Research Paper

Towards mass production of a spherical montmorillonite@covalent organic framework@gold nanoparticles heterostructure as a high-efficiency catalyst for reduction of methylene blue

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ABSTRACT

Gold nanoparticles (Au NPs) supported by a covalent organic framework (COF) exhibited a remarkably catalytic performance towards organic pollutants, while the application is limited by the recovery and reuse from the mixture due to the size of Au NPs@COF at the nanoscale. Herein, Au NPs were in situ reduced on the surface of thiol groups functionalized new COF with NaBH₄, followed by the deposition on polydopamine modified micron-sized porous spherical montmorillonite (SMT) to construct a spherical SMT@COF@Au NPs heterostructure. SMT was used here due to its excellent adsorption ability towards methylene blue (MB), increasing the concentration of MB near COF@Au NPs, thus accelerating the catalytic reaction. Hence, the optimized apparent reduction rate constant (K_{app}) and turnover frequency (TOF) in our experiment could reach 8.32 min⁻¹ and 3.2×10^5 h⁻¹, respectively, at 40 °C and pH values of 10, which is much better than the reported. Furthermore, micro-sized SMT with self-sedimentary property could be easily recovered from the mixture without any devices involved. More importantly, the granular micro-sized morphology of the SMT-based heterostructure could facilitate transport on the product line and reduce the fouling, facilitating mass production COF@Au NPs based catalyst for application.

1. Introduction

Heterogeneous catalysts have attracted great attention in the areas of science and industry due to their excellent physical and chemical properties (Gao et al., 2020; Liao et al., 2019; Wang and Zhuang, 2019). Nanomaterials such as metal oxides (Cao et al., 2020; Das et al., 2019), clay materials (Arora et al., 2018; Joseph et al., 2019; Peng et al., 2019; Zhang et al., 2018), carbon materials (Qin et al., 2019a; Qin et al., 2019b), and metal-organic frameworks (Gao et al., 2019) were commonly used as carriers due to their large special surface areas to provide more active sites. Recently, the combination of two nanoparticles, covalent organic framework (COF) and ultrafine noble metal nanoparticles (average diameter of less than 5 nm), as a nanocomposite

catalyst represents the type of the most investigated heterogeneous catalytic system because of the unique structure and property of COF to control the size of noble metal nanoparticles and the excellent organic pollutants adsorption/electron transfer/products desorption ability for catalytic reduction of organic pollutants (Cao et al., 2017; Zhang et al., 2020c). However, the synthesized COF/ultrafine noble metal nanoparticles nanocomposites are in favor of dispersion in the solution, while it is difficult to separate from the mixture and reuse even through high-speed centrifugation, heavily increasing the cost of toxic organic pollutants treatment.

Considered this troublesome, the magnetic carrier could be a good choice (Yang et al., 2020). Zheng et al. reported the synthesized Fe₃O₄ supported COF/gold metal nanoparticles (Au NPs) (Xu et al., 2020). Hou

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et al. reported the construction of core-shell structured $\text{CuFe}_2\text{O}_4/\text{Ag}$ NPs/COF (Hou et al., 2020). Although magnetic separation can be used to recover these prepared catalysts, the usage of a great number of magnetic equipment is not in favor of the application. Compared with these carriers with nano-size, the porous micro-size carrier assembled by nanomaterials can also provide a large surface area for supporting noble metal nanoparticles. In our previous work, porous spherical montmorillonite (SMt) prepared with the granulation of Mt. through spray-drying technology owning the characteristics of large surface area, strong adsorption ability, and outstanding acid-base stability (Wang et al., 2020; Xiao et al., 2018). Different from the pristine Mt. with the strong hydratability and difficulty to subside in the aqueous solution, the granular compacted SMt microsphere could easily self-sedimentary in the mixture (Wang et al., 2019).

The catalytic transformation occurred on the surface of the catalyst including a complex adsorption-transformation-desorption procedure, where the design of heterogeneous catalyst structure regulates the interaction between the substrates and catalysts, further influencing the catalytic performance (Iqbal et al., 2018). Herein, ultrafine gold metal nanoparticles (Au NPs) were in situ reduced on the surface of sulfhydryl groups functionalized new COF with NaBH_4 , followed by the deposition on polydopamine modified micron-sized porous SMt to construct a spherical SMt@COF@Au NPs heterostructure. The resultant heterostructure was examined as a heterogeneous catalyst for catalytic reduction of methylene blue (MB) in the presence of NaBH_4 . The influences of concentration of catalyst, reaction temperature, and pH value on catalytic activity were systematically investigated. Recyclability was further studied. The self-sedimentary granular SMt@COF@Au NPs heterostructure is not only facile recovery from the mixture without any devices involved but also facilitates the mass production of these types of heterogeneous catalysts due to the improvement of transport and the reduction of fouling in the product-line compared with other amorphous substrates. To the best of our knowledge, this is the first report of fabricated a granular porous micro size carrier supported COF@Au NPs heterostructure as a catalyst for reduction of organic pollutants, successfully solving an engineering problem via a physical method.

2. Experimental section

2.1. Chemical and materials

2, 4, 6-trihydroxybenzene-1, 3, 5-tricarbaldehyde and 2, 5-Diamino-1, 4-benzenedithiol dihydrochloride with purity above 98.0% were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., China. Other reagents and chemicals including 1, 4-Dioxane ($\geq 99.0\%$), Mesitylene ($\geq 98.0\%$), sodium borohydride (NaBH_4 , $\geq 99.0\%$), dopamine hydrochloride ($\geq 98.0\%$), acetic acid ($\geq 98.0\%$), methylene blue (MB, $\geq 99.0\%$), and montmorillonite were obtained from Sino-pharm Chemical Reagent Co. Ltd., China. All the reagents were of analytically pure grade and used without any further purification. The structures and properties of the prepared samples, including COF-SH, COF@Au NPs, and SMt@COF@Au NPs heterostructure, was characterized by scanning electron microscopy (SEM, Jeol S4800), transmission electron microscopy (TEM, JEM 2200), X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ^{13}C CP/MAS NMR (JNM-ECZ600R), X-ray diffraction (XRD, Bruker D8-Advantage powder diffractometer), surface area and pore analyzer (Micromeritics ASAP 2020), and inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer ELAN DRC II), respectively. The catalytic performance of the prepared samples was evaluated by a UV-vis spectrometer (PERSEE UT 1810).

2.2. Synthesis of COF-SH

The synthesis of COF-SH was performed via the condensation of 2, 4, 6-trihydroxybenzene-1, 3, 5-tricarbaldehyde and 2, 5-Diamino-1, 4-

benzenedithiol dihydrochloride. Typically, 2, 4, 6-trihydroxybenzene-1, 3, 5-tricarbaldehyde (25.21 mg, 0.12 mmol) and 2, 5-Diamino-1, 4-benzenedithiol dihydrochloride (44.11 mg, 0.18 mmol) were mixed with 1.1 mL of a 3:7:1 v/v/v solution of 1, 4-Dioxane/Mesitylene/6 M aqueous acetic acid. After frozen in a liquid nitrogen bath and three successive freeze-pump-thaw cycles, the tube was sealed and heated to 120 °C for 3 days. Then the yellow-brown precipitate was collected through filtration and fully washed with *N,N*-Dimethylformamide, acetone, and tetrahydrofuran. The product was dried under a vacuum at 60 °C to obtain COF-SH.

2.3. Fabrication of COF@Au NPs

200 mg of the synthesized COF-SH was dispersed in 60 mL of tetrahydrofuran, followed by the addition of HAuCl_4 solution (10 mL, 0.1 wt%). After stirring at room temperature for 2 h, NaBH_4 aqueous solution (10 mL, 0.53 M) was rapidly added and the mixture was continued reaction overnight. The products COF@Au NPs were collected by centrifugation, fully washed with DI water and ethanol, and finally dried under a vacuum at 60 °C overnight.

2.4. Fabrication of SMt@COF@Au NPs heterostructure

Porous spherical montmorillonite (SMt) was prepared with the granulation of Mt. through spray-drying technology. After coated with polydopamine (PDA), the PDA-coated SMt was introduced to the COF@Au NPs suspension to obtain a mixture with a PDA-coated SMt concentration of 20 g L^{-1} and COF@Au NPs concentration of 1 g L^{-1} , respectively. After being shaken for 12 h, the product was fully washed with DI water and dried at 60 °C in a vacuum oven for at least 12 h to a constant weight. The content of Au NPs was determined by the ICP-MS with the loading of 0.12 wt%. In addition, SMt@Au NPs heterostructure was fabricated through PDA chemistry for control.

2.5. Adsorption experiment

20 mg of samples were added to a 100 mL aqueous solution containing 40 $\text{mg}\cdot\text{L}^{-1}$ MB. The whole adsorption process was monitored by the UV-Vis absorption spectra. The removal percentage (*R*) was obtained from the Eq. (1):

$$R = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where C_0 and C_t are the initial organic pollutant concentration and concentration of the reaction time, respectively.

2.6. Evaluation of catalytic performances

MB was selected as a model and used to assess the catalytic activity of SMt@COF@Au NPs heterostructure. The time-dependent concentration of MB was monitored by UV-Vis spectrometry. Typically, 10 mL of MB solution with the concentration of 250 $\text{mg}\cdot\text{L}^{-1}$ and 10 mL of NaBH_4 aqueous solutions with the concentration of 0.5 M was first mixed with 80 mL DI water, then 40 mg of SMt@COF@Au NPs heterostructure was added. For recyclability, SMt@COF@Au NPs heterostructure was separated from the mixture through self-sedimentation and reused for the next cycle. The influences of the concentrations of SMt@COF@Au NPs heterostructure, reaction temperature, and pH values on apparent reduction rate constant (K_{app}) were investigated.

2.7. pH_{zpc} determination

SMt@COF@Au NPs heterostructure was added to 10 mL of an aqueous solution containing 0.1 M NaCl to obtain a suspension with a SMt@COF@Au NPs heterostructure concentration of 30 $\text{g}\cdot\text{L}^{-1}$. The pH of the solution was adjusted in the range of 3–11. Then the solution was

Scheme 1. The fabrication process of SMT@COF@Au NPs heterostructure including (a) the condensation reaction, (b) the chelation and reduction of Au ions on the COF substrate, and (c) the fabrication of SMT@COF@Au NPs heterostructure. The organic sheets and yellow points stand for COF and Au NPs, respectively.

fully mixed overnight and the SMT@COF@Au NPs heterostructure was picked up. The final pH was measured and the difference between the initial and final pH was plotted against the initial pH to obtain the pH_{zpc} .

3. Results and discussion

3.1. Synthesis and characterization of the SMT@COF@Au NPs heterostructure

COF with sulhydryl functional groups was first synthesized through the condensation reaction with the 2, 4, 6-trihydroxybenzene-1, 3, 5-tricarbaldehyde as the knot and 2, 5-Diamino-1, 4-benzenedithiol dihydrochloride as the organic linker at high temperature. After reaction 3 days, yellow precipitate COF-SH was obtained. Then the dried COF-SH

was used as a carrier to in situ supporting Au NPs to fabricate COF@Au NPs nanocomposites. On the other hand, granular SMT was surface-functionalized with polydopamine (PDA) and then used as the substrate to support COF@Au NPs nanocomposites to fabricate SMT@COF@Au NPs heterostructure, as shown in Scheme 1.

3.2. Structural studies

The synthesized COF was first characterized by the solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectrum. As shown in Fig. 1a, five intense peaks between 60 and 180 ppm could be observed and the chemical shift at 164.8 ppm indicated the condensation reaction happened between 1, 3, 5-Benzenetricarboxaldehyde and 2, 5-Diamino-1, 4-benzenedithiol dihydrochloride (Ma et al., 2019). The

Fig. 1. (a) ^{13}C CP/MAS NMR Spectrum of COF, (b) N_2 adsorption-desorption isotherms of samples, (c) XRD patterns, and (d) XPS spectrum of COF@Au NPs nanocomposites. Inset: high-resolution XPS spectrum of Au 4 f.

Table 1

Mesoscale properties of Mt., SMt, PDA@SMt, and SMt@COF@Au NPs heterostructure.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
Mt	8.1	0.10
SMt	61.2	0.38
PDA@SMt	46.4	0.25
SMt@COF@Au NPs	56.1	0.31

porous structures of the prepared samples were investigated by the measurement of N_2 sorption. As shown in Fig. 1b, all the samples exhibited regular pore structures typical of mesoporous materials. The pristine Mt. owned a specific surface area and pore volume of $8.1 \text{ m}^2 \text{g}^{-1}$ and $0.10 \text{ cm}^3 \text{g}^{-1}$, respectively (Table 1). After the granulation by the spray-drying technology, these values increased obviously to $61.2 \text{ m}^2 \text{g}^{-1}$ and $0.38 \text{ cm}^3 \text{g}^{-1}$, respectively (Table 1). This result reflected the efficient stacking and pore-making ability of spray drying (Stunda-Zujeva et al., 2017). The granular SMt coated by polydopamine (PDA) decreased these values to $46.4 \text{ m}^2 \text{g}^{-1}$ and $0.25 \text{ cm}^3 \text{g}^{-1}$, respectively, suggesting the weak N_2 adsorption ability of PDA. Conversely, these values increased to $56.1 \text{ m}^2 \text{g}^{-1}$ and $0.31 \text{ cm}^3 \text{g}^{-1}$, respectively, after supporting COF@Au NPs, demonstrating the efficient N_2 adsorption ability of COF (Table 1). Furthermore, XRD was used to confirm the crystallinity of the prepared COF and the loading of Au NPs on the SMt@COF@Au NPs heterostructure. As shown in Fig. 1c, three obvious peaks at 2θ of 11.0° , 26.3° , and 27.4° could be observed from the XRD curve of COF@Au NPs, resulting from the appearance of long-range order structure (Deng et al., 2020). Four strong peaks at 2θ of 38.1° , 44.4° , 64.5° , and 77.8° can be observed, which is well following the JCPDS

card no. 04–784, demonstrating the successful supporting of Au NPs on the COF surface (Xiao et al., 2019). Compared with SMt, the SMt@COF@Au NPs patterns exhibited similar features (JCPDS card no. 13–0135 for smectite and JCPDS card no. 46–1045 for quartz, respectively) and the same crystallite size (14.5 nm), indicating the higher content of SMt in the SMt@COF@Au NPs heterostructure (Gonçalves et al., 2017). XPS was further carried out to provide information on the surface elemental composition of the samples. As shown in Fig. 1d, the peaks corresponding to C, O, N, S, and Au could be observed, well consistent with the formation of COF@Au NPs nanocomposites. From the inset of Fig. 1d, the binding energies at 86.6 eV and 83.0 eV could be attributed to Au 4f_{7/2} and Au 4f_{5/2} of Au (0), respectively, confirming the loading of Au (0) NPs on the surface of COF. As shown in Fig. S1, the peaks corresponding to C, O, N, Si, and S could be observed, demonstrating the well supporting of COF@Au NPs nanocomposites on SMt. However, no Au peak could be observed, reflecting the lower content of Au on the SMt@COF@Au NPs heterostructure. ICP/MS was used to measure the loading of Au NPs. The content of Au NPs was quantified to be 0.12 wt% after dissolving the SMt@COF@Au NPs heterostructure in the strong acid. Besides, Au NPs were quantified to be 3.92 wt% in the COF@Au NPs nanocomposites. Thus, the loading of COF@Au NPs nanocomposites on the SMt@COF@Au NPs heterostructure could be calculated as 2.94 wt%.

The production of a catalyst with controllable morphology can not only improve the regularity of products and flowability but also decreases fouling, facilitating mass production for application (Qin et al., 2011). Therefore, SEM was used here to observe the morphologies of the fabricated samples. A granular morphology with a size distribution ($17 \pm 4 \text{ nm}$) was observed from Fig. 2a and Fig. S2. The synthesized COF exhibited a multilayer lamellar structure with a smooth surface

Fig. 2. SEM images of the (a) SMT@COF@Au NPs heterostructure with inset of pristine SMT and (b) COF with inset enlarging images, (c) TEM image of COF@Au NPs dispersed in aqueous solution, (d) TEM-EDX elemental mapping images, and (e) high resolution TEM image of the SMT@COF@Au NPs heterostructure.

(Fig. 2b). From the inset of Fig. 2b, the nanowires with an average diameter of about 40 nm could be observed. The morphology of COF@Au NPs nanocomposites after dissolving in an aqueous solution was observed by TEM. As shown in Fig. 2c, tiny Au NPs with a narrow size distribution (4 ± 1 nm) were uniformly dispersed on the surface of COF. The size of dispersed COF was about 50 nm, which is much suitable for supporting by micro-sized substrate SMT. Compared with SMT (inset of Fig. 2a), a smooth and lamellar structure could be seen on the surface of SMT@COF@Au NPs heterostructure, suggesting the good wrapping of COF@Au NPs nanocomposites on the surface of SMT. The uniform wrapping of COF@Au NPs on the surface of SMT is mainly due to the excellent adhesion ability of polydopamine coating. Corresponding to the TEM image, the EDX mapping of C, N, O, S, and Au elements exhibited in the same regions, demonstrating the fixed supporting of COF@Au NPs nanocomposites in the synthesized heterostructure (Fig. 2d). HR-TEM was employed to further prove the successful supporting of Au NPs on the SMT@COF@Au NPs heterostructure. As shown in Fig. 2f, Au NPs with the inter-planar spacing of 0.235 nm can be observed, which was assigning to the (111) plane of Au crystal (Xu et al., 2020). Although the content of Au NPs is lower in the SMT@COF@Au

NPs heterostructure, the small tiny size and uniform dispersion of Au NPs could supply the abundant active sites for catalytic reduction of organic pollutants.

3.3. Catalytic properties of SMT@COF@Au NPs heterostructure

Ultrafine noble metal nanoparticles with a diameter of less than 5 nm exhibited ultrahigh catalytic activities towards organic pollutants due to their large surface area to provide enough activity sites for electron transfer (Gong et al., 2019). Hence, the catalytic activity of the synthesized samples was evaluated by the reduction of carcinogenic toxic organic pollutant methylene blue (MB) in the presence of reduced agent NaBH_4 (Jana et al., 2019; Joseph et al., 2019; Lackovićová et al., 2019). The reduction process was monitored by a time-resolved UV–Vis spectroscopy. As shown in Fig. 3a, the peak at 665 nm gradually vanished within 3 min, reflecting the conversion of carcinogenic MB to inactive leuco-methylene blue. The sample prepared without COF was taken for control. As shown in Fig. S3, SMT@Au NPs with Au NPs with an average diameter size of 80 nm and content of 4 wt% were synthesized under similar conditions. More than 8 min was spent finishing the reaction

Fig. 3. (a) The time-resolved UV-vis spectra of MB. The effect of (b) SMT@COF@Au NPs heterostructure concentration, (c) temperature, and (d) pH values on the catalytic performance. (e) The time-resolved UV-Vis spectra of MB, the reaction conditions: 25 mg L⁻¹ MB, 400 mg L⁻¹ SMT@COF@Au NPs, pH 10, and temperature 40 °C. (f) pH_{zpc} determination of SMT@COF@Au NPs heterostructure.

Table 2

The comparison of catalytic activities of noble metal-based heterogenous catalysts reported recently for MB reduction with NaBH₄.

Catalyst	BET surface area (m ² g ⁻¹)	K_{app} (min ⁻¹)	TOF (h ⁻¹)	Ref.
Fe ₃ O ₄ @COF-Au	193.4	0.90	6.4×10^4	Appl. Catal. B Environ., 2020 (Xu et al., 2020)
SMT@Ag	45.0	0.24	110	App. Clay Sci., 2019 (Wang et al., 2019)
MgAlCe-LDH@Au NPs	–	1.80	2200	J. Mater. Chem. A, 2017 (Iqbal et al., 2017)
MGO-TA@Fe ³⁺ @Ag	126.8	3.24	6404	Chem. Eng. J., 2021 (Yang et al., 2021)
Graphene@Ag NPs	–	0.25	2120	ACS Sustain. Chem. Eng., 2018 (Sahoo et al., 2018)
Fe ₃ O ₄ @EDTA@Ag	81.0	1.83	198	ACS Appl. Nano Mater. 2019 (Sharif et al., 2019)
SMT@COF@Au NPs	56.1	8.24	3.2×10^5	this work

(Fig. S4). Considered the higher Au NPs, the rate was much less than our prepared SMT@COF@Au NPs heterostructure. These results demonstrated the good size control of COF towards the growth of Au NPs and

the excellent electron transfer ability of COF@Au NPs nanocomposites towards MB. Furthermore, the influences of the concentration of the catalyst, reaction temperature, and pH value were investigated.

Scheme 2. Mechanism of the catalytic reduction of MB with SMt@COF@Au NPs heterostructure.

Considering the excess concentration of NaBH_4 existing in the catalytic system, the kinetic equation $\ln(C_0/C_t) = K_{\text{app}}t$ was used to evaluate the catalytic performance, where the initial concentration of MB (C_0) and the concentration of MB at the time t (C_t) were calculated from the calibration curves (Fig. S5), where K_{app} is the apparent first-order rate

constant (Zhang et al., 2014). As shown in Fig. 3b, K_{app} increased from 0.48 min^{-1} to 1.24 min^{-1} with the concentration of SMt@COF@Au NPs heterostructure increasing from 200 mg L^{-1} to 400 mg L^{-1} . K_{app} reached a plateau with further increasing the concentration of SMt@COF@Au NPs heterostructure from 400 mg L^{-1} to 600 mg L^{-1} , reflecting enough

Fig. 4. The changes of apparent reduction rate constant K_{app} (a) and reduction efficiency E (b) of SMt@COF@Au NPs heterostructure in the reduction of MB with the prolonged cycle number. (c) SEM and (d) TEM images of SMt@COF@Au NPs heterostructure after cycled 20 times.

Fig. 5. The use of seawater as a sample for the color removal of MB by SMt@COF@Au NPs heterostructure. The initial concentrations of the reaction mixture were: MB (25 mg L^{-1}), NaBH_4 (0.05 M), and SMt@COF@Au NPs heterostructure (1000 mg L^{-1}).

active sites providing by SMt@COF@Au NPs heterostructure for electron transfer. The value of K_{app} increased from 1.24 min^{-1} to 3.80 min^{-1} with the reaction temperature increasing from 20°C to 40°C (Fig. 3c). The value of K_{app} increased from 1.24 min^{-1} to 2.36 min^{-1} with the increase of the pH values from 7 to 10. Hence, the optimal K_{app} (8.32 min^{-1} , Fig. 3e) in our experiment was obtained at the condition of 400 mg L^{-1} SMt@COF@Au NPs heterostructure and temperature 40°C and $\text{pH} = 10$. The reaction was finished within 30 s. Moreover, the turnover frequency (TOF) of SMt@COF@Au NPs heterostructure was calculated to be $3.2 \times 10^5 \text{ h}^{-1}$, demonstrating the excellent catalytic activity towards organic pollutant MB compared with those of noble metal-based catalysts reported recently (Table 2).

3.4. The catalytic reduction mechanism

The mechanism based on the high catalytic activity of SMt@COF@Au NPs heterostructure towards MB was proposed here. The main reason could be attributed to the special structure of the prepared heterostructure. Firstly, COF functionalized with sulfhydryl groups was designed and synthesized, by which the size of Au NPs was limited and Au NPs were immobilized on the surface of COF (Zhang et al., 2020c). The tiny small size Au NPs could provide abundant active sites for fast electron transfer. Secondly, COF was a good semiconductor, could serve as a cocatalyst to strengthen the electron transfer of Au NPs (Wang et al., 2021; Zhang et al., 2020a). Thirdly, the adsorption ability of

SMt@COF@Au NPs heterostructure could enhance the concentration of MB nearby the Au NPs, thus accelerating the catalytic reduction rate (Xiao et al., 2019). Furthermore, the influence of pH on the catalytic activities of SMt@COF@Au NPs heterostructure was investigated. As shown in Fig. S6, the R_{MB} increased from 13.0% to 25.4% as the increase of pH values from 4 to 11. Hence, pH_{zpc} was detected to prove the relationship between the adsorption and pH values (Zhang et al., 2020b). As shown in Fig. 3f, the value of pH_{zpc} was 7.1, that is, when the pH values exceeded 7.1, the surface of the SMt@COF@Au NPs heterostructure was negatively charged. For MB, a cationic organic pollutant, the electrostatic adsorption with the SMt@COF@Au NPs heterostructure would strengthen with the increase of pH values (Fig. S7). Therefore, a higher adsorption value was obtained at high pH values. The enhanced adsorption ability at high pH value could increase the concentration of organic pollutants around the active sites, thus accelerating the catalytic reaction (Scheme 2).

3.5. The stability of SMt@COF@Au NPs heterostructure

The recovery and reuse of noble metal-based catalysts are significantly important for the treatment of wastewater containing organic pollutants. Hence, successive 20 cycles were carried out to evaluate the stability of the SMt@COF@Au NPs heterostructure. As shown in Fig. 4a and Fig. 4b, the values of K_{app} slightly decreased 2% and R_{MB} maintained unaltered after 20 cycles. Besides, from the SEM images (Fig. 4c) and

TEM images (Fig. 4d), the morphology was unchanged after 20 cycles. The excellent stability of the prepared SMT@COF@Au NPs heterostructure can be attributed to the strong interfacial interaction between SMT and COF@Au NPs through the adhesion of polydopamine as well as the strong interfacial interaction between COF and Au NPs through the S–Au bonding (Zhang et al., 2020c).

3.6. Practical application

Seawater collecting from the Yellow Sea, Yantai, Shandong Province, China, was used here for practical application. As shown in Fig. 5, after adding NaBH₄ and SMT@COF@Au NPs heterostructure to the seawater/MB solution, the color vanished quickly within 30 s. SMT@COF@Au NPs heterostructure can quickly deposit on the bottom and can be easily reused without any devices involved. Therefore, the application of SMT@COF@Au NPs heterostructure for practical wastewater treatment is highly desirable.

4. Conclusions

A new covalent organic framework (COF) with sulfhydryl groups was designed to provide basic sites for Au ions, by which small size gold nanoparticles (Au NPs) were immobilized on the COF to form COF@Au NPs nanocomposites. The prepared nanocomposites were further stabilized supported by spherical montmorillonite (SMT) through the polydopamine chemistry method. The resultant heterostructure exhibited a high apparent reduction rate constant value (8.32 min^{-1}) and TOF ($3.2 \times 10^5 \text{ h}^{-1}$) towards organic pollutant methylene blue (MB). The high catalytic activity of our prepared heterostructure can be contributed to the strong adsorption ability of SMT towards MB, which increased the concentration of MB near COF@Au NPs, accelerating the catalytic reaction. Furthermore, the prepared heterostructure can be facile recovery due to the self-sedimentary ability of SMT. Moreover, the catalytic activity could maintain almost unaltered after a successive cycle for 20 times. This work demonstrated the design and synthesis of a new granular SMT@COF@Au NPs heterostructure for mass production and catalytic application through the integration of COF@Au NPs and SMT. We believed that our strategy would pave a new way for the application of noble-metal based heterogeneous catalyst for treating wastewater containing organic pollutants.

Author contributions

All authors have given approval to the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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