Highly Efficient Silver Catalyst Supported by a Spherical Covalent Organic Framework for the Continuous Reduction of 4-Nitrophenol

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ABSTRACT: Developing new materials and novel technologies for the highly efficient treatment of toxic organic pollutants is highly desirable. Chemical reduction based on heterogeneous substrate/noble metal catalysts and the reducing agent NaBH_4 has become an effective method in recent years. Here, a spherical covalent organic framework (SCOF) was designed to provide basic sites for Ag ions, by which small Ag NPs were immobilized on the SCOF to form Ag NPs@SCOF microspheres. The prepared microspheres exhibited a high catalytic reduction ability toward 4-nitrophenol (4-NP). An optimized permeation flux of $2000 \text{ L m}^{-2} \text{ h}^{-1}$ (LMH) and a more than 99% 4-NP reduction efficiency were obtained with flow-through experiments, which are far better than the reported results (below 200 LMH). Moreover, the microspheres could maintain stable catalytic performance under a continuous flow-through process. Our work provides an efficient material and technology that can be applied to easily treat toxic organic pollutants.

KEYWORDS: covalent organic framework, catalytic reduction, organic pollutants, flow-through, silver nanoparticles

INTRODUCTION

Noble metal nanoparticle-based heterogeneous catalysts have attracted considerable attention in recent years due to their potential outstanding catalytic activities toward toxic organic pollutants.^{1–16} Semiconductor material substrates, such as porous carbon,^{17,18} graphene oxide (GO),^{19–22} graphitic carbon nitride ($\text{g-C}_3\text{N}_4$),^{23–25} molybdenum disulfide (MoS_2),²⁶ metal organic frameworks (MOFs),^{27–32} and covalent organic frameworks (COFs),^{33,34} can not only immobilize and limit the aggregation of tiny noble metal nanoparticles but also provide abundant electrons to noble metal nanoparticles, thus effectively strengthening the electron transfer of noble metal nanoparticles from the reduction agents such as NaBH_4 to electron acceptor toxic organic pollutants to obtain nontoxic and beneficial forms.^{35,36} Compared with other substrates, COF materials have the characteristics of large specific surface areas (more than $300 \text{ m}^2 \text{ g}^{-1}$) and chemical stability and are more suitable substrates for supporting noble metal nanoparticles.^{37–40} In addition, the chemical structure of a COF can be tailored through the introduction of functionalized groups such as thioether groups

and nitrogen groups during the synthesis and post modification processes, which can impart strong interfacial interactions between noble metal nanoparticles and the COF skeleton, facilitating enhanced catalytic performance toward toxic organic pollutants.^{41,42}

The separation and reuse of noble metal nanoparticle-based heterogeneous catalysts is the key point affecting their application. Currently, due to its large surface area and low density, COF materials are difficult to sink in mixtures, even under high-speed centrifugation, which increases the cost of toxic organic pollutant treatment. To overcome these drawbacks, magnetic materials, such as Fe_3O_4 ^{43–46} and iron-rich materials,^{47–49} were used as substrates. Xu et al. reported the

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fabrication of Fe₃O₄ supported COF/Au composites for the catalytic reduction of 4-nitrophenol (4-NP).⁵⁰ After recycling 5 times, the catalytic activity was almost unaltered, exhibiting good stability. Nevertheless, treatment is still expensive because abundant equipment is involved.⁵¹ In addition, catalyst separation from the mixture and reuse process would also reduce the treatment efficiency. Therefore, developing a novel technology for the highly efficient treatment of toxic organic pollutants is highly desirable.

Membrane separation is an important research field of separation and purification technology due to its advantages of efficient and continuous treatment of organic pollutants.⁵² Recently, catalytic membranes with membrane supporting noble metal nanoparticles have drawn great attention due to their functionalization and treatment of toxic organic pollutants in addition to separation.^{53–55} For example, Dong et al. reported the fabrication of polysiloxane/COF/Pd NPs flat sheet membranes and use them to continuously treat organic pollutant chlorobenzenes.⁵⁶ A catalytic reduction efficiency of 98% was achieved, while the separation efficiency was unsatisfactory due to the lower loading of noble metal nanoparticles supported on the surface of these flat sheet membranes derived from the restriction of the membrane surface area. Thus, the efficiency of the separation system is limited.

Compared with COF-based flat sheet membranes, these membranes fabricated by the stacking of COF particles have more advantages, such as loose structures and large specific surface areas for the effective loading of noble metal nanoparticles. Among these COF particles with various structures (including lamella and dendritic structures), spherical COF particles have larger surface areas to provide more active sites for electron transfer and higher porosity for the fast pass through the feed solution.^{57,58} Furthermore, SCOF particles with good monodispersity are facile uniformly supporting the noble nanoparticles, facilitating improving the stability of the prepared catalyst.^{59,60} Here, a SCOF with a specific surface area of more than 500 m² g⁻¹ and an average diameter of approximately 2 μm was synthesized and first used as a substrate for supporting silver nanoparticles (Ag NPs). Microsized SCOF was selected due to their stability in the continuous flow process, which is no easy leach out. Compared with other noble metals, such as Au NPs and Pt NPs, Ag NPs have been widely used because of their excellent electron transfer ability and high-cost effectiveness.^{61–63} Phenolic compounds are considered hazardous pollutants by the U.S. EPA, which would affect the environment.⁶⁴ Catalytic reduction of 4-NP to low toxic amines 4-aminophenol (4-AP) is a green approach for environmental remediation. Furthermore, 4-AP can be reused in the chemical industry such as pharmaceuticals, pesticides, and urethane industries.^{65,66} Therefore, the catalytic performance toward 4-NP was systematically evaluated through the static and dynamic process. Stability and recyclability were investigated by testing the release of Ag NPs and a continuous catalytic performance during the flow-through process. To the best of our knowledge, few studies have explored fast treatment technology using the spherical COF materials and flow-through technology toward nitrophenol derivatives, providing a potential application for highly efficient and sustainable treatment.

MATERIALS AND METHODS

Materials and Chemicals. 1,3,5-Tris(4-aminophenyl) benzene (TPB) and 2,5-divinylterephthalaldehyde (DVA) with purities above 98.0% were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., China. Other reagents and chemicals including acetonitrile (ACN, ≥ 98.0%), 4-nitrophenol (4-NP, ≥ 98.0%), dopamine hydrochloride (DA, ≥ 98.0%), and sodium borohydride (NaBH₄, ≥ 99.0%) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All reagents were used without any further purification. The morphology, structure, and composition of the samples were characterized by scanning electron microscopy (SEM, Jeol S4800) and transmission electron microscopy (TEM, JEM 2200) coupled with energy-dispersive detection, ¹³C CP/MAS NMR (JNM-ECZ600R), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Thermo Escalab 250Xi), surface area and pore analysis (Micromeritics ASAP 2020), thermogravimetric analysis (TGA, Mettler SMP/PF7548/MET/400W instrument), and X-ray diffraction (XRD, Bruker D8-Advantage powder diffractometer). The concentration of Ag NPs was measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN DRC II). The catalytic activity was evaluated by a UV-vis spectrometer (PERSEE UT 1810).

Synthesis of the SCOF. TPB (0.04 mmol) and DVA (0.06 mmol) were mixed with 5 mL CAN and sonicated for 2 min. Afterward, acetic acid (12 M, 0.4 mL) was added to the mixture, which was incubated for 3 days at room temperature.⁶⁰ Then, the resulting yellow precipitate was collected through high-speed centrifugation, followed by washing with anhydrous acetone and anhydrous tetrahydrofuran three times. The product was dried under high vacuum at 60 °C for 24 h.

Fabrication of Ag NPs@SCOF. SCOF (0.5 g) was dispersed in 250 mL of DI water and then AgNO₃ (0.1 g) was added to the mixture. After reaction for 3 h, NaBH₄ (15 mL, 3 mM) was added dropwise. Then, the mixture was stirred for 12 h in the dark. After washing three times with DI water and collecting by centrifugation, the Ag NPs@SCOF product was obtained after drying under a high vacuum at 60 °C for 24 h. The content of the Ag NPs with a loading of 0.95 wt % was determined by ICP-MS.

Catalytic Experiment. Both static experiments and flow-through experiments were applied to evaluate the catalytic performance of the prepared Ag NPs@SCOF catalyst toward 4-NP. For static experiments, 25 mg of Ag NPs@SCOF microspheres were typically added to 100 mL of an aqueous solution containing 15 mg/L 4-NP and 0.2 M NaBH₄. The time-dependent concentration of the mixture was monitored by UV-vis absorption spectra. For the flow-through experiments, 50 mg of Ag NPs@SCOF microspheres were packed into a 6 mm PVC tube with an effective length of 10 mm and blocked with degreasing cotton, as shown in Figure S1 of the Supporting Information (SI). Through the flow filtration system, a feed solution containing 15 mg/L 4-NP and 0.05 M NaBH₄ was continuously catalytically reduced by the Ag NPs@SCOF microspheres.

The apparent reduction rate constant k_{app} and reduction efficiency (E) were calculated with eqs 1 and 2, respectively.

$$\ln(C_t/C_0) = -k_{app}t \quad (1)$$

$$E = (C_0 - C_t)/C_0 \quad (2)$$

where C_t and C_0 are the concentrations of the dyes at time t and 0, respectively, calculated from the calibration curves (Figure S2).

The flux (H , L m⁻²h⁻¹, LMH) was calculated with eq 3.

$$H = \frac{V}{S \times t} \quad (3)$$

where V and S are the cumulative permeability volume (L) and cross-section of the pipeline (m²), respectively.

Scheme 1. Fabrication Process of the Ag NPs@SCOF Catalyst Included a Condensation Reaction and the Chelation and Reduction of Ag Ions on the SCOF Substrate^a

^aThe blue and yellow spheres represent N groups and Ag NPs, respectively.

Figure 1. (a) ¹³C CP/MAS NMR Spectrum of SCOF, (b) N₂ adsorption–desorption isotherms of samples, and (c) XRD spectrum of Ag NPs@SCOF. Inset: high-resolution XPS spectrum of Ag 3d and (d) XPS patterns of samples.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ag NPs@SCOF. The SCOF was first synthesized through a condensation reaction with TPB as the organic linker and DVB as the knot at room

temperature. After reacting for 3 days, the SCOF in the form of a yellow precipitate was obtained.⁶⁰ Then, the dried SCOF was used as the substrate to fix the Ag NPs through the strong interfacial interaction between the abundant nitrogen func-

Figure 2. SEM images of the (a) the SCO and (b) Ag NPs@SCO with enlarged insets, (c) STEM-EDX elemental mapping images, and (d) high resolution TEM image of Ag NPs@SCO.

tional groups of the SCO and Ag NPs. Thus, Ag NPs@SCO was fabricated, as shown in Scheme 1.

Morphological and Structural Studies. The synthesized SCO was first characterized by solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. As shown in Figure 1a, five intense peaks between 100 and 180 ppm were observed, and the chemical shift at 137.2 ppm indicated that condensation occurred between TPB and DVB.^{41,60} The porous structures of the SCO and Ag NPs@SCO were investigated by measuring N_2 sorption. As shown in Figure 1b, the BET specific surface area of the SCO was calculated to be $505 \text{ m}^2/\text{g}$. This result indicated the large supported sites for loading Ag NPs. The value of Ag NPs@SCO decreased to $80 \text{ m}^2/\text{g}$ probably due to the deposition of nonporous Ag NPs altering the surface property of SCO microsphere.⁵⁰ XRD was used to confirm the crystallinity of the SCO and the loading of Ag NPs on the SCO. As shown in Figure 1c, three strong peaks at 2θ values of 4.7° , 5.5° , and 7.3° , which is in accordance with the previous report, demonstrated the good crystallinity of the prepared SCO.⁶⁰ After loading of Ag NPs, four strong peaks at 2θ of 38.1° , 44.4° , 64.5° , and 77.8° can be observed, which agrees with the JCPDS card no. 04–0783, demonstrating the successful loading of Ag NPs on the SCO surface.⁶² Although the content of Ag NPs is only 0.95 wt % (quantified by ICP/MS),

the intensity of peak is much higher than SCO, reflecting the good coverage of Ag NPs on the surface of SCO.⁶⁷ XPS was used to provide information on the elemental composition and chemical states of the synthesized samples. As shown in Figure 1d, peaks corresponding to C, O, N, and Ag can be observed, which is consistent with the formation of Ag NPs@SCO microspheres. From the inset of Figure 1d, the binding energies at 375.3 and 369.3 eV can be attributed to $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$ of Ag (0), respectively, confirming the loading of Ag (0) NPs on the surface of the SCO.⁶³ Furthermore, the binding energy from pyrrolic N shifted from the 399.3 to 399.8 eV after loading of Ag NPs, suggesting the strong interactions between Ag NPs and the pyrrolic N atoms of SCO (Figure S3).⁴¹

The morphologies of the SCO and Ag NPs@SCO were characterized by SEM and TEM. As shown in Figure 2a, the synthesized SCO exhibited a spherical morphology with a smooth surface. The mean diameter was calculated to be $2 \mu\text{m}$ from the inset of Figure 2a. The loading of Ag NPs had almost no effect on the surface morphology of the SCO (Figure 2b). To confirm the successful loading of Ag NPs on the surface of SCO, HR-TEM was used. As shown in Figure 2c, Ag NPs (yellow dots) were uniformly dispersed on the surface of SCO. The average size of Ag NPs was calculated as approximately 20 nm (Figure S4). Although the size of Ag

Figure 3. Time-resolved UV-vis spectra of 4-NP, (a) Ag NPs@SCOF and (b) the SCOF. (c) Plot of $\ln(C_t/C_0)$ versus reaction time for the catalytic reduction of 4-NP. The effect of (d) pH values, (e) Ag NPs@SCOF concentration, and (f) reaction temperature on the catalytic performance.

NPs is larger than the pore size of SCOF (3 nm), the Ag NPs can immobilize on the surface of SCOF due to the strong interfacial interactions between SCOF with abundant nitrogen and Ag NPs.⁴¹ The imaging of Ag NPs@SCOF (Figure 2d) exhibited the loading of Ag NPs and an interplanar spacing of 0.118 nm, which was assigned to the (222) plane of the Ag crystal.⁴¹ Considering that small Ag NPs are uniformly dispersed on the surface of the SCOF, the loaded Ag NPs can provide abundant active sites for the catalytic reduction of toxic organic pollutants.

Catalytic Properties of Ag NPs@SCOF Microspheres.

The catalytic properties of the fabricated Ag NPs@SCOF microspheres were examined in the catalytic reduction of 4-NP in the presence of NaBH_4 . The reduction process was monitored by the change in UV-vis absorbance at wavelengths of 300 and 400 nm.⁵¹ During the catalytic reduction process, the color of the 4-NP solution changed from green-yellow to colorless. Correspondingly, the characteristic absorbance of 4-NP at 400 nm rapidly decreased to 0 within 5 min and the characteristic absorbance of the reduced product

4-AP gradually increased at 300 nm (Figure 3a). To evaluate the catalytic performance of the fabricated Ag NPs@SCOF microspheres, the catalytic activity of the SCOF without Ag NPs was used as a control. As shown in Figure 3b, the characteristic absorbance of 4-NP at 400 nm was almost unaltered with prolonged reaction time, reflecting the effective catalytic performance of the Ag NPs@SCOF microspheres. Considering the excess concentration of NaBH_4 existing in the catalytic system, kinetic eq 1 was used to evaluate the catalytic performance. As shown in Figure 3c, a good linear relationship between $\ln(C_t/C_0)$ and t was exhibited by pseudo-first-order reaction kinetics. The slope k_{app} of the Ag NPs@SCOF microspheres was calculated to be 0.55 min^{-1} , which is much higher than that of 4-NP catalyzed by the SCOF (0.01 min^{-1}). Furthermore, the influences of the pH value, the concentration of the catalyst, and reaction temperature were investigated. In this work, the concentration of NaBH_4 is excessive, thus, the catalytic activity at different pH value can reflect the stability of the catalyst. As shown in Figure 3d, k_{app} was maintained 0.55 min^{-1} with increasing pH values from 7 to 11. The value of k_{app}

Figure 4. (a) Time-resolved UV-vis spectra of 4-NP solutions. (b) Plot of $\ln(C_t/C_0)$ versus reaction time for the catalytic reduction of 4-NP. The reaction conditions were as follows: 15 mg L^{-1} 4-NP, 300 mg L^{-1} Ag NPs@SCOF, pH 7, and temperature of 40°C .

Table 1. Comparison of the Catalytic Activities of Noble Metal-Based Heterogeneous Catalysts Reported Recently for 4-NP Reduction with NaBH_4

catalyst	k_{app} (min^{-1})	TOF (h^{-1}) ^a	ref
GO-Au	0.12	42	<i>Appl. Catal. B Environ.</i> , 2016 ²²
Au@g-C ₃ N ₄	0.90	12	<i>Appl. Catal. B Environ.</i> , 2019 ²⁴
Au@g-C ₃ N ₄	0.36	87	<i>Appl. Catal. B Environ.</i> , 2017 ²⁵
SBA-15/PDA _{0.6} /Ag	0.44		<i>ACS Appl. Mater. Inter.</i> , 2018 ⁶⁸
HCB-Au	0.05		<i>Appl. Catal. B Environ.</i> , 2019 ⁶⁹
Pt@COF	—	56	<i>J. Am. Chem. Soc.</i> , 2017 ⁷⁰
Fe ₃ O ₄ @PPy-MAA/Ag	0.17		<i>Appl. Catal. B Environ.</i> , 2019 ⁷¹
Au@PDA@Au	0.50		<i>ACS Appl. Mater. Inter.</i> , 2017 ⁷²
Pd-GA/RGO	0.12		<i>J. Hazard. Mater.</i> , 2017 ⁷³
MP@Void-Pt@mSiO ₂	0.35		<i>ACS Sustain. Chem. Eng.</i> , 2018 ⁷⁴
Ag-L NPs/LCG ₃	0.37		<i>ACS Sustain. Chem. Eng.</i> , 2020 ⁷⁵
Au@TR-HCP-TPMT	0.37	18	<i>ACS Appl. Nano Mater.</i> , 2019 ⁷⁶
Ag@CMP	0.08	17	<i>ACS Appl. Mater. Inter.</i> , 2017 ⁷⁷
Au@SMt	1.05	13	<i>App. Clay Sci.</i> , 2018 ⁷⁸
Ag NPs@SCOF	1.06	81	this work

^aThe moles of 4-NP catalytically reduced per mole of Ag under the consumed time.

increased linearly with the concentration of Ag NPs@SCOF microsphere (Figure 3e) and increased from 0.42 min^{-1} to 0.67 min^{-1} as the temperature increased from 20 to 40°C (Figure 3f). Thus, the reduction reaction can be finished within 3 min (Figure 4a). The optimal k_{app} value (1.06 min^{-1} , Figure 4b) was obtained at 300 mg L^{-1} Ag NPs@SCOF and a temperature of 40°C . Accordingly, the color of 4-NP vanished within 3 min. 300 mg L^{-1} Ag NPs@SCOF was selected here due to the unaltered the turnover frequency (TOF, the moles of 4-NP catalytically reduced by per mole of Ag under the consumed time) as the concentration of Ag NPs@SCOF microsphere above 300 mg L^{-1} (Figure S5). TOF of the Ag NPs@SCOF microspheres was calculated to be 81.2 h^{-1} , suggesting better catalytic activity toward 4-NP reduction than the noble metal-based heterogeneous catalysts recently reported (Table 1). For example, Cao et al. reported the fabrication of conjugated microporous polymer@Ag NPs nanocatalyst for the reduction of 4-NP.⁷⁷ Although the Ag particle size of 3.9 nm was achieved, the value of TOF only reached 17 h^{-1} , which is much lower than our work. This result suggested the significant importance of SCOF as a substrate to fabricate catalyst.

Recyclability Examination. Five successive cycles were carried out. For one cycle, after finishing the catalytic reduction process, the catalyst was recovered by high speed centrifuga-

tion and reused for the next cycle. As shown in Figure S6, the value of k_{app} decreased by less than 10%. The mass loss after separation from the mixture was determined. The mass loss percent of the Ag NPs@SCOF microspheres after 1, 3, and 5 cycles of the catalytic reduction of 4-NP decreased by 97.5, 95.5, and 92.2 wt %, respectively, agreeing with the decreased value of k_{app} . These results reflected the excellent stability of the Ag NPs@SCOF microspheres. Nevertheless, the catalyst was difficult to recover from the solution. Even high-speed centrifugation equipment was carried out, the mass loss of the catalyst is unbearable, which heavily increased the cost. Furthermore, although the catalytic reduction can be finished within a few minutes, the recovery process would spend lots of time, decreasing the efficiency of the treatment.

Flow-through Catalytic Performance of Ag NPs@SCOF Microspheres. By taking advantage of the micro-sized SCOF and the support of the Ag NPs to fabricate the Ag NPs@SCOF microspheres, we designed a continuous flow setup for flow-through catalytic reduction of 4-NP. Compared with the static experiment, in a typical experiment, a feed solution containing a certain concentration of 4-NP and NaBH_4 was pumped through a PVC tube containing Ag NPs@SCOF. The catalytic processes performed with fluxes varying from 150 to $4000 \text{ L m}^{-2} \text{ h}^{-1}$ (LMH) were monitored by a UV-vis spectrometer. As shown in Figure 5a, the characteristic

Figure 5. UV-vis spectra of the 4-NP solution in the flow-through system with a flux from 150 to 4000 LMH (a), and the corresponding reduction efficiency (b).

Table 2. Comparison of the Catalytic Activities of Noble Metal-Based Heterogeneous Catalysts Reported Recently for 4-NP Reduction with NaBH₄ under a Flow-through Process

catalyst	concentration of 4-NP (mM)	noble metal content (mg)	flow rate (LMH)	reduction efficiency (%)	ref.
PET-DOPA-PEI-AuNPs	0.30	0.44	40	99	<i>Chem. Eng. J.</i> , 2016 ⁵⁴
Ag-PDA-IOs	0.10	0.42	150	99	<i>ACS Appl. Mater. Interfaces</i> , 2016 ⁷⁹
NTEMs/PDA/Pd	0.50		34	80	<i>ACS Appl. Mater. Interfaces</i> , 2018 ⁸⁰
C-BCGO-Au-stc-M membrane	0.27	0.96	87	96	<i>J. Hazard. Mater.</i> , 2020 ⁸¹
Ag NPs@SCOF	0.11	0.53	2000	99	this work

Figure 6. Release of Ag ions from the Ag NPs@SCOF microsphere in the flow-through system with a flux of 1000 LMH (a) and the corresponding reduction efficiency with prolonged reaction time (b). (c, d) TEM images of Ag NPs@SCOF microspheres after catalysis for 24 h.

Scheme 2. Catalytic Mechanism Proposed for 4-NP Reduction with NaBH_4 in the Presence of Ag NPs@SCOF Microspheres

absorbance of 4-NP at 400 nm rapidly decreased to almost zero; correspondingly, the characteristic absorbance of the reduced product 4-AP increased at 300 nm as the feed solution flowed through the Ag NPs@SCOF microspheres under a flux of less than 2000 LMH. The reduction efficiency can be maintained at more than 99% as the flux increases from 150 to 2000 LMH (Figure 5b). When the flux was higher than 2000 LMH, a peak at 400 nm can be observed. The reduction efficiency decreased from 99% to 84% as the flux increased from 2000 LMH to 4000 LMH. The higher the flux was, the greater the concentration of 4-NP became. The shorter residence time between the 4-NP solution and the Ag NPs@SCOF microsphere decreased the reduction efficiency.⁷⁹ Thus, the reduction efficiency and flux can be further optimized by increasing the concentration of catalysts.⁵⁵

The reduction rate and reduction efficiency are two significant aspects for practical applications in organic pollutants treatment. Our fabricated Ag NPs@SCOF catalyst exhibited a better catalytic performance than the reported catalysts (Table 2). For example, Tripathi et al. fabricated flat membrane supported Au NPs and obtained an optimized flux of 40 LMH with a reduction efficiency of 99% under flow-through experiments.⁵⁴ Compared with the flat sheet membrane, our prepared Ag NPs@SCOF microspheres had more advantages, such as loose structures and large specific surface areas, facilitating the fast and continuous catalytic treatment of organic pollutants.

Stability of Ag NPs@SCOF Microspheres. For practical applications, continuous flow-through catalytic reduction was carried out under a flux of 1000 LMH. The feed solution containing 15 mg/L 4-NP and 0.05 M NaBH_4 was continuously pumped through a PVC tube containing 50 mg of Ag NPs@SCOF microspheres. The catalytic processes and the concentrations of Ag ions in the filtrate were monitored by UV-vis spectrometry and ICP-MS, respectively. As shown in Figure 6a, the concentration of Ag ions in the filtrate linearly increased with prolonged time, and the concentration after testing for 24 h was calculated to be 4.3 ppb, which is much lower than the limit of Ag ions (100 ppb) in drinking water.⁸² Furthermore, the cumulative Ag ions in the filtrate after testing for 24 h was only 325 ng, which accounted for 0.07 wt % of the total Ag supported on the Ag NPs@SCOF microspheres. That is, more than 99.9 wt % Ag NPs were maintained on the surface of the Ag NPs@SCOF microspheres. The excellent stability of our prepared Ag NPs@SCOF microsphere during the continuous catalytic process can be contributed to the strong interactions between Ag NPs and SCO and the large size of the catalyst avoiding leaching out.⁴¹ Correspondingly,

the reduction efficiency was maintained at more than 99% after testing for 24 h (Figure 6b). From the TEM images (Figure 6c,d), the morphology of the synthesized Ag NPs@SCOF microspheres was almost unchanged after testing for 24 h. Moreover, the XRD pattern of the Ag NPs@SCOF microspheres was also unaltered after testing for 24 h (Figure S7). All these results reflected the good stability of our prepared Ag NPs@SCOF microspheres.

Catalytic Reduction Mechanism. A mechanism was proposed based on the good catalytic performance of the prepared Ag NPs@SCOF microspheres toward 4-NP with a high k_{app} value (1.06 min^{-1})/TOF (81.2 h^{-1}) achieved for the static experiments and high flux (2000 LMH)/high reduction efficiency (more than 99%) achieved for the flow-through experiments. The main reason for the excellent catalytic performance can be attributed to the unique structure of the prepared catalyst. First, the SCO was designed and functionalized with nitrogen groups, which can immobilize Ag ions and restrict the size of Ag NPs grown on the surface of the SCO. Small Ag NPs can provide more catalytic sites than large Ag NPs for fast electron transfer from an electron donor (NaBH_4) to an electron acceptor (4-NP) to catalytically reduce 4-NP. Moreover, the large surface area of the SCO supplies abundant sites for supporting Ag NPs. In addition, the SCO, a good semiconductor, serves as a cocatalyst, providing basic sites that strengthen the electron transfer of the noble metal nanoparticles (much better than the conjugated microporous polymer substrate⁷⁷ and the montmorillonite substrate reported in our previous work;⁷⁸ TOF, 17 h^{-1} and 13 h^{-1} , respectively).^{57–60} Furthermore, Ag NPs@SCOF microspheres with a zeta potential of -9.8 mV more easily adsorb 4-NP with a relatively more positive charge than the product 4-AP, facilitating the acceleration of the catalytic reduction reaction and the detachment of 4-AP from the surface of catalysts to refresh the free active sites for the continuous flow-through reaction (Scheme 2).⁴³

CONCLUSIONS

In summary, a spherical COF with nitrogen groups was designed to provide basic sites for Ag ions, by which small Ag NPs were immobilized on the SCO to form Ag NPs@SCOF microspheres with superior catalytic performance toward 4-NP. A high k_{app} value (1.06 min^{-1})/TOF (81.2 h^{-1}) was achieved for the static experiments. A high flux (2000 LMH)/high reduction efficiency (more than 99%) was achieved for the flow-through experiments, which is far better than the reported results. Furthermore, only 0.07 wt.% Ag NPs were released from the catalytic system under a continuous flow-

through process for the 24 h test, reflecting the good stability of our prepared Ag NPs@SCOF microspheres. The excellent stability of our prepared Ag NPs@SCOF microspheres during the continuous catalytic process can be contributed to the strong interactions between Ag NPs and SCOF and the large size of the catalyst avoiding leach out. This work demonstrated the design and synthesis of a heterostructure used for catalytic application through the integration of small Ag NPs and a functionalized spherical COF, which can be extended to the fabrication of other functional catalysts based on the covalent organic framework supported nanostructured metal. We believe that our work will provide an efficient new material and applicable technology for the facile treatment of toxic organic pollutants.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c20444>.

Calibration curves of 4-NP, a lab-scale continuous filtration setup and Ag NPs@SCOF with cotton blocking the ends of the loaded polyvinyl chloride tube, TEM and EDX image of Ag NPs@SCOF microsphere, recyclability of Ag NPs@SCOF in the reduction of 4-NP, and photographs of synthesized samples (PDF)

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Notes

The authors declare no competing financial interest.

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