1 Fabrication of ploydopamine-kaolin supported Ag nanoparticles as effective

2 catalyst for rapid dye decoloration

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Abstract: In this work, silver nanoparticles supported on polydopamine-kaolin 13 composite (PDA-kaolin-Ag) was fabricated by an *in-situ* reduction method with PDA 14 as both reductant and stabilizer. The morphology, composition, and structure of 15 PDA-kaolin-Ag composite were characterized by transmission electron microscopy 16 (TEM), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy 17 (XPS). The catalytic reduction tests confirmed the importance of PDA modification 18 and high catalytic activities of this as-prepared PDA-kaolin-Ag composite towards a 19 model dye Rhodamine B. The catalytic reduction processes followed pseudo-first 20 21 order kinetics. Meanwhile, this catalyst showed excellent stability and recyclability for dye decoloration. Furthermore, this composite also exhibited good catalytic 22

performance on methylene blue, methyl orange, and Congo red. These results suggest
that PDA-kaolin-Ag composites can be used as efficient and cost-effective catalyst for
the decoloration of various organic dyes.

Keywords: Polydopamine functionalized kaolin; Silver nanoparticles; Catalytic
Performance; Dye decoloration; Catalytic stability

28 1. Introduction

Environment pollution is a severe threat on ecosystem and human health. (Ye et al., 29 2017; Ren et al., 2018a; Ren et al., 2018b; Wang et al., 2018a) Various contaminants 30 released into water bodies have caused serious water pollution and water resource 31 shortage. (Xu et al., 2012; Tang et al., 2018; Wang et al., 2018b; Xiong et al., 2018; 32 Yang et al., 2018a; Yi et al., 2018; Zhou et al., 2018) Organic dyes are a kind of 33 34 common chemicals that are widely used in textile, paper, leather, and other industries. It is estimated that their annual production is over 7×10^5 ton and a portion of dyes will 35 be inevitably discharged into water bodies during their production, usage, and 36 transport. (Gong et al., 2009; Adeyemo et al., 2017; He et al., 2018b) Consequently, 37 multifarious undesirable colors appearing on water surface will impede the sunlight 38 penetration, thereby endangering the survival of aquatic organisms.(Yagub et al., 2014; 39 He et al., 2018a) Owing to their undesirability, high visibility, and toxicity, therefore, 40 41 it is imperative to solve this pollution challenge.

42 As is well-known, catalysis is a vital subject for water purification. (Yang et al., 43 2018b) Nowadays, with the development of nanoscience, nanoscaled noble metal 44 nanoparticles such as silver (Ag) and gold used as nanocatalysts have been attracting

growing scientific interest in catalysis field. (Ganapuram et al., 2015; He et al., 2018c; 45 Qin et al., 2018) Hitherto, the application of Ag nanoparticles (Ag NPs) as catalyst for 46 47 water purification, such as dye decoloration, organic compound reduction and degradation, has been widely reported due to its fascinating characteristics and 48 49 important catalytic potential. (Kurtan et al., 2015; Li et al., 2015; He et al., 2018c) Unfortunately, the easy aggregation of nanoparticles will impede their catalytic 50 activity and practical application. To improve the dispersity of Ag NPs, the 51 immobilization of Ag NPs on various support materials has been developed, which is 52 beneficial to maintain its catalytic activity and facilitate the solid-liquid separation. 53 (He et al., 2018c) However, some support materials such as graphene materials and 54 carbon nanotube are usually limited to apply due to their complicate preparation 55 56 processes and high cost. In other words, seeking an appropriate material as support of Ag NPs for dye wastewater treatment is a significant subject. 57

Recently, clay minerals as nanoparticle supports have been attracting great attention 58 due to their environmental and economical advantages in comparison with many other 59 support materials such as graphene and carbon nanotube. (Zhou, 2011; Lin et al., 2014; 60 Ramprakash Upadhyay and Srivastava, 2016; He et al., 2018c) Kaolin, one of the 61 common clay minerals, has been studied as the nanoparticle support owing to its 62 low-cost, abundance, and eco-friendly. (Chen et al., 2012; Hashemian and Reza 63 Shahedi, 2013; Liu et al., 2013) In particular, its exceptional properties such as high 64 65 versatility, thermal and mechanical stability make it important to act as nanocatalyst support. (Wang et al., 2011) As one of the powerful methods, chemical reduction is 66

usually applied to fabricate the Ag-based composites in the presence of reductants 67 such as hydrazine, sodium borohydride (NaBH₄), sodium citrate, and dopamine. (He 68 69 et al., 2018c; Huang et al., 2018; Zhang et al., 2018) Nowadays, dopamine, a simple nontoxic organic chemical, has been widely used as green reductant for the synthesis 70 71 of Ag-based composites due to its dual-functional properties including reduction and self-polymerization. (Zhang et al., 2013; Lin et al., 2014; Xie et al., 2014) It has been 72 verified that dopamine can be polymerized into polydopamine (PDA) at weakly 73 alkaline solution condition. (Hu et al., 2014) The self-polymerization makes the 74 substrate materials coated with abundant amine and hydroxyl groups, which is 75 beneficial to the efficient bind with metal ions. Importantly, the in-situ reduction of 76 the adsorbed metal ions occurred on the active surface of PDA. (Yu et al., 2014) 77 78 Therefore, dopamine has been employed as an effective and green reductant for the synthesis of Ag NPs rather than the hazardous reductants such as hydrazine and 79 NaBH₄. (Zhang et al., 2013; Lin et al., 2014; Xie et al., 2014) However, the 80 application of dopamine as reductant for the preparation of cost-effective 81 PDA-kaolin-Ag composite has not been reported. Thus, this work was conducted to 82 verify the application potential of this composite as catalyst for the removal of dye 83 solution. 84

In this work, a novel PDA-kaolin-Ag catalyst was synthesized through a facile *in-situ* reduction route. In order to investigate the catalytic performance of this as-prepared composite on dye decoloration, Rhodamine B (RhB), a kind of common dye, was used as a model pollutant for the catalytic reduction tests. Herein, this

89	catalyst exhibited excellent catalytic performance and good stability for dye
90	decoloration, and could be used in environmental remediation.
91	2. Materials and methods
92	2.1 Materials
93	Kaolin ($Al_2Si_2O_9H_4$), dopamine hydrochloride, tris(hydroxymethyl) aminomethane
94	(Tris), hydroxylamine hydrochloride (NH ₂ OH HCl), and silver nitrate (AgNO ₃) used for
95	the synthesis of catalyst were purchased from Sinopharm chemical reagent Co., Ltd.
96	NaBH ₄ was purchased from Sinopharm chemical reagent Co., Ltd. Rhodamine B
97	(RhB), methylene blue (MB), methyl orange (MO), and Congo red (CR) were
98	purchased from Sigma-Aldrich. Ultrapure water was used for the preparation of
99	solutions in all experiments.
100	2.2 Synthesis of PDA-kaolin-Ag composites
101	Firstly, the PDA coated kaolin composite was prepared. 1.6 g kaolin powder was
102	dispersed in 200 mL Tris-HCl buffer solution (10 mM, pH=8.5) by ultrasonication for
103	2 h. Afterwards, 200, 400, and 800 mg dopamine hydrochloride were added into the
104	mixture under stirring, resulting in the corresponding concentrations of dopamine
105	hydrochloride were 1, 2, and 4 mg/mL, respectively. After stirring for 24 h at room
106	temperature, the solid product was separated by filtration and washed with ultrapure
107	water for three times. Then the obtained three PDA-kaolin samples were dried in a
108	vacuum oven at 60 $^{\circ}$ C overnight.

For the synthesis of PDA-kaolin-Ag composites, three different PDA-kaolin
powders (200 mg) were dispersed in 200 mL ultrapure water, respectively. And then 2

mL of silver ammonia solution (as Ag precursor solution) was added to the above 111 reaction system under stirring for 12 h at room temperature. Herein, 10 mg/mL of 112 113 AgNO₃ was prepared and ammonia solution was dropwise added to it until the brown 114 precipitation just disappeared, then silver ammonia solution (10 mg/mL) was obtained. 115 The solid products were separated by filtration and washed with ultrapure water for three times, and dried in a vacuum oven at 50 $\,^{\circ}$ C overnight. The resultant composites 116 were named as PDA-kaolin-Ag/1, PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4, 117 respectively. The synthesis of kaolin-Ag without PDA was according to Leopold's 118 method (Leopold and Lendl 2003; Qi et al., 2014) In brief, 200 mg kaolin was 119 dispersed in 100 mL ultrapure water, and 2 mL above silver ammonia solution was 120 added into the mixture for stirring 12 h. Afterwards, 40 mg NH₂OH HCl was added to 121 122 the mixture under stirring for 4 h to obtain kaolin-Ag composite. For further comparison, different concentrations of silver ammonia solution were used for the synthesis of 123 PDA-kaolin-Ag composites. Herein, 0.5 mL and 1 mL of silver ammonia solution 124 were added to prepare PDA-kaolin-Ag/2(0.5) and PDA-kaolin-Ag/2(1) as the same 125 procedure, respectively. 126

127 2.3 Characterization

The surface morphology and chemical compositions of as-prepared samples were characterized using Transmission Electron Microscope (TEM) (JEOL, Japan) and X-ray photoelectron spectroscopy (XPS) on ESCALAB 250Xi (Thermo Fisher Scientific, USA), respectively. The crystal structures of samples were determined by X-ray diffraction (XRD) patterns that recorded on a D8 Advance powder X-ray 133 diffractometer (Bruker, German) with a Cu Kα X-ray generator (40 kV, 100 mA).

134 2.4 Catalytic performance of PDA-kaolin-Ag composite

135 To investigate the catalytic performance of as-prepared catalysts, a comparative experiment on the decoloration of RhB with PDA-kaolin and PDA-kaolin-Ag samples 136 137 was firstly carried out. 10 mg sample was added into 50 mL RhB aqueous solution (10 mg/L) under continuous stirring at room temperature, respectively. Then, 1mL of 138 fresh NaBH₄ solution (0.25 M) was rapidly injected into the mixture solution. With 139 the reaction proceeding, the color of dye solution gradually vanished due to the 140 catalytic reduction. The catalytic activities of as-prepared samples were estimated by 141 monitoring the absorption spectra change (in the range of 300-700 nm) at the 142 maximum absorption wavelength of dye with a UV-vis spectrometer (UV-2550, 143 144 SHIMADZU, Japan). Another comparative experiment on the decoloration of RhB with kaolin-Ag, PDA-kaolin-Ag/1, PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4 was 145 conducted to investigate the effect of dopamine concentration on the synthesis and 146 catalytic performance of PDA-kaolin-Ag composites. Afterwards, PDA-kaolin-Ag/2 147 composite was further used to investigate the catalytic activity towards RhB solution 148 under the conditions of different dye concentration and catalyst dosage. In addition, 149 three other dyes including methylene blue (MB), methyl orange (MO), and congo Red 150 (CR) were also used for the catalytic reduction tests. 151

152 3. Results and discussion

153 3.1 Synthesis and characteristics of PDA-kaolin-Ag composite

154 The PDA-kaolin was first prepared by mixing the kaolin powder into dopamine

solution (10 mM, pH=8.5) with stirring, and the PDA layers could be coated on the surface of kaolin due to the self-polymerization of dopamine at weakly alkaline condition. Afterwards, silver ammonia solution was added, owing to the reducing ability of PDA, and then Ag NPs were deposited on the PDA layers by the *in-situ* reduction. The successful synthesis of PDA-kaolin-Ag composite has been verified by both the characteristic analysis and catalytic tests below. The facile synthesis process of PDA-kaolin-Ag composite is presented in Fig. 1.

In order to determine the morphological feature of PDA-kaolin-Ag composites, 162 TEM analysis was conducted. As shown in the TEM images (Fig. 2A, B), a thin PDA 163 layer was obviously coated on kaolin surface. After the formation of Ag NPs, large 164 amount of small black particles were well dispersed on the surface of PDA-kaolin 165 without the agglomeration (Fig. 2D, E, F). However, the dispersity of Ag NPs was 166 poor, and particles were aggregated to form larger size without PDA as stabilizer (Fig. 167 2C). These observations confirmed that PDA could act as an efficient reductant and 168 stabilizer for the synthesis of Ag NPs on the clay support. 169

The composition and structure of kaolin have been characterized in our previous study. (He et al., 2018b; He et al. 2019) Herein, a detailed characteristic description of PDA-kaolin-Ag composite was presented. The XRD patterns of kaolin-Ag and PDA-kaolin-Ag composites are shown in Fig. 3A. According to previous studies, the main diffraction peak of kaolin found at $2\theta = 26.5$ °was ascribed to quartz, and some kaolinite peaks could also be seen at $2\theta = 45.8$ °and 21.0 °(Fig. S1a). (Ma et al., 2007; Zhao et al., 2011; Liew et al., 2012; He et al., 2014) Compared with the XRD patterns

177	of kaolin and PDA-kaolin samples, in the case of kaolin-Ag and PDA-kaolin-Ag
178	composites, several obvious diffraction peaks at $2\theta = 37.9$ °, 44.2 °, 64.4 °, and 77.3 °
179	that corresponded to the reflections of (111), (200), (220), and (311) crystalline planes
180	were observed, which could be readily indexed to face-centered-cubic structure of Ag
181	crystal according to JCPDS card No. 04-0783. Furthermore, the typical XRD peaks of
182	Ag crystal revealed that the crystallized Ag NPs could be successfully incorporated on
183	the surface of kaolin composite. (Ai et al., 2011) With the increase of dopamine
184	concentration, XRD peaks of Ag crystal in the PDA-kaolin-Ag composites were more
185	intense and sharp, indicating that the dopamine mass was an important factor for the
186	synthesis of Ag NPs. In addition, with the increase of Ag concentration, the intensities
187	of typical Ag NPs XRD peaks of PDA-kaolin-Ag composite became stronger,
188	indicating the relative amount of Ag NPs in PDA-kaolin-Ag/2 was higher than that in
189	PDA-kaolin-Ag/2(1) and PDA-kaolin-Ag/2(0.5) (Fig. S1). In addition, the
190	introduction of Ag NPs could not change the structure of kaolin.

Furthermore, XPS analysis was performed to further verify the composition of 191 PDA-kaolin-Ag composites. The XPS survey spectra (Fig. 3B) showed that Ag 192 element was emerged in the composite in addition to the characteristic elements of 193 kaolin such as Al, Si, and O. (Huang et al., 2016; He et al., 2018b) The element 194 contents of kaolin-Ag and PDA-kaolin-Ag composites are listed in Table 1. Without 195 PDA modification, the content of Ag atom was low (0.5%). Obviously, the increased 196 contents of carbon and nitrogen atoms were attributed to the PDA modification. The 197 contents of Ag atom were 1.79%, 2.02%, and 2.18% in PDA-kaolin-Ag/1, 198

199	PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4, respectively. The increased PDA content
200	resulted in larger Ag content in PDA-kaolin-Ag composites. Thus, PDA modification
201	on kaolin was beneficial for the synthesis of kaolin-Ag composites. The
202	high-resolution scan of Ag3d spectrum of PDA-kaolin-Ag/2 revealed the presence of
203	typical $Ag3d_{5/2}$ and $Ag3d_{3/2}$ peaks, which were centered at binding energy of 368.02
204	eV and 374.02 eV, respectively (Fig. 9). (Wei et al., 2015) Meanwhile, the binding
205	energy gap of 6 eV suggested that the zero valence state of metallic Ag was deposited
206	on the surface of PDA-kaolin. (Cai et al., 2012; Wei et al., 2015; Gilea et al., 2018)
207	Thus, the successful preparation of PDA-kaolin-Ag composite could be verified by
208	taking the analysis of the characteristic results of XRD, TEM, and XPS together.

209 3.2 Catalytic performance

210 3.2.1 Catalytic activity of PDA-kaolin-Ag for RhB decoloration

To investigate the catalytic performance of PDA-kaolin-Ag on dye decoloration, 211 herein, RhB was used as a model dye pollutant. Generally, the catalytic reduction 212 process can be monitored by the variations of absorbance spectra with time, resulting 213 from the dye color gradually vanishing after the addition of NaBH₄ and catalyst. (Xie 214 et al., 2014; Kurtan et al., 2016) Without Ag NPs in the composite, only a slight 215 decrease of absorbance spectra within 30 min was monitored (Fig. S2A, 216 Supplementary information). Compared with PDA-kaolin composite, an obvious 217 decrease trend of absorption peak could be observed as shown in Fig. S2B, indicating 218 that the successful incorporation of Ag NPs on PDA-kaolin. Theoretically, the 219 catalytic reaction involves the adsorption of dye molecules and BH₄⁻ ions onto the 220

catalyst surface and the electron transfer from the donor BH_4^- to the acceptor dye molecules, which has been collectively demonstrated in previous studies.(Joseph and Mathew, 2015; Kurtan et al., 2015) Herein, the electrons donated by BH_4^- will transfer to the electron relay of Ag NPs, then RhB molecules can capture them from Ag NPs, thereby resulting in the redox reduction of RhB and genarating its reduced form (leuco RhB) (Fig. 4).(Kurtan et al., 2015; Kurtan et al., 2016) Therefore, the presence of Ag NPs could enhance the decoloration of RhB.

Furthermore, the loading content of Ag could influence the catalytic activity on the 228 dye decoloration. On one hand, the increase of PDA content could increase the Ag 229 loading content (Table 1). The catalytic performance of kaolin-Ag, PDA-kaolin-Ag/1, 230 PDA-kaolin-Ag/2, and PDA-kaolin-Ag/4 could be seen from Fig. 5. Obviously, the 231 decoloration of RhB was much easier with PDA-kaolin-Ag/2 and PDA-kaolin-Ag/4 232 than that of kaolin-Ag and PDA-kaolin-Ag/1, owing to the higher content of Ag NPs 233 on kaolin. On the other hand, the increase of silver ammonia solution in the 234 preparation of PDA-kaolin-Ag could enhance the catalytic performance (Fig. S3, 235 Supplementary information). As shown in Fig. S3, the maximum absorbance peak of 236 RhB was measured to be at 553 nm (λ_{max} = 553 nm). Obviously, the absorbance peak 237 at 553 nm almost disappeared within 4 min in the presence of PDA-kaolin-Ag/2, 238 which was more rapid than that of PDA-kaolin-Ag/2(0.5) (12 min) and 239 PDA-kaolin-Ag/2(1) (6 min), indicating the better catalytic activity 240 of PDA-kaolin-Ag/2 in dye decoloration. Therefore, choosing an appropriate Ag 241 concentration for the preparation of Ag-based composites is necessary. Since 242

PDA-kaolin-Ag/2 exhibited a satisfactory catalytic performance on RhB reduction, it
was selected as catalyst for the following experiments.

- 245 3.2.2 Effect of dye concentration and catalyst dosage on the catalytic activity of
- 246 PDA-kaolin-Ag/2 composite

To evaluate the catalytic activity of PDA-kaolin-Ag/2 composite towards RhB 247 aqueous solution with different concentrations, three different concentrations (10 248 mg/L, 20 mg/L, and 40 mg/L) of RhB solution were used for the tests. As shown in 249 Fig. 6, the decoloration time increased with the increase of RhB concentration. The 250 intensity of maximum absorption peak dropped sharply within 1 min, 3 min, and 10 251 min after adding the catalyst into the corresponding RhB solution with concentration 252 of 10 mg/L, 20 mg/L, and 40 mg/L, respectively. Furthermore, the complete 253 254 decoloration of higher concentration of dye solution required more time at the same conditions. The increase of dye concentration would lead to the increased competition 255 of elctron capture among dye molecules, whereas the catalytic capacity was finite at a 256 fixed mass of catalyst, thus the dye reduction decreased at a higher dye concentration. 257 The effect of catalyst dosage on the catalytic processes was also investigated. As 258 shown in Fig. 7, it clearly indicated that the catalytic reduction of RhB was faster at 259 the reaction system with higher catalyst dosage. Furthermore, the catalytic rate of 260 RhB fitted by pseudo-first order reaction kinetic was applied to evaluate the catalytic 261 activity. Herein, the kinetic equation was described as $ln(A_t/A_0)$ =-kt, where A_t and A₀ 262 263 are the absorbance of RhB at time t and 0, respectively, and k is the rate constant that can be calculated from the slope of the linear plot. (Du et al., 2015) The rate constants 264

(k) were calculated to be 0.076 min⁻¹, 0.643 min⁻¹, and 1.316 min⁻¹ at the 265 corresponding catalyst dosage treatment of 5 mg, 10 mg, and 15 mg, respectively 266 267 (Table 2). Obviously, the reaction rate increased with the increase of catalyst dosage due to the increased electron transfer ability. In addition, good linear correlation 268 269 coefficient values of the plots can be observed from Table 2, indicating that the reactions could be well described by pseudo-first order kinetics. Thus, an appropriate 270 catalyst dosage used for the dye reduction is necessary to make the reaction more 271 effective. By comparison with the catalytic reduction of RhB using other different 272 nanocatalysts, (Ai et al., 2011; Kurtan et al., 2015) we concluded that this as-prepared 273 PDA-kaolin-Ag nanocatalyst showed a satisfactory catalytic performance on dye 274 decoloration. 275

276 3.3 Catalytic stability

The stability and recyclability of catalyst are important for its application in 277 wastewater treatment. As shown in Fig. 6, the conversion percentage just had a slight 278 decrease after several reusing, indicating the good stability of PDA-kaolin-Ag catalyst. 279 In order to determine the characteristic of recycled catalyst, XRD and XPS analyses 280 were performed. As seen from Fig. 9A, the typical XRD diffraction peaks of 281 crystallized Ag NPs were still prominent. Furthermore, it can be seen from Fig. 9B 282 that there was no significant change on the valence state of Ag after the third cycles. 283 These results are agreement with the previous report, which suggested that the PDA 284 285 film played an important role in preventing the loss of Ag NPs. (Xie et al., 2014; Ye et al., 2014) The good stability indicated that PDA-kaolin-Ag catalyst might has a 286

287 satisfactory application in dye wastewater treatment.

288 3.4 Catalytic performance of PDA-kaolin-Ag towards other dye solutions

289 Undoubtedly, organic dye pollution has been a serious environment challenge. It is a pressing task to remove various dye pollutants from water bodies. In this study, the 290 291 catalytic reduction tests toward other dyes including methylene blue (MB), methyl orange (MO), and Congo red (CR) by PDA-kaolin-Ag/2 composite were also carried 292 out. Similarly, the color of dyes faded after the catalytic reduction. It can be seen from 293 the Fig. S4 that the maximum absorption peaks of three dyes dropped drastically 294 within 20 min. These same reduction phenomena collectively reinforce the potential 295 of PDA-kaolin-Ag composites as efficient catalysts for rapid dye decoloration in the 296 presence of NaBH₄. The potential reduction mechanism could be explained by 297 298 electron relay system as reported by previous studies. (Kurtan et al., 2015; Kurtan et al., 2016) However, the reduction differences among various dyes could be noted by 299 the comparison of reduction trends and rate constants, which might be ascribed to the 300 different dye nature such as charge and hydrophobicity.(Joseph and Mathew, 2015; 301 Kurtan et al., 2015) Therefore, more efforts should be paid to conduct a 302 comprehensive research on a specific dye pollutant. 303

304 4. Conclusions

In summary, PDA-kaolin-Ag catalyst has been successfully fabricated by a facile *in-situ* reduction route without additional reductant, which was determined by the characteristic analysis of XRD, XPS, and TEM. The results show that appropriate dopamine concentration is important for the synthesis of PDA-kaolin-Ag composites and PDA-kaolin-Ag composites can be used as an efficient catalyst for the catalytic
reduction of RhB dye in the presence of NaBH₄. Meanwhile, an appropriate catalyst
dosage is necessary for the rapid dye decoloration. Importantly, this catalyst remains
good stability and recyclability in dye wastewater treatment. In addition,
PDA-kaolin-Ag composite also shows excellent catalytic activities toward other
organic dyes such as MB, MO, and CR, indicating that this cost-effective catalyst has

- 315 great potential in environmental applications.
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507 Figures











608 PDA-kaolin-Ag/1 (B), PDA-kaolin-Ag/2 (C), and PDA-kaolin-Ag/4 (D).



Fig. 6. Sucessive UV-vis absorption spectra of different concentration of RhB aqueous
solution (50 mL) with (A) 10 mg/L, (B) 20 mg/L; (C) 40 mg/L, in the presence of
NaBH₄ (5 mM) and PDA-kaolin-Ag/2 (10 mg). (D) Absorption rate curves of RhB
aqueous solution with different concentration. Note: *2 indicates the double dilution
of initial RhB solution before measurement.







