Promoting Effect of the Core-Shell Structure of MnO$_2$@TiO$_2$ Nanorods on SO$_2$ Resistance in Hg$^0$ Removal Process

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Abstract: Sorbent of αMnO$_2$ nanorods coating TiO$_2$ shell (denoted as αMnO$_2$-NR@TiO$_2$) was prepared to investigate the elemental mercury (Hg$^0$) removal performance in the presence of SO$_2$. Due to the core-shell structure, αMnO$_2$-NR@TiO$_2$ has a better SO$_2$ resistance when compared to αMnO$_2$ nanorods (denoted as αMnO$_2$-NR). Kinetic studies have shown that both the sorption rates of αMnO$_2$-NR and αMnO$_2$-NR@TiO$_2$, which can be described by pseudo second-order models and SO$_2$ treatment, did not change the kinetic models for both the two catalysts. In contrast, X-ray photoelectron spectroscopy (XPS) results showed that, after reaction in the presence of SO$_2$, S concentration on αMnO$_2$-NR@TiO$_2$ surface is lower than on αMnO$_2$-NR surface, which demonstrated that TiO$_2$ shell could effectively inhibit the SO$_2$ diffusion onto MnO$_2$ surface. Thermogravimetry-differential thermosgravimetry (TG-DTG) results further pointed that SO$_2$ mainly react with TiO$_2$ forming Ti(SO$_4$)$_2$O in αMnO$_2$-NR@TiO$_2$, which will protect Mn from being deactivated by SO$_2$. These results were the reason for the better SO$_2$ resistance of αMnO$_2$-NR@TiO$_2$.

Keywords: core-shell structure; αMnO$_2$: nanorods; elemental mercury removal; SO$_2$: resistance

1. Introduction

The emission of mercury from coal-fired power plants has drawn wide public concern in modern society. Mercury emissions are a long-term threat to human health and the environment because of extreme toxicity, persistence, and bioaccumulation. Therefore, controlling mercury emitted from coal-fired power plants has practical significance. Mercury in coal combustion flue gas is mainly present in three forms: Elemental mercury (Hg$^0$), oxidized mercury (Hg$^2$), and particulate-bound mercury (Hg$^+$). Particulate-bound mercury (Hg$^+$) can be removed by electrostatic precipitators (ESP) and fabric filters (FF), while oxidized mercury (Hg$^2$) can be captured by wet flue gas desulfurization system (WFGD). However, existing air pollution control devices can hardly remove Hg$^0$ due to its high volatility and low solubility.

Hg$^0$ capture with specific adsorbents is a usual way to control Hg$^0$ emissions from coal-fired power plants [1]. Activated carbon (AC) has been widely used for the adsorption of Hg$^0$ in coal-fired flue gas [2,3]. However, a huge amount of AC needs to be injected into flue gas because of its low Hg$^0$ capture capacity, which leads to a high operating cost of this technology. Sulfur or halogen modification can enhance adsorption ability of AC [4,5]. However, the injected AC is usually captured together with fly ash by particulate control device, and the Hg$^0$ adsorbed on AC will influence the fly ash utilization [6]. Therefore, alternative economic sorbents with high Hg$^0$ removal efficiency are necessary.
Oxides, such as CuO [7,8], FeO [9,10], CeO [11,12] and MnO [13–15], with high redox properties, exhibit great potential for Hg removal. Among these oxides, MnO is a commonly available and inexpensive material that has received extensive attention due to the redox couples of Mn²⁺/Mn³⁺ and Mn³⁺/Mn⁴⁺ [16]. Electronic shift between the different valence states of Mn is active and leads to a high redox capacity. Stefano Cimino et al. [14] investigated the Hg⁰ removal performance of Mn/TiO₂ and found that Hg⁰ capture efficiency was about 57% at 70 °C. After modification by some other transition metal oxides, Mn-based materials, such as Mn-FeO [15], Mn-ZrO [17], Mn-CeO [18], and Mn-CuO [19] can remove Hg⁰ better. Furthermore, it has been reported that the shape and crystallographic phases of Mn based sorbents have serious effects on Hg⁰ removal performance. Xu et al. [20] synthesized three different crystallographic phases of MnO and found that α-MnO₂ had the highest capacity due to its larger surface area and oxidizability. Chalkidis et al. [21] pointed out that MnO₂ nano-rods possessed good Hg⁰ removal capacity owing to the higher surface adsorbed oxygen species.

However, Mn-based sorbents usually have a poor SO₂ resistance as SO₂ can easily react with Mn, thereby forming MnSO₄ and leading to a largely suppressed Hg⁰ removal activity. Even a little amount of SO₂ will result in serious inhibited effects on Hg⁰ removal process. Our previous work has indicated that Ce-Zr modified Mn sorbent will be totally deactivated in 1 h after the introduction of 50 ppm SO₂ due to SO₂ poisoning Mn forming MnSO₄ [22]. TiO₂ is a traditional way to enhance the SO₂ resistance of MnO [23] as TiO₂ can inhibit the deposition of sulfates on sorbents surface [24]. But the Hg⁰ removal activity of MnO/TiO₂ is unsatisfactory because the active component of Mn is still exposed in SO₂ atmosphere. Core-shell is a structure with active component core and supporting components shell. The shell can inhibit the interaction between SO₂ and sorbent surface and efficiently protect active component core [25]. Therefore, synthesizing a core-shell structure with MnO core and TiO₂ shell may obtain a better SO₂ resistance.

Inspired by this, α-MnO₂ nanorods and αMnO₂ nanorods coating TiO₂ shell were synthesized in the present work to investigate the Hg⁰ removal efficiency in the presence of SO₂. Thermo-gravimetric (TG) and X-ray photoelectron spectroscopy (XPS) were performed to determine the role of SO₂ in the Hg⁰ oxidation and adsorption processes and a probable mechanism of SO₂ influence was deduced based on XPS and TG results. The kinetic model of the Hg⁰ adsorption process was examined as well.

2. Results and Discussion

2.1. Structure Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed to investigate the morphologic and structural properties of αMnO₂-NR and αMnO₂-NR@TiO₂. Figure 1a,a’ show SEM and TEM images of αMnO₂-NR. It can be seen that αMnO₂-NR has a uniform nanorod structure with an average diameter of about 100 nm. As shown in Figure 1b, for αMnO₂-NR@TiO₂, the uniform nanorod structure is well-retained after being coated with TiO₂ and the packing state of this sample is similar to αMnO₂-NR. The surface of αMnO₂-NR@TiO₂ are rougher when compared to αMnO₂-NR, and the average diameter increases to 150 nm due to the TiO₂ coating. The average length of the αMnO₂-NR@TiO₂ is about 2–3 μm (shown in Figure 1c). As shown in Figure 1b’, an obvious dividing line can be detected between MnO₂ core and TiO₂ shell, and the shell with thickness of about 30 nm is well dispersed outside of the αMnO₂-NR.
Figure 1. Scanning electron microscopy (SEM), and transmission electron microscopy (TEM) images of (a) and (a’) αMnO$_2$-NR; (b), (b’), and (c) αMnO$_2$-NR@TiO$_2$.

$\text{N}_2$ sorption-desorption isotherms of the samples are shown in Figure 2. Both αMnO$_2$-NR and αMnO$_2$-NR@TiO$_2$ exhibit a type IV adsorption isotherm, according to the definition of IUPAC, which means that αMnO$_2$-NR and αMnO$_2$-NR@TiO$_2$ have a mesoporous structure. The surface areas, pore volumes, and average pore diameters of the sorbents are illustrated in Table 1. BET surface areas of the two sorbents are similar, suggesting that TiO$_2$ coating does not change the structure of αMnO$_2$-NR a lot. This result consists with SEM results.

Figure 2. $\text{N}_2$ sorption-desorption isotherms for the sorbents.
Table 1. Pore structure analysis of the sorbents.

| Samples           | BET Surface Area (m²/g) | Pore Volume (cm³/g) | Average Pore Diameter (nm) |
|-------------------|-------------------------|---------------------|----------------------------|
| αMnO₂-NR          | 29.103                  | 0.192               | 5.428                      |
| αMnO₂-NR@TiO₂     | 32.985                  | 0.207               | 4.186                      |

X-ray diffractometer (XRD) patterns of the two catalysts are shown in Figure 3. All the peaks in XRD pattern of αMnO₂-NR and αMnO₂-NR@TiO₂ were indexed to cryptomelane type α-MnO₂ (JCPDS 44-0141, tetragonal, I₄/m, a = b = 0.978 nm, c = 0.286 nm). The intensity of diffraction peaks for the two samples is almost the same. It means that TiO₂ shell does not influence the dispersion of αMnO₂-NR, which is great agreement with BET and SEM results.

2.2. Hg⁰ Adsorption

2.2.1. Hg⁰ Adsorption Performance

Breakthrough experiments were performed to investigate the Hg⁰ adsorption performance of the two sorbents. A blank test was also performed and the results is shown in Figure S1. It can be seen that the outlet Hg⁰ concentration is stable when no sorbent was loaded in the fixed-bed reactor. As shown in Figure 4, the Hg⁰ removal efficiency of αMnO₂-NR is about 92% at the beginning of the test and it decreases to 41% after 130 min reaction. When it comes to αMnO₂-NR@TiO₂, the Hg⁰ removal efficiency at the beginning of the test is about 81% which is lower than that of αMnO₂-NR. But it is about 43% at the end of the test suggesting a more stable removal activity. These results indicate that TiO₂ shell does not inhibit the Hg⁰ diffusion from gas phase to the surface of αMnO₂-NR.
Figure 4. Hg\textsuperscript{0} breakthrough curves of αMnO\textsubscript{2}-NR and αMnO\textsubscript{2}-NR@TiO\textsubscript{2} under pure N\textsubscript{2} atmosphere. Reaction condition: 150 °C, GHSV = 180,000 h\textsuperscript{-1}.

Figure 5 shows the effects of SO\textsubscript{2} on Hg\textsuperscript{0} adsorption performance. For αMnO\textsubscript{2}-NR, Hg\textsuperscript{0} removal efficiency sharply declines from 55% to 14% during the 35 min reaction, when SO\textsubscript{2} is injected into flue gas. However, for αMnO\textsubscript{2}-NR@TiO\textsubscript{2}, the downward trend of Hg\textsuperscript{0} removal efficiency is much slower and decreases from 76% to 43% in a 30 min test, and still has a Hg\textsuperscript{0} removal efficiency of 25% after 80 min. These results confirm that TiO\textsubscript{2} shell can inhibit the direct interaction between SO\textsubscript{2} and MnO\textsubscript{2} surface, which will efficiently protect MnO\textsubscript{2} core from SO\textsubscript{2} poisoning.

αMnO\textsubscript{2}-NR@TiO\textsubscript{2} was used to investigate reusability for Hg\textsuperscript{0} removal. The results are shown in Figure 6. After 10 h Hg\textsuperscript{0} adsorption test, αMnO\textsubscript{2}-NR@TiO\textsubscript{2} reaches a Hg\textsuperscript{0} adsorption equilibrium. And then, the sorbent was heated at 450 °C for 2 h to release the HgO on sorbent surface. It can be found that, after heated treatment, the Hg\textsuperscript{0} adsorption efficiency and capacity of αMnO\textsubscript{2}-NR@TiO\textsubscript{2} recovers to its original level. After two recycling, it still shows a good Hg\textsuperscript{0} adsorption efficiency. Furthermore, SEM results of the fresh and used αMnO\textsubscript{2}-NR@TiO\textsubscript{2} (shown in Figure S2) show that recycle have no
effect on the microstructure. These results suggest an outstanding reusability of αMnO₂-NR@TiO₂. The Hg⁰ adsorption capacity of αMnO₂-NR@TiO₂ is 0.11 mg/g, it is good enough compared to other sorbents (shown in Table S1). The surface areas of the sorbents in the present work are relatively low thereby lowering the available surface active sites. αMnO₂-NR@TiO₂ with higher surface area will be studied in our following works, and may give a better Hg⁰ adsorption capacity.

![Image of Hg²⁺ breakthrough curves of αMnO₂-NR@TiO₂ under pure N₂ atmosphere. Reaction condition: 150 °C, GHSV = 180,000 h⁻¹.](image)

**Figure 6.** Hg⁰ breakthrough curves of αMnO₂-NR@TiO₂ under pure N₂ atmosphere. Reaction condition: 150 °C, GHSV = 180,000 h⁻¹.

Hg⁰ adsorption test of αMnO₂-NR@TiO₂ at different Hg⁰ concentration was also investigated and the results are shown in Figure S3. With a doubled Hg⁰ concentration, the breakthrough curve gets steep suggesting that αMnO₂-NR@TiO₂ will easily reach Hg⁰ adsorption equilibrium at a higher Hg⁰ concentration.

### 2.2.2. Structure-Activity Relationship

Fourier Transform Infrared Spectrometer (FTIR) was used to confirm the kind of surface active site for Hg⁰ adsorption. As can be seen in Figure 7, the peaks at 429, 503, and 700 cm⁻¹ correspond to Mn-O vibration [26], which becomes much weaker after reaction. It suggests that Mn-O group participates in Hg⁰ adsorption process. According to previous work, the surface active oxygen species in Mn-O group should be the active sites for Hg⁰ adsorption.
2.3. Models of Adsorption Kinetics

In order to better illustrate the Hg\(^0\) adsorption mechanisms of αMnO\(_2\)-NR and αMnO\(_2\)-NR@TiO\(_2\), two popular models of pseudo-first order and pseudo-second order kinetic models, which have been widely used to investigate the adsorption process [27], were employed to fit the above experimental data. These two kinetic equations are displayed as follows [28]:

\[
\lg (q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t - \text{pseudo-first order}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} - \text{pseudo-second order kinetic}
\]

where \(q_e\) and \(q_t\) are the adsorption capacity of Hg\(^0\) on the sorbents at equilibrium, and at reaction time \(t\) (min), respectively. The parameters \(k_1\) (min\(^{-1}\)) and \(k_2\) (g/(μg·min)) are the rate constants of the pseudo-first order, and pseudo-second order models, respectively.

The fitting results are shown in Figure 8, and the obtained values of correlation coefficient (R\(^2\)) are summarized in Table 2. The values of R\(^2\) of the pseudo-second order model for αMnO\(_2\)-NR and αMnO\(_2\)-NR@TiO\(_2\) are 0.991 and 0.995, respectively, which are higher than those of pseudo-first order kinetic model (0.944 and 0.938 for αMnO\(_2\)-NR and αMnO\(_2\)-NR@TiO\(_2\)). It indicates that the pseudo-second order model can better fit the experimental data and Hg\(^0\) removal process are dominantly controlled by chemisorption. After SO\(_2\) introduction, the values of R\(^2\) of the pseudo-second order model for αMnO\(_2\)-NR and αMnO\(_2\)-NR@TiO\(_2\) are 0.997 and 0.992, which are still much higher than those of the pseudo-first order model. These results show that Hg\(^0\) adsorption process in the presence of SO\(_2\) atmosphere are also dominantly controlled by chemisorption.
2.4. The Mechanism of SO₂ Effects on Hg⁰ Adsorption

XPS analysis was employed to explore the relative proportion of elements on the sample surface. The XPS spectra of Mn 2p, O 1s and S 2p for the fresh and used samples are shown in Figure 9. The surface atomic concentrations and surface atomic ratios are summarized in Table 3.
Catalysts for αMnO

The intensity of the used αMnO 170.0 eV are of MnO 163.2 eV shown in salts during the slight shift to higher binding energy after αMnO treatment, which correspond 530.8 eV, denoted as O

corresponding to the core.

MnO the reaction between SO 2 and Mn

separated into three peaks at 640.2–641.2 eV, 641.2–642.1 eV, and 642.2–643.4 eV corresponding to Mn 2+, Mn 3+, and Mn 4+, respectively [29,30]. As shown in Table 3, the ratio of Mn 4+/Mn is about 37.8% for the fresh αMnO-NR and it decreases to 33.4% after the SO 2 resistance test. Compared to αMnO-NR, Mn 4+ content is almost constant for αMnO-NR@TiO 2 before, and after, SO 2 resistance test. These results indicate that, for αMnO-NR, Mn 4+ is easily reduced to Mn 2+ during SO 2 resistance process via the reaction between SO 2 and MnO 2 [31]. For αMnO-NR@TiO 2, the interaction between SO 2 and MnO 2 is inhibited by the TiO 2 shell structure, which can efficiently protect active component Mn 4+ in the core.

Figure 9a shows the XPS spectra of Mn 2p. A doublet due to spin orbital coupling can be detected which corresponds to Mn 2p 3/2 (around 641.24 eV) and Mn 2p 1/2 (around 652.82 eV). Due to the high intensity of Mn 2p 3/2, it was fitted to give detail information of valence state of Mn and it can be separated into three peaks at 640.2–641.2 eV, 641.2–642.1 eV, and 642.2–643.4 eV corresponding to Mn 2+, Mn 3+, and Mn 4+, respectively [34]. As shown in Table 3, the ratio of Mn 4+/Mn is about 37.8% for the fresh αMnO-NR and it decreases to 33.4% after the SO 2 resistance test. Compared to αMnO-NR, Mn 4+ content is almost constant for αMnO-NR@TiO 2 before, and after, SO 2 resistance test. These results indicate that, for αMnO-NR, Mn 4+ is easily reduced to Mn 2+ during SO 2 resistance process via the reaction between SO 2 and MnO 2 [31]. For αMnO-NR@TiO 2, the interaction between SO 2 and MnO 2 is inhibited by the TiO 2 shell structure, which can efficiently protect active component Mn 4+ in the core.

Figure 9b shows O 1s XPS spectra. For the fresh catalysts, O 1s bands can be split into two peaks, corresponding to lattice oxygen (peak at 529.5 eV, denoted as O l) and chemisorbed oxygen (peak at 530.8 eV, denoted as O c), respectively [32]. Whereas, a new peak appears around 532.3 eV after SO 2 treatment, which corresponds to SO 4 2− (denoted as O 4) [33]. The intensity of the peak around 532.3 eV for αMnO-NR@TiO 2 is weaker than that for αMnO-NR suggesting a lower amount of SO 4 2− on the used αMnO-NR@TiO 2 surface. Furthermore, the peaks of O l and O 4 in αMnO-NR have an obvious slight shift to higher binding energy after SO 2 treatment. It might be due to the formation of sulfate salts during the sulfating process [34].

To determine the above deduction, S 2p bands was further investigated and the results are shown in Figure 9c. For the fresh αMnO-NR and αMnO-NR@TiO 2, two peaks around 162.2 eV and 163.2 eV attributed to S 2− and S 3− can be detected [35,36], which may come from MnSO 4 (the precursor of MnO 2). But for the used αMnO-NR and αMnO-NR@TiO 2, two new peaks at about 168.8 eV and 170.0 eV are observed, which may be assigned to SO 4 2− and HSO 4 −, respectively [37,38]. The peak intensity of the used αMnO-NR is much higher than that of αMnO-NR@TiO 2. As shown in Table 3, for αMnO-NR, the surface atomic concentrations of S increases from 3.17% to 4.97% after SO 2.

Table 3. The surface atomic concentrations and the relative concentration ratios of samples based on XPS.

| Samples                        | S   | Mn 4+/Mn | O 4/O 2 |
|--------------------------------|-----|----------|---------|
| αMnO-NR (fresh)                | 3.17| 37.8     | 26.0    |
| αMnO-NR@TiO 2 (fresh)          | 2.27| 33.4     | 24.7    |
| αMnO-NR (used)                 | 4.97| 34.0     | 22.8    |
| αMnO-NR@TiO 2 (used)           | 2.66| 33.0     | 20.0    |
treatment while it increases from 2.27% to 2.66% for αMnO$_2$-NR@TiO$_2$. These results confirm that TiO$_2$ shell can inhibit the S accumulation on catalyst surface.

To obtain more information about the SO$_2$ poisoning mechanism, Thermo-gravimetric-differential thermos-gravimetry (TG-DTG) was performed to investigate the weight loss of αMnO$_2$-NR and αMnO$_2$-NR@TiO$_2$ after SO$_2$ treatment, and the results are presented in Figure 10. It can be seen that the used αMnO$_2$-NR has an obvious weight loss step in the temperature range of 680–780 °C with a weight loss of about 2.4%, which can be attributed to manganese sulfate decomposition [39–41]. There is no weight loss step between 680–780 °C with respect to αMnO$_2$-NR@TiO$_2$, but there is a new weak step around 780–850 °C can be detected, and it may be due to the decomposition of Ti(SO$_4$)O [42]. This result demonstrates that SO$_2$ tends to react with titanium oxides instead of manganese oxides over αMnO$_2$-NR@TiO$_2$. Based on these results, TiO$_2$ shell can lead to the preferential adsorption of SO$_2$ on Ti surrounding forming Ti(SO$_4$)O to protect Mn active component from being deactivated.

![Figure 10. Thermo-gravimetric (TG) and differential thermos-gravimetry (DTG) of spectras of αMnO$_2$-NR and αMnO$_2$-NR@TiO$_2$ after SO$_2$ treatment.](image)

3. Materials and Methods

3.1. Catalysts Preparation

The αMnO$_2$ nanorods were synthesized through a hydrothermal method [43]. KMnO$_4$ (2.5 g, AR) and MnSO$_4$·H$_2$O (1.05 g, AR) were dissolved in 80 mL distilled water. The mixed solution was transferred into a Teflon-line stainless steel autoclave, sealed, and kept in an oven at 160 °C for 12 h. After cooling to room temperature, the precipitates were filtered off, washed several times using deionized water and dried at 110 °C overnight. Finally, the product was calcined at 400 °C in a muffle furnace for 4 h and the obtained sample is denoted as αMnO$_2$-NR.

MnO$_2$@TiO$_2$ core-shell nanorods were synthesized through a versatile kinetics-controlled coating method [44]. αMnO$_2$-NR (0.075 g) and aqueous ammonia (0.28 mL, 28 wt.%), were dispersed in 100 mL absolute ethanol under ultrasound for 30 min. Afterwards, titanium tetrabutoxide (TBOT) (0.75 mL) was added drop-wise into the mixture and then kept at 45 °C for 24 h. The mixed solution was filtered, washed and dried at 60 °C for 12 h. Finally, the solid was calcined under flow air at 500 °C for 2 h to obtain the sample (denoted as αMnO$_2$-NR@TiO$_2$).

ALL reagents are from Aladdin company, Shanghai, China.
3.2. Hg\textsuperscript{0} Adsorption Experiments

The Hg\textsuperscript{0} removal test has been described in detail in our previous work [45]. The experimental reactor contains a gas distribution system, a Hg\textsuperscript{0} vapor generating device, a fixed-bed quartz reactor (ID = 8 mm), an online mercury analyzer and a tail gas treating unit. The mercury permeation tube was placed in a U-shape glass tube, which was immersed in a water bath at a constant-temperature (38 °C) to ensure a constant Hg\textsuperscript{0} permeation rate. The total gas flow was 600 mL/min, and the sorbent volume was generally 0.2 mL, resulting in a GHSV of 1.8 × 10\textsuperscript{3} h\textsuperscript{-1}. The concentrations of Hg\textsuperscript{0} and SO\textsubscript{2} were monitored by a VM-3000 online mercury analyzer (Mercury Instruments, München, German), and flue gas analyzer (KM950, Kane International Ltd., London, United Kingdom), respectively.

During each test, the Hg\textsuperscript{0} gas first bypassed the fixed-bed reactor, and then introduced into the reactor for 2 h to obtain a stable Hg\textsuperscript{0} concentration. Hg\textsuperscript{0} breakthrough ratio was quantified by the following formula,

\[
\text{Breakthrough ratio(%) = } \frac{C}{C_0} \times 100\%
\]

where \(C\) and \(C_0\) represent the inlet and outlet Hg\textsuperscript{0} concentrations (μg/Nm\textsuperscript{3}) in the fixed-bed reactor.

3.3. Characterization

The morphology and microstructure of the samples were observed using SEM (Nova NanoSEM 450, FEI) and TEM (Tecnai G2 F30 S-Twin, FEI). The surface areas and pore parameters of the samples were determined by Nitrogen adsorption/desorption method at liquid nitrogen temperature at −196 °C on an automated gas sorption analyzer (Autosorb-iQ-C, Quantachrome Instruments, Boynton Beach, FL, USA). The pore size and pore volume were derived from the desorption branches using the Barrette-Joyner-Halenda (BJH) model. The crystal structures of the samples were characterized by an XRD (XRD-7000S, SHIMADZU Corporation, Kyoto, Japan) operating at 40 kV and 100 mA using a Cu Kα radiation. The scanning range (2θ) was from 10° to 90° with a scan speed of 5°/min. The element (Mn, O, and Hg) valence state was analyzed by XPS (ESCALAB250 Thermo Fisher Scientific, Wilmington, DE, USA) with a monochromatic Al Kα source. The C 1s binding energy value of 284.8 eV was used to calibrate the observed spectra. TG was performed on TGA/DSC1 analyser (METTLER TOLEDO, Schwerzenbach, Switzerland), under a nitrogen flow of 20 mL/min, using a heating rate of 10 °C/min from room temperature to 900 °C (NETZSCH Corporation, Selb, Germany). DTG analysis was obtained based on residual weight of the sample with respect to time. FTIR spectra were obtained on a Nicolet Maquina-IR 750 spectrometer to measure the surface groups of the samples (Thermo Nicolet Corporation, Madison, WI, USA).

4. Conclusions

\(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\) was prepared by versatile kinetics-controlled coating method to compare with \(\alpha\text{MnO}_2\cdot\text{NR}\) in the Hg\textsuperscript{0} removal process. SEM, BET, and XRD results showed that TiO\textsubscript{2} shell did not change the structure of \(\alpha\text{MnO}_2\cdot\text{NR}\). Therefore, the two sorbents had similar Hg\textsuperscript{0} removal performance in N\textsubscript{2} atmosphere. When SO\textsubscript{2} was introduced, \(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\) had a much better performance than \(\alpha\text{MnO}_2\cdot\text{NR}\). XPS and TG-DTG results showed that \(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\) had lower surface S concentration after treatment of SO\textsubscript{2} and no manganese sulfate could be detected in \(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\). It suggests that the TiO\textsubscript{2} shell can effectively protect MnO\textsubscript{2} from being deactivated by SO\textsubscript{2}. Adsorption kinetic results showed that Hg\textsuperscript{0} adsorption process over both the two sorbents obeys pseudo-second order model with, or without, SO\textsubscript{2}.

**Supplementary Materials:** The following are available online at www.mdpi.com/xxx/s1, Figure S1: Outlet Hg\textsuperscript{0} concentration without sorbent, Figure S2: The image of \(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\) after adsorption, Figure S3: Breakthrough curve of \(\alpha\text{MnO}_2\cdot\text{NR}@\text{TiO}_2\) with different Hg\textsuperscript{0} feed concentration, Table S1: Comparison of the adsorption capacities of the sorbents.
Author Contributions: X.S. and H.Z. designed the experiments; X.H. and C.L. performed the experiments and analyzed the data; X.Z. wrote the paper; J.B., N.Z. and G.H. contributed reagents/materials/analysis tools. All authors have read and agreed to the published version of the manuscript.

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