

Spray synthesis of rapid recovery ZnO/polyaniline film ammonia sensor at room temperature

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Supplementary materials

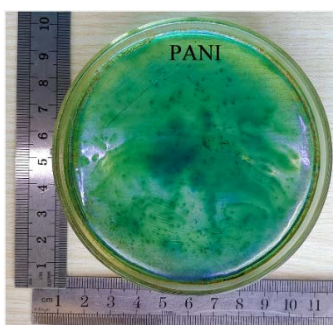


Fig. S1 Photograph of the PANI film prepared at reaction time of 24 h.

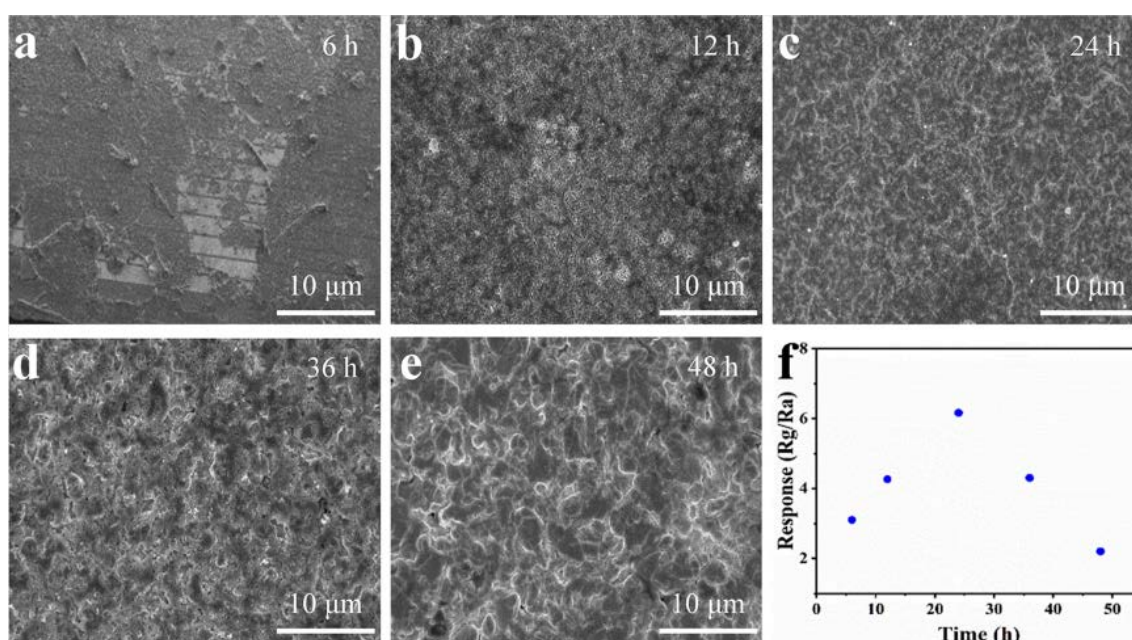


Fig. S2 SEM images of the PANI films prepared at reaction time of (a) 6 h, (b) 12 h, (c) 24 h, (d) 36 h, and (e) 48 h. (f) The response of the sensors with the reaction time of PANI films to 100 ppm (1 ppm = 10⁻⁶) NH₃ at room temperature after sprayed with 10 mg ZnO.

The morphology of PANI films prepared with different aniline diffusion time was observed by scanning electron microscope. It is found that when the diffusion time is 6 h, the film formed is difficult to transfer completely. When the diffusion time is 12 h, the PANI film can be obtained. When the diffusion time is 24 h, the obtained PANI film is relatively flat. When the diffusion lasts for 36 h or even 48 h, the surface of PANI film appears obvious protrusion. 10 mg ZnO powder was sprayed on the PANI film prepared with different aniline diffusion time. The responses of the materials to 100 ppm NH₃ were tested at room temperature. It is found that 24 h is the best diffusion time of aniline. The response of the sensor to 100 ppm NH₃ is 6.21.

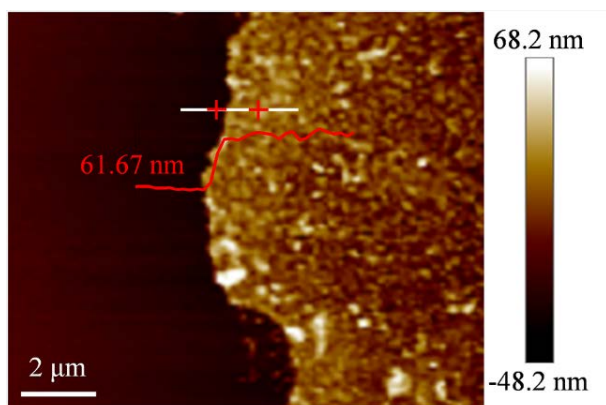


Fig. S3 AFM image and thickness of the PANI film obtained by aniline diffusion for 24 h.

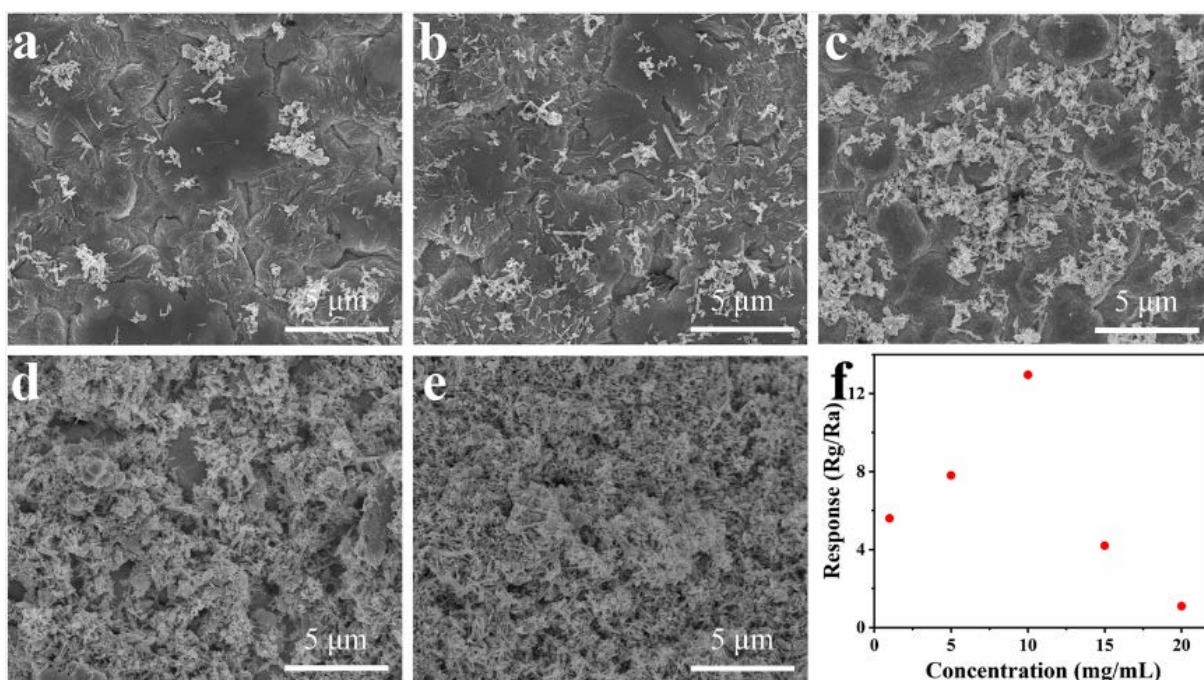


Fig. S4 SEM images of the PANI films sprayed with (a) 2, (b) 10, (c) 20, (d) 40, and (e) 80 mg ZnO. (f) The response of the sensors with different amounts of ZnO to 100 ppm NH₃ at room temperature.

The morphology of the PANI films sprayed with different amounts of ZnO was observed by scanning electron microscope. It is found that when the concentration of sprayed ZnO is lower than 10 mg·mL⁻¹, with the increase of the concentration of sprayed ZnO, the more contact between ZnO and the PANI film, the greater the response of the composite to 100 ppm NH₃. At the same time,

when the concentration of sprayed ZnO is higher than $10 \text{ mg}\cdot\text{mL}^{-1}$, the sprayed ZnO accumulates so much that completely covers the PANI film. This makes the p-n heterogeneous energy levels formed by the contact between ZnO and the PANI film completely wrapped by ZnO, which is almost unresponsive to NH_3 at room temperature, resulting in the decrease of the composite response to 100 ppm NH_3 . The response of the composite to 100 ppm NH_3 at room temperature first increases and then decreases with the increase of the amount of sprayed ZnO, indicating that the effective interaction between ZnO and the PANI film changes with the concentration of sprayed ZnO. When the concentration of sprayed ZnO is $10 \text{ mg}\cdot\text{mL}^{-1}$, the prepared ZnO/PANI film sensor has the best response to 100 ppm NH_3 at room temperature, which is 12.93.

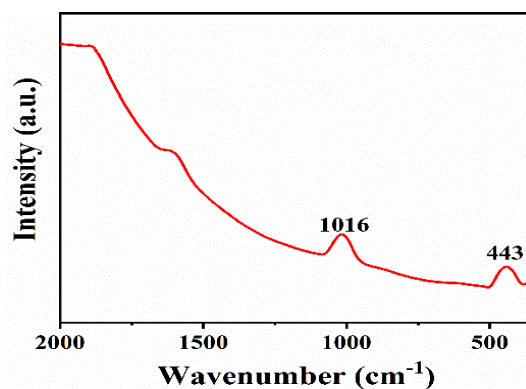


Fig. S5 Raman spectrum of ZnO.

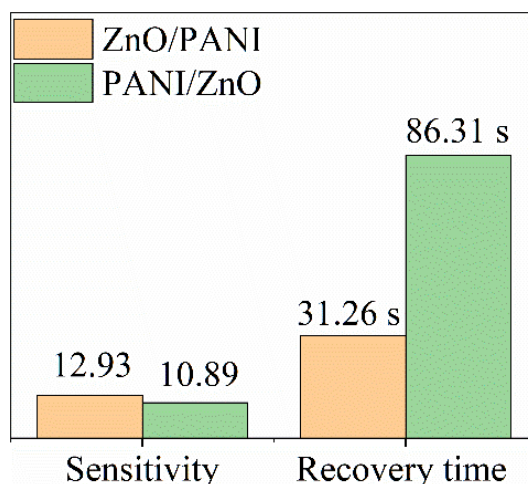


Fig. S6 Comparison of sensitivity and recovery time to 100 ppm NH_3 at room temperature of the sensor prepared by spraying 20 mg ZnO powder and then covering the prepared PANI (PANI/ZnO) and spraying the same amount of ZnO powder on the PANI film (ZnO/PANI).

The performance of the sensor sprayed with 20 mg ZnO powder and then covered with PANI film (PANI/ZnO) was compared with that of the sensor sprayed with the same amount of ZnO powder on the PANI film (ZnO/PANI). It is found that the response values of the two sensors to 100 ppm NH_3 at room temperature are 10.89 and 12.93, respectively, which are close to each other. But the 31.26 s recovery time of of ZnO/PANI sensor is significantly shorter than that of 86.31 s of PANI/ZnO sensor. The method of coating ZnO on PANI film in recovery time has obvious advantages. This may be because the formed heterostructure is not directly exposed to the surface, which makes it difficult for NH_3 to desorb.

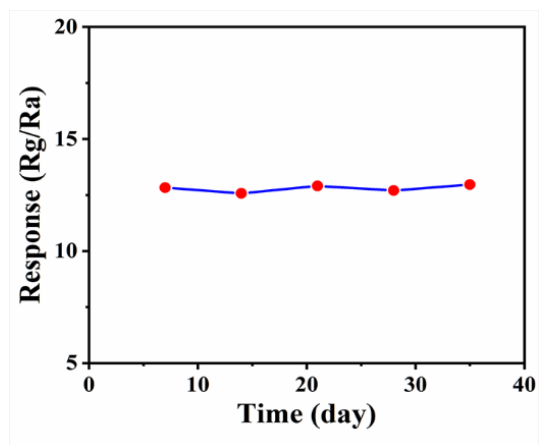


Fig. S7 The responses of the ZnO/PANI film sensor to 100 ppm NH₃ at room temperature within 35 d.

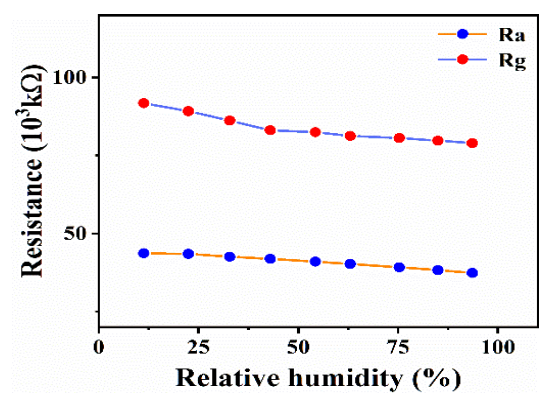


Fig. S8 The changes of the initial resistance (R_a) and response resistance (R_g) of the ZnO/PANI film sensor with different values of relative humidity.