

# Cascade assembly of carbon nanoflasks as a potential high-efficient nanoreactor

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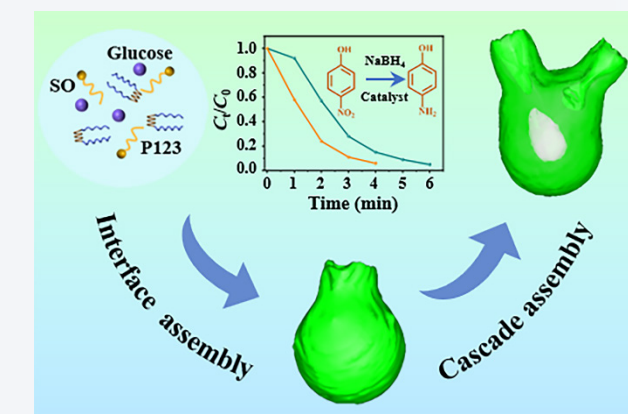
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**ABSTRACT:** Asymmetric carbon nanomaterials have shown unique performance merits over their symmetric counterparts, particularly in multifunctional tunability and active site availability. However, precisely manipulating the geometric structure of asymmetric carbon nanoparticles while integrating functional components remains a major challenge. Herein, a facile and cost-effective cascade assembly strategy is proposed towards double-necked carbon nanoflasks (DCFs) at the emulsion interface formed by PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub> (P123) and sodium oleate. Electron tomography and three-dimensional (3D) reconstruction analysis reveal that the newly-designed DCFs contain larger initial flasks with smaller ones grown into their body. Importantly, precursor-guided reaction kinetics regulation drives the morphological evolution of primary products from hemispherical to single-necked carbon flasks (SCFs). Furthermore, only those well-grown SCFs can enable the subsequent cascade assembly of DCFs via unique geometric constraint and hydrogen-bonding interactions. Remarkably, this newly developed cascade assembly route enables the functional modification of asymmetric carbon nanomaterials. As a proof of concept, the potential nanoreactors are further constructed by *in-situ* encapsulating ultra-small Ag nanoparticles (~ 5 nm) into the carbon nanoflasks. Benefiting from the stable immobilization of Ag nanoparticles, the resultant catalyst exhibits an outstanding catalytic activity for the reduction of 4-nitrophenol. This work offers a promising strategy for designing functionally integrated asymmetric nanoreactors.

**KEYWORDS:** carbon nanoflasks, asymmetric structure, cascade assembly, three-dimensional (3D) tomography, nanoreactor

## 1 Introduction

Asymmetric nanomaterials generally offer unique performance merits over their symmetric counterparts, particularly in multifunctional tunability and active site availability [1–3]. Over the past few decades, significant efforts have been devoted to manipulating the geometric structure of asymmetric nanomaterials, aiming to optimize their performance for customized applications such as catalysis, energy storage, and biomedicine. To date, asymmetric nanomaterials with diverse structures, including



dumbbell-type, bowl-shaped, and tadpole-like architectures, have been successfully developed through different synthetic strategies. However, the current research mainly focuses on silica-based asymmetric nanomaterials owing to their good controllability in design [4, 5]. In contrast, carbon nanomaterials possess charming advantages including abundant raw material availability, excellent chemical stability, as well as diverse morphology and structure [6–10]. Therefore, constructing asymmetric carbon nanomaterials is expected to not only amplify the intrinsic merits of carbon, but also unlock unprecedented functionalities for advanced applications [11–14].

Precisely manipulating the geometric structure of asymmetric carbon nanomaterials is highly desirable via developing advanced synthesis methods. Among available strategies, emulsion-guided interfacial assembly has emerged as a promising route for

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fabricating asymmetric carbon nanoparticles with unique morphology [15–17]. For example, Mai et al. synthesized asymmetric carbon nanoparticles through the polymerization of *m*-phenylenediamine at the trimethylbenzene/water emulsion interface. By adjusting the oil droplet sizes, they prepared mushroom-like, wheel-shaped, and acorn-like carbon nanoparticles. Thanks to their large specific surface area, the resulting asymmetric carbon nanoparticles demonstrated enhanced catalytic performance for the oxygen reduction reaction [18]. Similarly, Guo et al. proposed a droplet-directed anisotropic assembly method for synthesis of asymmetric carbon nanoparticles [19]. Their morphology can be tailored from non-porous sphere to semifootball-like architecture, and finally to nano-ellipsoid by tuning the polarity of the oil phase. Finite element analysis and experimental results demonstrated that the unique structure can not only provide abundant active sites but also facilitate the efficient diffusion of molecules. That, in turn, endows the prepared carbon nanomaterial with excellent electrochemical performance. Despite these advances, achieving fine control over the kinetic assembly process in such a strategy remains challenging. Additionally, the preparation processes usually rely on some toxic precursors such as aniline and aminophenol, thereby raising the environmental concerns. On the other hand, asymmetric nanoreactors have shown their own merits in practical applications. For example, hydrogen peroxide-driven asymmetric nanomotors were fabricated by selectively loading  $\text{Fe}_3\text{O}_4$  catalysts into the cavities of streamlined silica nanoparticles. Owing to the large inner cavities and high specific surface areas, these nanomotors exhibited excellent diffusion performance [5]. However, an *in-situ* integration of functional materials into asymmetric carbon nanomaterials during the assembly process is still a formidable obstacle.

Herein, we propose a facile cascade assembly strategy that integrates biomass conversion with interfacial engineering in a synergistic manner to prepare double-necked carbon nanoflasks (DCFs). In this innovative approach, single-necked carbon nanoflasks (SCFs) is firstly synthesized via the hydrothermal carbonization of glucose at an emulsion interface formed by  $\text{PEO}_{20}$ - $\text{PPO}_{70}$ - $\text{PEO}_{20}$  (P123) and sodium oleate (SO). These initially formed SCFs subsequently serve as substrates to guide subsequent cascade assembly towards DCFs. Precursor-guided reaction kinetics studies indicate that the formation of the double-necked structure is highly dependent on the initial flask-like morphology of primary nanoparticles. Importantly, a high-efficient nanoreactor can be further constructed by this newly-developed cascade assembly route, where ultra-small Ag nanoparticles are *in-situ* encapsulated into DCFs. The resulting Ag@DCF catalyst shows a superior catalytic activity for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with sodium borohydride ( $\text{NaBH}_4$ ) as the reducing agent.

## 2 Experimental section

### 2.1 Materials

P123 was purchased from Sigma-Aldrich. Sodium oleate ( $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{Na}$ , SO), glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), D-galactose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), D-xylose ( $\text{C}_5\text{H}_{10}\text{O}_5$ ), D-ribose ( $\text{C}_5\text{H}_{10}\text{O}_5$ ), silver nitrate ( $\text{AgNO}_3$ ), sodium borohydride ( $\text{NaBH}_4$ ), and 4-nitrophenol ( $\text{C}_6\text{H}_5\text{NO}_3$ ) were purchased from Chinese Sinopharm Chemical Reagent Co., Ltd. Deionized water was applied in all the experiments.

### 2.2 Synthesis of carbon nanoflasks

In a typical experiment, 54 mg of P123 and 54 mg of SO were dissolved in 24 mL of deionized water and stirred for 30 min. Subsequently, 46 mL of aqueous solution containing 1.5 g of glucose was added. After stirring for 30 min, the mixed solution was placed into a 100 mL of Teflon-lined autoclave and treated at 180 °C for 12 h. Then, the resulting brown precipitate was collected, washed repeatedly with distilled water and ethanol for several times, and then dried at 60 °C overnight to get the single-necked carbon nanoflasks, designed as SCFs.

Following the above procedures, DCFs were then prepared. The main difference was that 1.5 g of glucose was further added to the solution after the first reaction and then heated at 180 °C for another 12 h. Afterwards, the resulting brown precipitate was collected, washed repeatedly with distilled water and ethanol for several times, and then dried at 60 °C overnight, achieving the DCFs product.

### 2.3 Synthesis of Ag@SCFs and Ag@DCFs

The assembly method developed in our work was further employed to construct the nanoreactors by an *in-situ* encapsulation of Ag nanoparticles into the carbon nanoflasks. In a typical synthesis of Ag@SCFs, 54 mg of P123 and 54 mg of SO were dissolved in 24 mL of deionized water and stirred for 30 min. Then, 8 mg of  $\text{AgNO}_3$  and 46 mL of aqueous solution containing 1.5 g of glucose were added. After stirring for 30 min, the resultant solution was put into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. Afterwards, the resulting brown precipitate was collected, washed repeatedly with distilled water and ethanol for several times, and then dried at 60 °C overnight towards Ag@SCFs. The synthesis of Ag@DCF followed the similar procedures, only 1.5 g of glucose was further added to the Ag@SCFs solution and then heated at 180 °C for another 12 h.

### 2.4 Structural characterizations

The crystal structure of the samples was systematically investigated by X-ray powder diffraction (XRD, Rigaku D/max-2550) and Raman microscope (Renishaw inVia). Scanning electron microscopy (SEM, Zeiss SUPRA 55), transmission electron microscopy (TEM, Hitachi HT7700), and high-resolution TEM (HRTEM, JSM-2010F) were conducted to observe the morphology and microstructure of the products. FEI Tecnai F30 transmission electron microscope was used to perform the electron tomography (ET) analysis at the operating voltage of 300 kV with bright-field TEM mode. Malvern Zetasizer Nano S was used to test the surface electrical properties. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Thermo Scientific K-Alpha photoelectron apparatus. Ultraviolet-visible (UV-Vis) spectra were analyzed by Hitachi U-3010 spectrophotometer.

### 2.5 Catalytic reduction of 4-nitrophenol

The catalytic performance of Ag@SCFs and Ag@DCF catalysts for the reduction of 4-NP using sodium borohydride ( $\text{NaBH}_4$ ) as the reducing agent was evaluated in aqueous media at room temperature. In brief, 1 mL of  $\text{NaBH}_4$  solution (0.5 M) was firstly added to the 200  $\mu\text{L}$  of 4-NP solution (0.005 M). Thereafter, 1.5 mL of Ag@SCFs or Ag@DCF solution (0.1  $\text{mg}\cdot\text{mL}^{-1}$ ) was added to initiate the catalytic reduction. Immediately, the solution was quickly subjected to UV-Vis measurement in the range of 200–600 nm. In addition, the reusability of the catalyst was also

investigated under the same reaction conditions.

### 3 Results and discussion

The carbon nanoflasks with single-necked and double-necked structures were prepared through a facile emulsion-induced interfacial and cascade assembly route (Fig. 1(a)). Firstly, glucose, P123, and SO were uniformly dispersed in an aqueous solution to form a homogeneous mixture. During the hydrothermal process, SO dissociated into oleate anions and then self-assembled to produce oleic acid (OA) droplets in the aqueous phase, forming an oil-in-water emulsion system, which was then stabilized by P123 through the hydrophobic interaction [20]. Meanwhile, glucose molecules underwent dehydration and condensation to form oligomers, which were then anchored onto the surface of oil droplets via hydrogen bonding interactions [21–23]. With the hydrothermal reaction proceeded, the oligomers gradually polymerized at the oil–water interface, resulting in the formation of SCFs. After that, additional glucose was further introduced into the reaction system, initiating a cascade assembly process onto the SCFs surface, ultimately achieving the unique DCFs.

SEM and TEM images show that SCFs have a uniform and flask-like structure with a rough surface and hollow structure, and the

particle size is approximately 560 nm (Figs. S1–S3 in the Electronic Supplementary Material (ESM)). Through precise measurement, the cavity diameter and shell thickness of SCFs are 350 and 107 nm, respectively. HRTEM image confirms the amorphous structure of SCFs (Fig. S4 in the ESM). ET is a powerful technique for precisely analyzing the three-dimensional (3D) configurations of intricate nanostructures. The unique morphology of the products prompts us to further identify their fine structure using ET analysis. As displayed in Figs. S5(a) and S5(b) in the ESM, the resulting SCFs are hollow structure with the neck connecting to the cavity inside the body. The top and side views of 3D reconstruction images (Figs. S5(c) and S5(d) in the ESM) further confirm the formation of hollow carbon nanoflasks, which can be directly observed through 3D visualization (Video S1 in the ESM). Interestingly, after cascade assembly, the morphology of the product undergoes significant transformation, changing from the original single-necked to newly double-necked structure (Fig. 1(b)). Moreover, large-scale SEM images display that the obtained DCFs exhibit the uniform structure with double-necked configuration, and no other distinct morphologies can be found (Fig. S6 in the ESM). To the best of our knowledge, this unique double-necked structure is reported here for the first time. Meanwhile, this morphological evolution highlights the critical role of our proposed cascade assembly strategy in

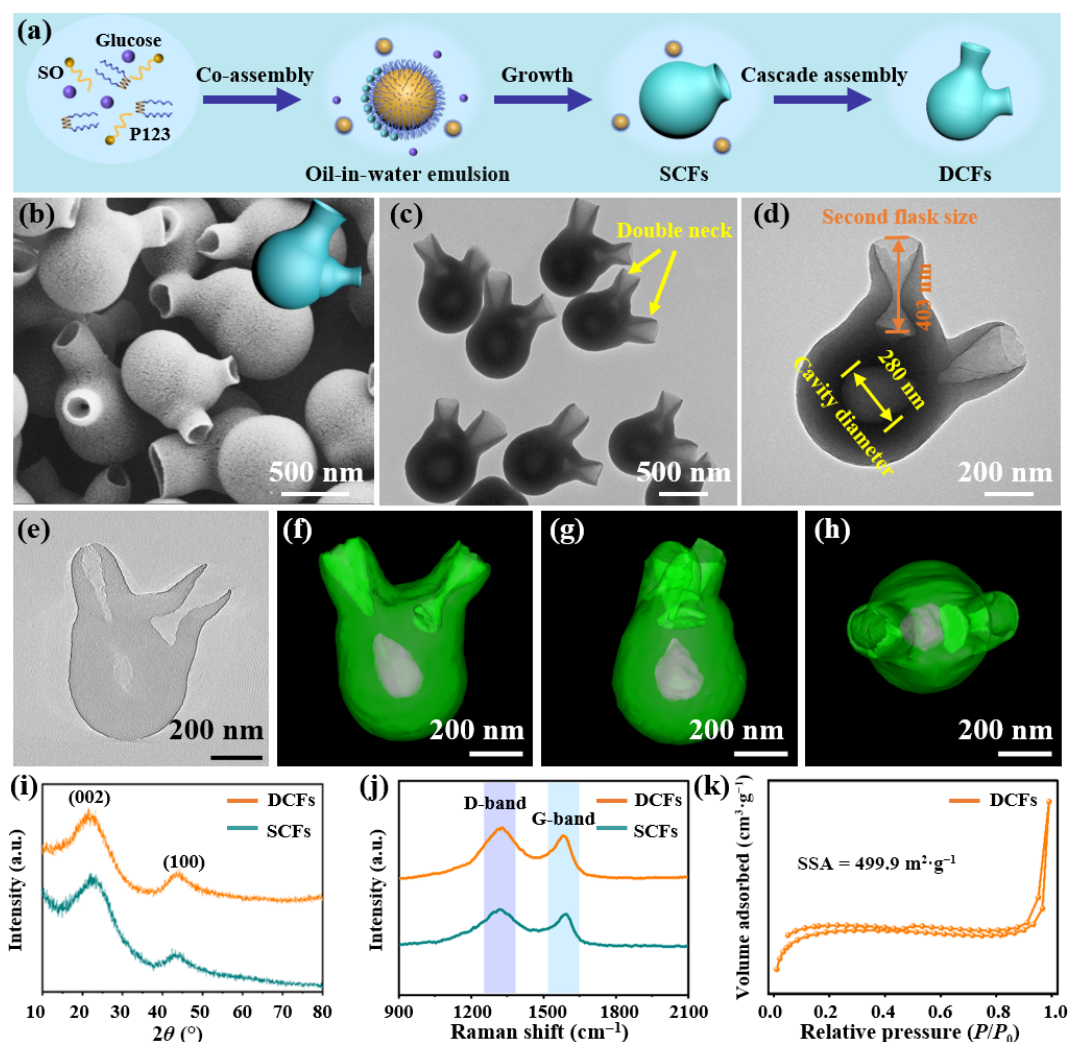


**Figure 1** (a) Schematic illustration of the preparation process of carbon nanoflasks. (b) SEM and ((c) and (d)) TEM images of DCFs. (e) ET slice and ((f)–(h)) 3D reconstruction images of DCFs. (i) XRD patterns and (j) Raman spectra of SCFs and DCFs. (k) N<sub>2</sub> adsorption–desorption isotherm of DCFs.

precisely manipulating geometric structure of asymmetric carbon nanoparticles. TEM images further confirm a distinctive dual-flask configuration of DCFs (Figs. 1(c) and 1(d)), with a smaller flask with a size of 403 nm positioned on the surface of a larger flask. Additionally, the particle size of DCFs increases to  $\sim 590$  nm (Fig. S7 in the ESM), while the diameter of the central cavity decreases to 280 nm. HRTEM image also verifies their amorphous structure (Fig. S8 in the ESM). The ET cross-sectional view of DCFs clearly shows the existence of two flask-like hollow structures (Fig. 1(e)). Notably, the neck of the larger flask is isolated from the internal cavity, indicating that the cascade assembly process not only generates the new flask, but also facilitates the growth of the initial flask. The 3D reconstruction images from various angles vividly illustrate the unique double-necked structure (Figs. 1(f)–1(h) and Video S2 in the ESM).

The crystal phase of the products was characterized by the XRD technique. As shown in Fig. 1(i), two distinct peaks at  $23.5^\circ$  and  $43.7^\circ$  are observed for both SCFs and DCFs, corresponding to the (002) and (100) crystal planes of amorphous carbon, respectively [24]. Raman spectroscopy provides another effective method for analyzing the carbon materials. Figure 1(j) clearly displays two prominent peaks at  $1343$  and  $1581\text{ cm}^{-1}$  for SCFs and DCFs, which are attributed to the D band and G band, respectively [25–28]. The  $I_D/I_G$  values for SCFs and DCFs are calculated to be 1.15 and 1.21, respectively, indicating the presence of abundant defects [29]. This result is consistent with the above XRD and HRTEM results. Besides, the Brunauer–Emmett–Teller (BET) surface area of DCFs is calculated to be  $499.9\text{ m}^2\cdot\text{g}^{-1}$  (Fig. 1(k)), which is higher than  $415.8\text{ m}^2\cdot\text{g}^{-1}$  of SCFs (Fig. S9 in the ESM). This result suggests that DCFs with distinctive double-necked structure can provide more available sites for the catalytic reaction.

To gain insight into the formation mechanism of carbon nanoflasks, a series of synthetic parameter-dependent experiments were then conducted. The influence of the P123 and SO amounts on the structure of products was firstly explored. When the surfactant quantity is 18 mg, spherical carbon nanoparticles with hollow structure were formed, but these particles showed a certain degree of aggregation (Fig. S10(a) in the ESM). That mainly stems from the insufficiency of surfactants, which cannot effectively stabilize oil droplets in the emulsion system. Thermodynamically, such oil–water interfaces are energetically unfavorable. To minimize the total surface free energy of the system, the oil droplets spontaneously coalesce during hydrothermal treatment, thus resulting in the agglomeration of carbon nanoparticles. With increasing P123 and SO amounts, the dispersibility of carbon nanoparticles was significantly improved (Figs. S10(b) and S10(c) in the ESM). The possible reason is that excess surfactant molecules can enable complete coverage of the oil droplet surface, thereby forming a stable steric barrier that prevents droplet coalescence and ensures uniform dispersion of carbon nanoparticles. Besides, the particle size analysis exhibits a positive correlation between P123/SO amounts and product size (Fig. S10(d) in the ESM). This result indicates that the size of the oil droplet template can be regulated by tuning the SO usage.

The type of carbon precursors on the structure of the products was then investigated. Firstly, galactose, possessing a similar chemical structure to glucose, was used as a replacement for glucose (Fig. 2(a)). As shown in Figs. 2(b) and 2(c), the initial assembly yielded an obvious single-necked structure, which transformed into a double-necked configuration after the cascade assembly. This

structural evolution pathway is highly consistent with that observed when glucose was used as the carbon precursor, confirming that the formation of SCFs and their subsequent conversion to DCFs are a general characteristic of hexose-based carbon precursors. Next, ribose (Fig. 2(e)), a typical pentose, was employed as the carbon precursor. After the first assembly, the product exhibits a hemispherical morphology rather than the flask-like structure (Fig. 2(f)). This distinct structural divergence stems from the intrinsic molecular properties of ribose, which differ fundamentally from those of hexoses (glucose and galactose) in terms of dehydration–polymerization behavior. For hexose precursors, they first undergo dehydration to yield 5-hydroxymethylfurfural (HMF), which then polymerizes to form the flask-like carbon material (Fig. 2(d)). In contrast, ribose, as a pentose, generates furfural as its dominant dehydration product (Fig. 2(h)). Notably, HMF exhibits generally higher reactivity than furfural [30], enabling hexose-driven reactions to proceed in a rapid and ordered manner that favors the formation of SCFs. By comparison, furfural possesses significantly slower reaction kinetics, which disrupts the ordered assembly process and leads to premature termination of the reaction, ultimately resulting in the formation of hemispherical nanoparticles. Cascade assembly on these hemispherical particles only resulted in increased thickness while retaining the hemispherical shape (Fig. 2(g)). To validate the generality of this phenomenon for pentose precursors, xylose, another pentose, was selected as the carbon precursor. Seen from Fig. S11 in the ESM, the resulting product also exhibits a hemispherical structure, confirming the conclusion that hexose as precursors tends to form single-necked flasks, while pentose favors the formation of hemispherical structure due to their distinct dehydration–polymerization behavior. Meanwhile, these findings also provide a compelling evidence that the formation of DCFs highly depends on the unique geometry structure of SCFs, highlighting the importance of cascade assembly.

Time-evolution experiments were further performed to better elucidate the formation mechanisms of SCFs and DCFs. In terms of SCFs, hemispherical structure was obtained after 3 h of hydrothermal reaction (Fig. 3(a)). However, these particles exhibited a structural instability, marked by shell collapse and even rupture. This observation reflects that the oligomers just begin to adsorb and cross-link at the emulsion droplet interface. As the reaction progressed to 6 h (Fig. 3(b)), the hemispherical particles gradually evolved into a spherical structure with an open hole, with the carbon shell thickening to 52 nm (Fig. 3(e)). This progression indicates that prolonged hydrothermal treatment can promote the continuous dehydration–condensation of glucose. After 12 h (Fig. 3(c)), SCFs with a well-defined flask-like morphology was formed, accompanied by a further increase in particle size and shell thickness. These observations collectively indicate that the SCF formation undergoes a kinetically-controlled assembly process (Fig. 3(d)). For DCFs, a nascent cascade neck began to nucleate on the SCF surface after 3 h (Fig. 3(f)). As the reaction progressed to 6 h (Fig. 3(g)), this cascade neck structure matured, with increased length and defined geometry, reflecting progressive deposition of carbonaceous components on the emulsion template. After another 12 h of cascade assembly, relatively perfect DCFs were achieved (Figs. 3(h) and 3(i)). Quantitative analysis (Fig. 3(j)) reveals a positive correlation between cascade neck length and reaction time. This behavior strongly supports that the cascade assembly process on SCFs follows the same emulsion-induced interfacial polymerization mechanism as the primary SCFs formation.

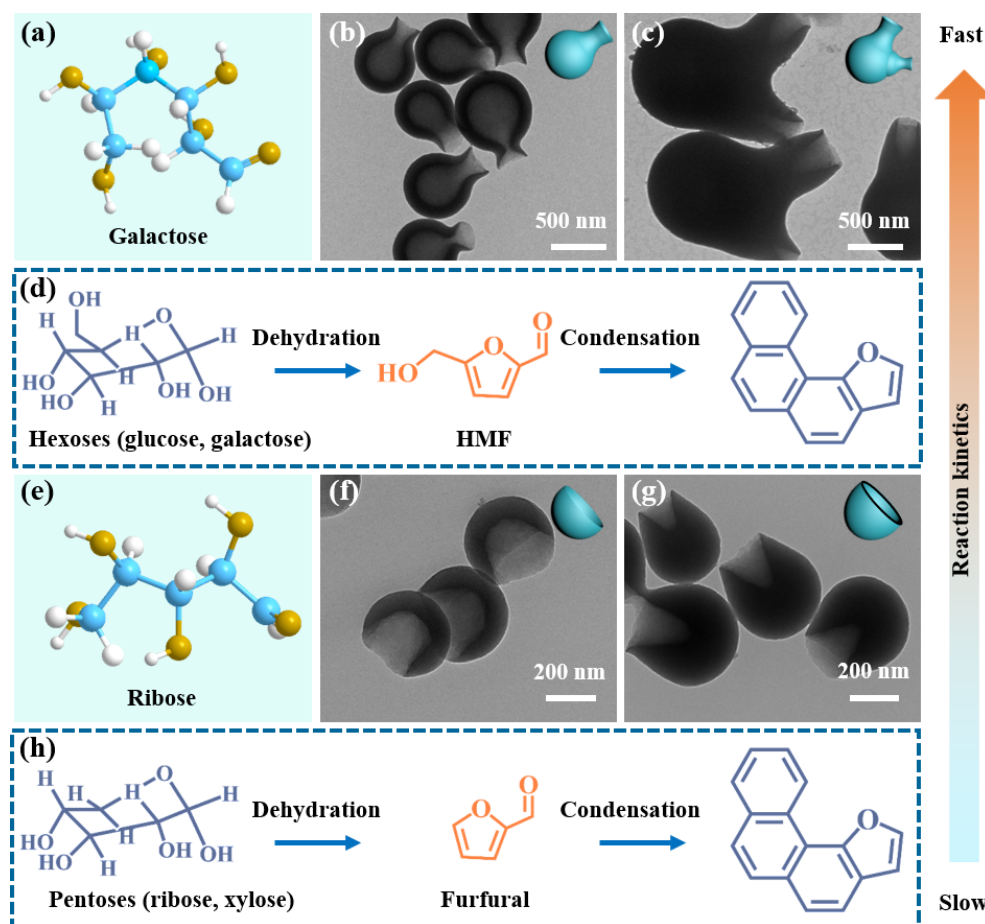


**Figure 2** Molecular structures, TEM images of products prepared with different precursors, and corresponding reaction pathways: ((a)–(d)) galactose and ((e)–(h)) ribose.

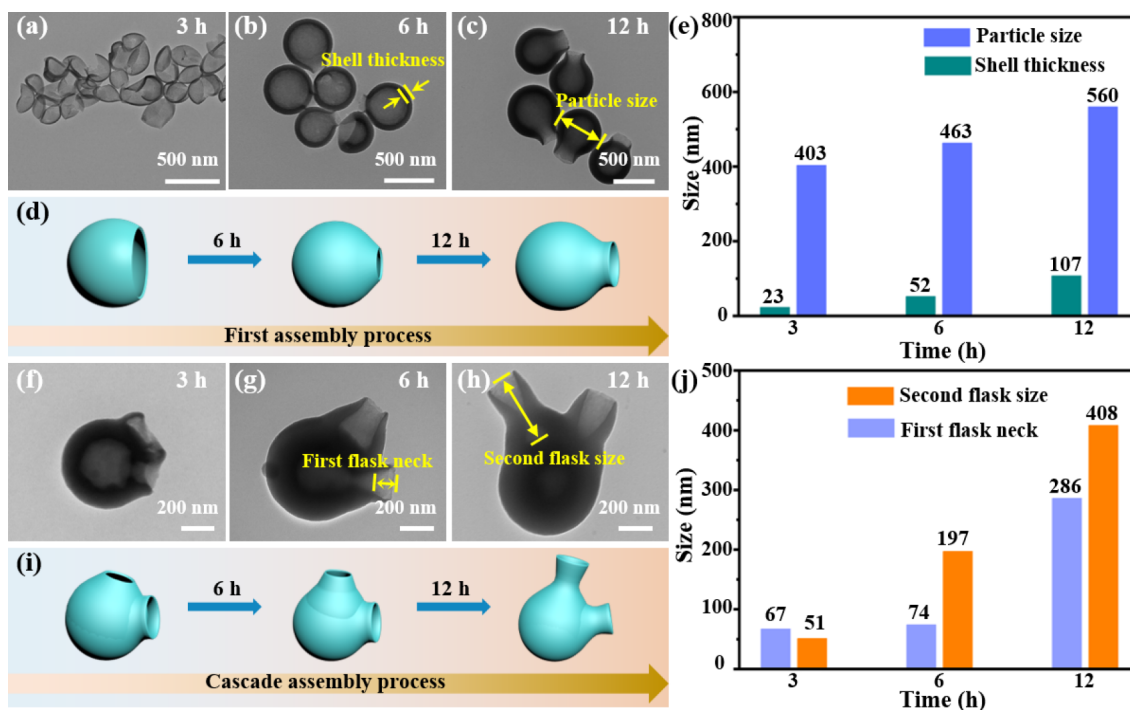


**Figure 3** ((a)–(d)) TEM images and corresponding 3D schematic diagram of SCFs at different hydrothermal time: (a) 3, (b) 6, and (c) 12 h. (e) Statistics of SCFs particle size and shell thickness at different hydrothermal time. ((f)–(i)) TEM images and corresponding 3D schematic diagram of DCFs at different hydrothermal time: (f) 3, (g) 6, and (h) 12 h. (j) Statistics of second flask size and first flask neck in DCFs at different hydrothermal time.

To further identify the effect of SCF structure on the DCF product, a customized cascade assembly was performed on the spherical SCFs with open-hole structure, obtaining from 6 h of hydrothermal treatment (Fig. 3(b)). As shown in Fig. S12 in the ESM, the resultant product maintained the single-necked structure, with an increased shell thickness evolving into a bilayer configuration. This finding indicates that only those well-grown SCFs can lead to the formation of double-necked nanoflasks. In contrast to the highly curved body region of the flask-like structure, the neck area exhibits much lower interfacial curvature. According to the thermodynamic principle of interfacial energy minimization, this low-curvature flask-neck surface serves as a preferential nucleation site, selectively promoting the polymerization of residual emulsion droplets in the solution. Additionally, it should be noted that if an equivalent amount of P123/SO surfactant to that employed in the initial assembly was added into the cascade assembly process, only some hollow nanoparticles were surrounded on the surface of SCFs (Fig. S13 in the ESM). Furthermore, if the as-obtained SCFs were firstly centrifuged, dried, and then re-dispersed in water, followed by the addition of P123/SO and glucose for cascade assembly, the resulting product fails to grow on the surface of the pre-formed SCFs (Fig. S14 in the ESM). This result clearly demonstrates that the remaining emulsions in the system serve as core nucleation templates, facilitating the occurrence of subsequent cascade assembly. On the other hand, it also indicates that the newly-developed cascade assembly is an eco-friendly and cost-effective strategy. The zeta potential analysis demonstrates a distinct increase in potential following the addition of glucose to the P123/SO (Table S1 in the ESM), confirming that electrostatic attraction is the main driving force for the efficient assembly process.

Inspired by these findings, we proposed a cascade assembly process governed by a spatial confinement effect that is dependent on interfacial curvature. This mechanism integrates the dynamic evolution of emulsions, interfacial interactions, and site-specific

polymerization, extending the principles of dynamic interplay and active-site growth central to liquid active surface growth. As shown in Fig. 4, the assembly initiates with the construction of monodisperse oil-in-water emulsion droplets, a foundational template analogous to the liquid nanoparticles. Under hydrothermal conditions, SO decomposed into oleic acid ions, which subsequently converted into OA, while the hydrophobic PPO segments of P123 inserted into the oil phase of OA, and the hydrophilic PEO segments extend into the aqueous phase to form a steric stabilization layer. This results in the formation of a stable oil-in-water emulsion. The PEO segments on the surface of P123-stabilized emulsion droplets form hydrogen bonds with the hydroxyl groups of glucose molecules in the aqueous phase, realizing the selective immobilization of the carbon precursor at the oil-water interface, and the adsorbed glucose molecules undergo dehydration and intermolecular condensation at the interface, gradually forming glucose oligomers. When the concentration of glucose oligomers at the oil-water interface reaches a critical nucleation threshold, heterogeneous nucleation is triggered at the emulsion interface (rather than in the bulk aqueous phase), as the interface provides a lower-energy nucleation site compared to the homogeneous phase. This nucleation initiates the *in-situ* surface polymerization of glucose oligomers, and the oligomers undergo further cross-linking and carbonization to form a continuous carbon shell on the emulsion droplet surface. Just as the previous reported mechanism [31, 32], the emulsion droplets exhibit dynamic extrusion behavior under hydrothermal conditions, and the droplet surface is continuously renewed with fresh oil-water interface sites. Oligomers preferentially polymerize on these renewed interface sites, and the slight kinetic imbalance between emulsion extrusion and carbon shell passivation induces symmetry breaking of the initially spherical carbon shell. It is worth noting that the rate of emulsion extrusion and carbon shell passivation is related to the reaction kinetics of the precursor. The reaction kinetics of the carbon precursor used in this work is slower,

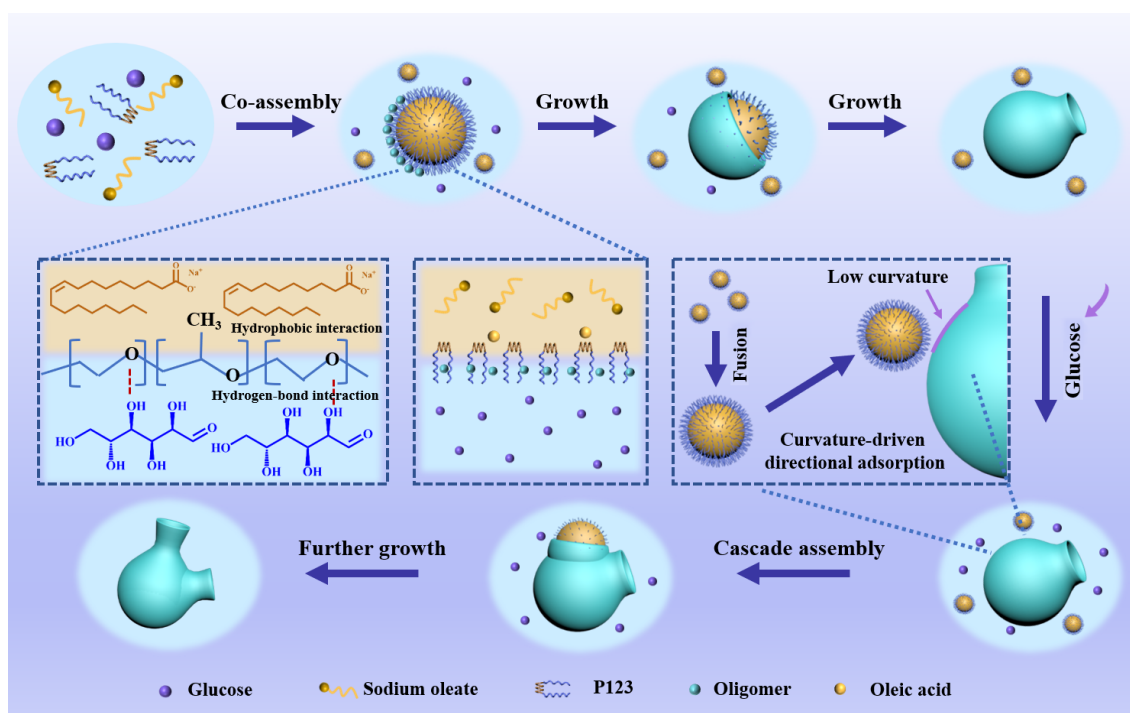


**Figure 4** Schematic illustration of the formation mechanism of carbon nanoflasks via a spatial constraint effect-oriented cascade assembly route.

resulting in a lower passivation rate of the carbon shell compared to the emulsion extrusion rate. This imbalance leads to focused growth at a specific interface site, forming a flask-neck structure. After the formation of primary SCFs, a small excess of unreacted emulsion droplets remain in the reaction system. These residual emulsion droplets are stably dispersed in the aqueous phase and interact with the SCF surface via hydrogen bonding (between the PEO segments on the residual droplet surface and the hydroxyl groups on the SCF surface). The spatial distribution of these residual emulsion droplets on the SCF surface is not random but is governed by the principle of minimizing the system's total interfacial energy. SCFs exhibit a pronounced interfacial curvature gradient: The flask-neck region has a low curvature (flat or gently curved surface), while the spherical flask body has a high curvature (convex curved surface). For colloidal particles, adsorption on a low-curvature surface results in a smaller increase in the system's interfacial area and thus a lower interfacial energy compared to adsorption on a high-curvature surface. As a result, residual emulsion droplets are selectively and preferentially adsorbed onto the low-curvature flask-neck region of SCFs, forming a localized emulsion template layer at the neck, and this curvature-dependent adsorption is the molecular basis for the site-specificity of subsequent cascade assembly. The final step of cascade assembly is triggered by further introduction of glucose. Due to the hydrogen bonds interactions between the PEO of emulsion droplets and the hydroxyl groups of glucose molecules, the polymerization of glucose proceeds along the surface of the neck-localized emulsion droplets, replicating the growth pattern of the primary SCFs and forming new flask-like subunits at the flask-neck of SCFs. Ultimately, this site-specific cascade assembly generates the DCFs.

In addition to the structural regulation, the functionalized design of asymmetric carbon nanoparticles is critical for optimizing their performance in the practical application. The successful assembly of asymmetric carbon nanoflasks inspires us to explore the possibility for rational constructing high-performance nanomaterials following the new assembly route. Especially, previous study has demonstrated that the P123/SO emulsion can be employed as the reducing agent for the synthesis of noble metal nanoparticles [33, 34]. As a proof of concept, we encapsulate ultra-small Ag nanoparticles into the carbon nanoflasks by the *in-situ* assembly process. The preparation of Ag@SCFs and Ag@DCFs is closely resembled that of SCFs and DCFs (Fig. 5(a)). The primary difference is the addition of AgNO<sub>3</sub> during synthesis, where silver species can be adsorbed onto the surface of the emulsion droplets [33]. During the hydrothermal process, the silver salt underwent *in-situ* reduction by the P123/SO emulsions, while carbon nanoflasks as the nanoreactor were simultaneously formed. Due to the relatively faster reaction kinetics of metal salts, the Ag nanoparticles were effectively encapsulated within the carbon nanoflasks.

XRD patterns demonstrates that both Ag@SCFs and Ag@DCFs show new diffraction peaks at 38.1°, 44.2°, 64.4°, and 77.4°, corresponding to the (111), (200), (220), and (311) crystal planes of metal Ag (JCPDS No. 087-0597), respectively (Fig. 5(b)) [35, 36]. TEM images show that Ag nanoparticles with an average particle size of 5 nm are firmly deposited within each carbon nanoflask, while keeping the perfect structure of the nanoflasks (Fig. 5(c) and Fig. S15 in the ESM). Meanwhile, TEM images also witness the *in-situ* reduction process of Ag@SCFs. As shown in Fig. S16(a) in the ESM, silver nanoparticles began to form after 3 h of hydrothermal treatment. As the hydrothermal reaction time increased, carbon

nanoparticles gradually transformed into flask-like structure, while the size of Ag nanoparticles remained unchanged (Figs. S16(b)–S16(d) in the ESM). These observations unequivocally validate the successful encapsulation of Ag nanoparticles within the carbon nanoflasks via an *in-situ* reduction method. XPS was conducted to elucidate the surface chemical composition of Ag@DCFs. The survey full spectrum confirms the presence of Ag, C, and O (Fig. 5(d)), and their specific atomic contents are 0.16 at.%, 77.59 at.%, and 22.25 at.%, respectively (Table S2 in the ESM). For the high-resolution Ag 3d spectrum (Fig. 5(e)), two peaks corresponding to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> are observed at binding energies of 368.4 and 374.4 eV, respectively, indicating the formation of metallic Ag [37]. The C 1s spectrum is deconvoluted into four components, corresponding to C=C (~ 284.8 eV), C–C (~ 286.2 eV), C–O (~ 288.7 eV), and C=O (~ 289.6 eV) bonds (Fig. 5(f)) [25]. Additionally, the O 1s spectrum is fitted into two peaks assigned to C–O (~ 531.9 eV) and C=O (~ 533.1 eV) (Fig. S17 in the ESM) [38]. These results conclusively demonstrate the successful incorporation of Ag nanoparticles into the carbon nanoflasks.

The catalytic performance of asymmetric Ag@SCFs and Ag@DCFs catalysts was evaluated through a classical reduction of 4-NP to 4-AP by NaBH<sub>4</sub>. UV-Vis spectroscopy was used to monitor the reaction progress (Fig. 5(g) and Fig. S18 in the ESM). At the absence of the catalysts, an absorption peak centered at 400 nm belongs to the typical characteristic peak of 4-NP [39–41]. Once adding the catalysts, the peak intensities at 400 nm decreases rapidly, which almost disappear within 6 and 4 min for Ag@SCFs and Ag@DCFs, respectively. Simultaneously, a new absorption peak at 295 nm emerges and gradually increases [42–44]. That means the efficient reduction of 4-NP to 4-AP in two catalysts, suggesting that Ag@DCFs has better catalytic activity. Furthermore, as the reaction proceeded, the color of the 4-NP solution underwent a distinct change from light yellow to colorless (Figs. S19 and S20 in the ESM), further verifying the successful occurrence of the reduction process.

Figure 5(h) shows the time-dependent conversion processes of 4-NP for two catalysts, which provides a compelling evidence for the superior catalytic activity of Ag@DCFs. With excess NaBH<sub>4</sub>, the pseudo first-order kinetics were applied to evaluate the catalytic rate [42]. As shown in Fig. 5(i), the rate constant (*k*) was calculated to be 0.53 min<sup>-1</sup> for Ag@SCFs, much lower than that of Ag@DCFs (0.72 min<sup>-1</sup>), further confirming the better catalytic performance of Ag@DCFs in converting 4-NP to 4-AP. In addition, the reusability of the Ag@DCFs catalyst was also evaluated. After five cycles, the conversion of 4-NP was maintained at approximately 95.4% (Fig. 5(j)), demonstrating an excellent catalytic stability of Ag@DCFs. The above result highlights the unique advantages of carbon nanoflasks as nanoreactors for catalytic applications.

## 4 Conclusions

In summary, carbon nanoflasks with single-necked and double-necked structures were successfully fabricated through a scalable and cost-effective interfacial and cascade assembly route. Experimental results demonstrate that suitable carbon precursors determine the structural evolution of primary nanoparticles, guiding their morphological transformation from hemispherical to single-necked flasks. The spatial confinement provided by such a unique SCFs architecture facilitates the subsequent hydrogen-

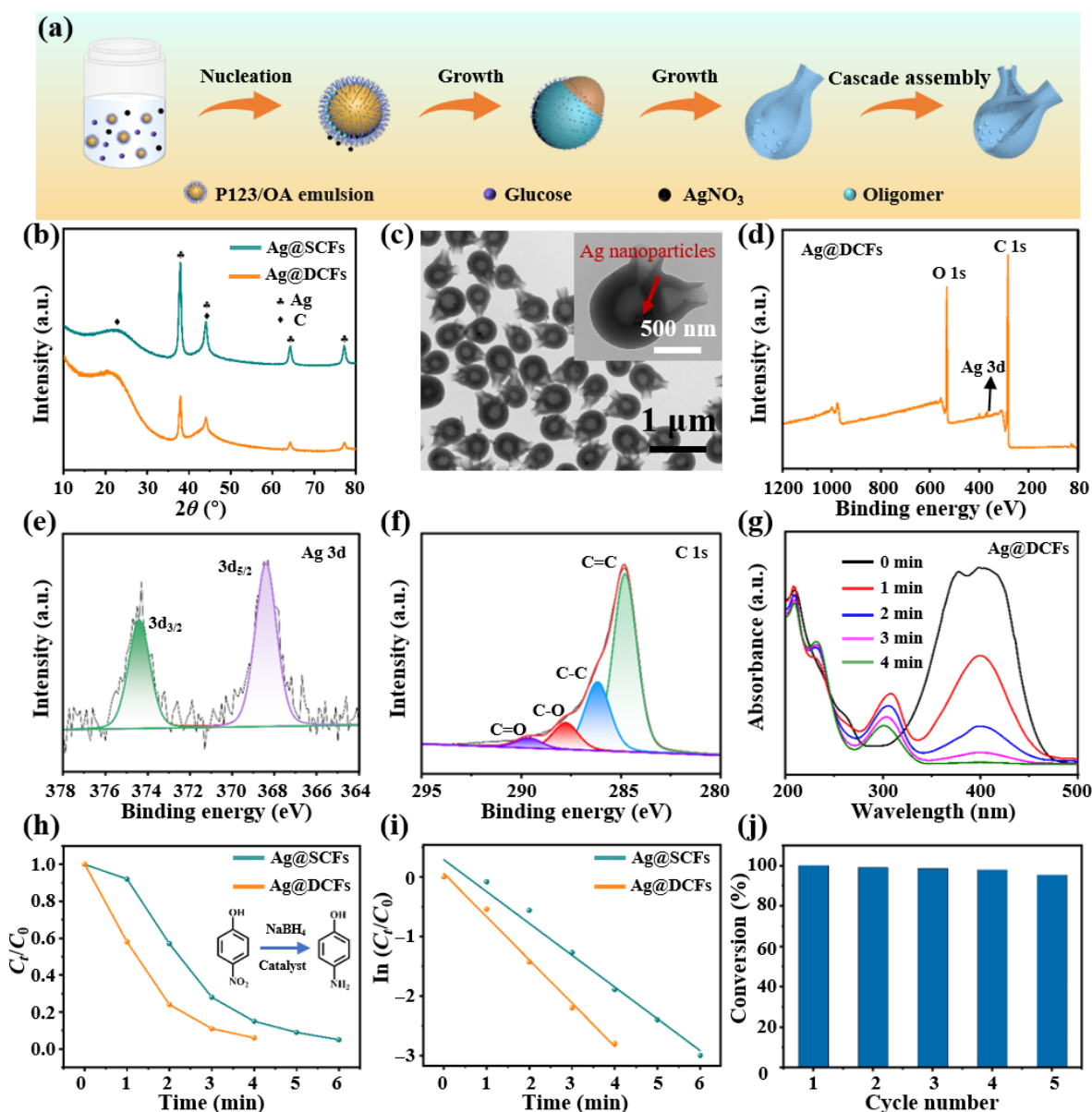


**Figure 5** (a) Schematic illustration of the synthetic process of Ag@SCFs and Ag@DCF. (b) XRD patterns of Ag@SCFs and Ag@DCF. (c) TEM image of Ag@DCF. (d) XPS survey spectrum of Ag@DCF. (e) and (f) High-resolution spectra of Ag 3d and C 1s. (g) Time-dependent UV-Vis spectra for the reduction of 4-nitrophenol with Ag@DCF. (h) Comparison of catalytic activities and (i)  $\ln(C_t/C_0)$  versus time for the reduction of 4-NP of Ag@SCFs and Ag@DCF. (j) Recyclability of Ag@DCF for the reduction of 4-nitrophenol.

bonding driven cascade assembly towards the final DCFs. As observed by ET analysis and 3D reconstruction, DCFs consist of a larger primary flask decorated with smaller flask-like units on the flask body. Used as asymmetric nanoreactors, both Ag@SCFs and Ag@DCF catalysts are well constructed by the *in-situ* encapsulating ultra-small Ag nanoparticles within the carbon nanoflasks. Owing to the unique spatial confinement and stable immobilization of Ag nanoparticles, the resultant Ag@DCF catalyst exhibits a superior catalytic activity for the NaBH<sub>4</sub>-mediated reduction of 4-NP to 4-AP. This work highlights the promising potential of structurally engineered nanoreactors for advanced catalytic applications.

**Electronic Supplementary Material:** Supplementary material (SEM, TEM, HRTEM, ET slices, and 3D reconstruction images,

particle size distribution, Zeta potential and atomic contents tables, high-resolution XPS spectra of O 1s, along with digital photos of 4-NP solutions) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908617>.

### Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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## Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

## Author contribution statement

H. T. L.: Data curation, validation, writing manuscript, experimental design. H. S.: Electron tomography analysis. S. Y. H.: Data analysis, characterizations. Z. Z. K.: Characterizations. C. Z. Y.: Manuscript discussions, revised manuscript. H. J. Z.: Conception, funding acquisition, writing manuscript. All the authors have approved the final manuscript.

## Use of AI statement

None.

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