm in dihedral angle were prepared by reduc-
ing Na2PdCl4 with l-ascorbic acid (AA) in an aqueous solution, with the aid of Br
ions as a capping agent.[37] Figure S1 in the Supporting Infor-
mation shows typical TEM images of the as-prepared Pd
nanocubes. The average edge length of these Pd nanocubes
was calculated to be (18 ± 4) nm with purity approaching
100%. Subsequently, these nanocubes were used as seeds
for epitaxial growth of Au shells, by reducing Cu** ions with
chlorine in an aqueous solution using HDA as a capping
agent. By using different amounts of Pd seeds, the size of
the Pd@Cu core–shell nanocubes could be easily tuned from
45 to 100 nm.[15]

We chose 100 nm Pd@Cu core–shell nanocubes to react
with a solution of HAuCl4 in ethylene glycol (1.0 mm) at
room temperature and investigate the details of a galvanic
replacement reaction between Cu sacrificial template and
HAuCl4. Figure 1a shows SEM and TEM images of the as-
obtained Pd@Cu core–shell nanocubes of 100 nm in edge
length. All of the nanoparticles were cubic in shape, with
slight truncation at the corners. The inner Pd cores can be
clearly observed in the TEM image, as well as the HAADF-
STEM image in Figure S2 (Supporting Information) due to
the difference in contrast between Pd and Cu elements.
Although these Pd@Cu core–shell nanocubes had been
washed by water and ethanol several times before being
used for the replacement reaction, the surface was still
capped by a thin layer of HDA (Scheme S1 in the Support-
ing Information).[33] This hydrophobic layer tended to cause
the Pd@Cu core–shell nanocubes to aggregate in an aqueous
solution. As a result, we used ethylene glycol rather than
water as a solvent for the replacement reaction, with the ad-
dition of a certain amount of PVP as the colloidal stabilizer.

Figure 1b–d, shows the morphological evolution of
Pd@Cu core–shell nanocubes when they were titrated with
0.25, 0.50, and 1.0 mL of the solution of HAuCl4 (1.0 mm) in
ethylene glycol. As shown by the TEM images, all the prod-
ucts still retained the cubic shape. The TEM images in the
insets reveal that a hollow shell was already formed at the
very beginning of the reaction. The proportion of Cu being
dissolved gradually increased with the introduction of more
HAuCl4. When the titrated volume of HAuCl4 solution

reached 1.0 mL, the Cu shell was completely dissolved, leaving behind a Pd nanocube inside each nanocage (Figure 1d). Elemental analysis by ICP-MS indicated that the atomic mole ratio of Au/Cu for the hollow product at this stage was close to 1:2, suggesting that the shells of the nanocages were made of a Au–Cu alloy. This result also demonstrates that alloying also accompanied the galvanic replacement reaction, which is similar to previous studies involving Ag nanostructures.[36,38] We denote the hollow metal nanostructure as Pd@Au$_x$Cu$_1$/C$_0$ yolk–shell nanocages. Since there was no solid matrix around the Pd core, the Pd nanocube would randomly attach to the wall when the sample was dried. If excessive HAuCl$_4$ was added into the reaction, the hollow structures would collapse and turn into disordered aggregation of small particles (Figure S3 in the Supporting Information), which could be attributed to a de-alloying process for the Au–Cu walls.[18]

We also applied high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM), high-resolution TEM (HRTEM), and energy dispersive X-ray (EDX) analysis to further characterize the structure and composition of the Pd@Au$_x$Cu$_1$/C$_0$ yolk–shell nanocages obtained with 1.0 mL of the solution of HAuCl$_4$ (1.0 mL, 1.0 mM) in ethylene glycol. Due to the large difference in contrast between the Pd core and the Au–Cu alloyed walls under TEM and HAADF-STEM (Figure 2, a and b), we were able to clearly observe a Pd cube in the interior of each nanocage, confirming the formation of yolk–shell nanocages in high yields. Figure 2c shows a HRTEM image of an individual Pd@Au$_x$Cu$_1$/C$_0$ yolk–shell nanocage, indicating that the walls of the nanocage were made of a random assembly of small crystallites. Figure S4 in the Supporting Information shows the selected area electron diffraction (SAED) pattern taken from a single Pd@Au$_x$Cu$_1$/C$_0$ nanocage, giving a combination of polycrystalline diffraction rings from the porous walls and a set of single-crystal diffraction spots from the Pd core. The formation of small crystallites for the walls could be attributed to the presence of a thin, oxide layer (CuO) on the surface of the Pd@Cu core–shell nanocube, which was also observed in our previous study.[35] The thin oxide layer might cause non-uniform deposition of the resultant Au atoms during the galvanic replacement process by forming multiple nucleation sites. The lattice spacing of the small crystallites was measured to be 0.224 nm (Figure 2d), which is between the {111} lattice spacing of Cu (0.208 nm, JCPDS NO. 001-1241) and Au (0.235 nm, JCPDS NO. 001-1172), and very close to that of AuCu alloy (0.223 nm, JCPDS NO. 025-1220), indicating a composition of Au–Cu alloy. The elemental distributions of a single Pd@Au$_x$Cu$_1$/C$_0$ yolk shell nanocage was resolved by EDX mapping and line scan profiles (Figure 2e and f). Distinct Cu and Au signals were detected from the walls, while the Pd signal was only observed from the core. The faint signal of oxygen could be ascribed
to the contribution of the residual trace oxides form the surface of a Pd@Cu core–shell template.

Figure 3 illustrates the changes in morphology and structure for the samples at different stages of the replacement reaction between Pd@Cu core–shell nanocubes and HAuCl₄. As shown in the TEM image of a single Pd@Cu core–shell nanocube (Figure 3a), the Pd@Cu template was slightly truncated at the corners. This means the facets exposed on the Cu shell were mainly [100] together with a small portion of [111] (Scheme S1 in the Supporting Information). At the beginning of galvanic replacement, cavities started to appear at the corner sites of the Cu cubic shell with the formation of a polycrystalline cage-like frame, indicating that Cu was initially dissolved from the corner sites (Figure 3b). With the further addition of HAuCl₄, the Cu shell was continuously dissolved from the corners toward the interior, and the cavity was simultaneously enlarged (Figure 3c). Finally, when 1.0 mL of the solution of HAuCl₄ was added, the Cu shell was completely dissolved, leaving behind a Pd cube inside each nanocage (Figure 3d). According to our previous study, the surface capping could substantially influence the galvanic replacement process by controlling the sites at which the replacement was initiated.⁵⁶ In this case, when HAuCl₄ was added into the solution, the corners terminated in [111] facets were unprotected by HDA and thus served as the primary sites for the oxidation of Cu since the [100] facets were passivated by HDA (Scheme S1 in the Supporting Information).⁵⁵ Figure 3e summarizes the major steps involved in the formation of Pd@Au, Cu₁ₓ/Cuₐₓ, yolk–shell nanocages through the galvanic replacement reaction between Pd@Cu nanocubes and HAuCl₄. We notice that, at a later stage of the replacement, the newly formed Auₐₓ/Cu₁ₓₖ small particles preferred to be dispersed in the solution phase rather than being deposited on the walls. As a result, the thickness of the walls for the Pd@Au, Cu₁ₓₖ, yolk–shell nanocages would not increase further as the reaction proceeded.

We also examined the extinction spectra taken from the samples at different stages of the galvanic replacement reaction. As shown in Figure 4, the extinction peak of Pd@Cu core–shell nanocubes was located at about 605 nm, which was consistent with our previous report.⁵⁵ When 0.25 mL of the HAuCl₄ solution was added, it turned into a broad peak that started at about 550 nm and extended into the near-IR region. However, unlike the gradual red-shift of extinction peaks for Au–Ag nanocages during the addition of HAuCl₄ into Ag nanocubes,⁷ further addition of HAuCl₄ into Pd@Cu nanocubes did not cause any shift for the peak. Instead, the intensity of the broad extinction peak declined with the dissolution of more Cu from the Pd@Cu nanocubes. Since the cross section of extinction (Cₑₓₜₜ) contains both absorption (Cₑₐₑ) and scattering (Cₛₓₜₜ), this drop in extinction can be attributed to the enlargement of the hollow interior, which would greatly reduce the scattering cross-section of the nanocages. Owing to the extinction in the near-IR region, the yolk–shell metal nanostructures may find potential use in photothermal cancer therapy.⁵⁹–⁶¹

Compared with other routes for preparing hollow metal nanostructures, galvanic replacement is a universal and better controlled approach. We also applied Pd@Cu core–shell nanocubes with smaller sizes as the sacrificial template to tune the interior void space of the Pd@Au, Cu₁ₓₖ, yolk–shell nanocages. Figure 5a and b show TEM images of Pd@Cu core–shell nanocubes of 75 and 45 nm in edge length, respectively. After being titrated with sufficient HAuCl₄ solution, yolk–shell nanocages with smaller sizes were obtained (Figure 5c and d). Furthermore, for the purpose of regulating the composition of the porous walls of the nanocages, other noble-metal salt precursors could also be introduced to replace HAuCl₄. Theoretically, the replacement based on Cu nanostructures can be executed with any other metals whose reduction potentials are more positive than that of Cu²⁺/Cu pair. Figure 6 shows typical TEM
images of Pd@Pd\(\times\)Cu\(_1\)\(\times\) and Pd@Pt\(\times\)Cu\(_1\)\(\times\) yolk–shell nanocages obtained by titrating Pd@Cu core–shell nanocubes of 100 nm in edge length with solutions of Na\(_2\)PdCl\(_4\) (1.0 mL, 1.5 mM) and K\(_2\)PtCl\(_4\) (1.0 mL, 1.5 mM) in ethylene glycol, respectively, at room temperature. The Pd- and Pt-based nanocages might exhibit improved performance in catalysis, because the yolk–shell structure could enhance their stability and dispersibility, and the hollow structure could greatly improve their activities relative to those of their solid counterparts.

When nanostructures made of pure Cu without Pd seeds inside were applied as the sacrificial templates, hollow metal nanostructures with only porous alloy walls were obtained. Figure 7a and c show TEM images of Cu nanocubes before and after reacting with HAuCl\(_4\) solution (1.0 mL, 1.0 mM) in ethylene glycol. The sequential TEM images from Cu nanocubes to Au\(_x\)Cu\(_1\)\(\times\)nanocages (Figure S5 in the Supporting Information) suggest that the galvanic replacement of a pure Cu nanocube also started at the corner sites further confirming the mechanism that involved in the galvanic replacement between Pd@Cu core–shell nanocubes and HAuCl\(_4\). In addition, by simply changing the morphology of Cu templates, hollow Au\(_x\)Cu\(_1\)\(\times\)nanostructures with other morphologies could be obtained. Figure 7b shows TEM image of Cu nanowires with an average diameter of 24 nm that were prepared by using a previously reported protocol. After titrating with sufficient HAuCl\(_4\), Au\(_x\)Cu\(_1\)\(\times\)nanotubes with porous walls and a slightly enlarged diameter were obtained (Figure 7d). It is clear that hollow metal nanostructures with other different morphologies and compositions can also be obtained by using other combinations of Cu-based nanostructures and metal salt precursors.

**Conclusion**

In summary, Pd@M\(_x\)Cu\(_1\)\(\times\) (M = Au, Pd, and Pt) yolk–shell nanocages have been successfully synthesized through galvanic replacement reactions between Pd@Cu core–shell nanocubes and solutions of HAuCl\(_4\), Na\(_2\)PdCl\(_4\), and K\(_2\)PtCl\(_4\) in ethylene glycol, respectively. As a substitute for the commonly used Ag templates, the Cu sacrificial templates could react with a broader range of different metal salts under relatively milder conditions owing to the lower reduction po-
tential of Cu^{2+}/Cu. Because the [100] facets on the Pd@Cu nanocubes were blocked by the surface capping layer made of HDA, the dissolution of Cu preferentially start from the corner sites and then progress toward the interior. The UV/Vis extinction spectra taken from the Pd@Au,Cu_{1−x}, yolk–shell nanocages showed a broad peak extending from the visible to the near-IR region, suggesting potential application in photothermal therapy. In addition, the Pd@M,Cu_{1−x} (M=Pd or Pt) yolk–shell nanocages are useful for catalytic applications.

**Experimental Section**

**Chemicals and materials:** Ethylene glycol (EG, lot no. K43B24) was obtained from J. T. Baker. Gold(III) chloride trihydrate (HAuCl₄·3H₂O, ≥ 99.9%), sodium palladium(II) tetrachloride (Na₂PdCl₄, 99.98%), potassium platin(II) tetrachloride (K₂PtCl₄, 99.99%), copper chloride dihydride (CuCl₂·2H₂O), poly(vinyl pyrrolidone) (PVP, MW = 55,000), L-ascorbic acid (AA), hexadecylamine (CH₃(CH₂)₁₄CH₂NH₂, HDA), potassium bromide (KBr), and glucose (C₆H₁₂O₆) were all obtained from Sigma–Aldrich. Ethanol (200 proof) was obtained from Pharmco Products. All the chemicals were used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ. All the chemicals were used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ.

**Synthesis of Pd cubes of 18 nm in edge length:** The Pd nanocubes to be used as seeds for the synthesis of Pd@Cu core–shell nanocubes were synthesized according to our previous report.[37] Typically, PVP (105 mg), AA (60 mg), and KBr (600 mg) were dissolved in DI water (8.0 mL), and then placed in a vial and heated at 80°C in an oil bath under magnetic stirring for 10 min. Subsequently, Na₂PdCl₄ (57 mg) was dissolved in DI water (3.0 mL) and injected into the pre-heated solution with a pipette. The mixture of reagents was capped, and maintained at 80°C for 3 h. The product was collected by centrifugation, washed three times with water to remove excess PVP and inorganic ions, and then re-dispersed in DI water (11 mL).

**Synthesis of Pd@Cu core–shell cubes:** The Pd@Cu core–shell nanocubes were synthesized through a seed-mediated overgrowth approach according to our previous report.[39] In a standard synthesis, an aqueous solution (10 mL) containing CuCl₂·2H₂O (21 mg), HDA (90 mg), and glucose (50 mg) was placed in a vial and magnetically stirred at room temperature overnight. For the synthesis of Pd@Cu core–shell cubes of 100 nm in edge length, the aqueous suspension of Pd seeds (1.8 mgmL⁻¹) was used. The vial was then capped and maintained at 100°C in an oil bath for another 3 h. The size of Pd@Cu core–shell nanocubes was tuned by adding different amounts of the 18 nm Pd seeds. For 75 and 45 nm Pd@Cu core–shell nanocubes, 0.05 and 0.30 mL of the 18 nm Pd seeds were used, respectively. The product was collected by centrifugation, washed three times with water, and twice with ethanol, and then re-dispersed in EG (50 mL).

**Synthesis of Cu nanowires and nanocubes:** The Cu nanowires and nanocubes without Pd seeds inside were synthesized according to our previous report.[39] For a standard synthesis, CuCl₂·2H₂O (21 mg), HDA (180 mg for Cu nanowires, 90 mg for Cu nanocubes), and glucose (50 mg) were dissolved in DI water (10 mL) in a vial and magnetically stirred at room temperature overnight. The capped vial was then transferred into an oil bath and heated at 100°C for 6 h under magnetic stirring. The product was collected by centrifugation, washed three times with water, and twice with ethanol, and then re-dispersed in EG (50 mL).

**Synthesis of Pd@M,Cu_{1−x} (M=Pd, Pt) yolk–shell nanocages:** The Pd@M,Cu_{1−x} nanocubes with a yolk–shell structure were synthesized through a galvanic replacement reaction between the Pd@Cu core–shell nanocubes and [MCl₄]⁻ ions in EG. For the Pd@Au,Cu_{1−x} yolk–shell nanocages, typically, PVP (30 mg) was added into a solution of the as-prepared Pd@Cu core–shell nanocubes suspended in EG (10 mL) and then heated in a 50 mL flask, and then magnetically stirred for 10 min at room temperature. Subsequently, a solution of HAuCl₄ in EG (1.0 mL, 1.0 mg) was pumped into the above solution at the rate of 0.1 mLmin⁻¹. After that, the reaction was continued for additional 30 min. In order to obtain Pd@Pd,Cu_{1−x} and Pd@Pt,Cu_{1−x} yolk–shell nanocages, solutions of Na₂PdCl₄ (1.0 mL, 1.5 mg) or K₂PtCl₄ (1.0 mL, 1.5 mg) in EG was used to replace HAuCl₄ solution, and the reaction time after pumping was prolonged to 3 h. The product was collected by centrifugation, washed three times with ethanol, and then re-dispersed in water.

**Morphological, structural, and elemental characterization:** Transmission electron microscopy (TEM) images were taken using a Tecnai G2 Spirit Twin microscope (FEI, Hillsboro, OR) and a JEM-1400 microscope (JEOL, Tokyo, Japan) operated at 120 kV by dropping the nanoparticle dispersions on carbon-coated copper grids and drying under ambient conditions. High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) mapping analyses were performed using a JEOL 2100F microscope (JEOL, Tokyo, Japan) operated at 200 kV. Scanning electron microscopy (SEM) images were captured using a Nova Nano SEM 230 field-emission microscope (FEI, Hillsboro, OR) operated at 30 kV. UV/Vis spectra were taken with a diode array spectrophotometer (Cary 50, Varian). The concentrations and ratios of metal elemental the suspension of as-prepared nanostructures were determined using inductively coupled plasma mass spectrometry (ICP-MS, Perkin–Elmer Elan DRC II).

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Y. Xia et al.


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