1 Ultralong ZnO/Pt Hierarchical Structures for Continuous-Flow Catalytic Reactions

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10 Abstract

11 Grass-like double-layer ZnO micro-nanostructures in the confined microchannels is
12 fabricated via fluid construction methods, with the vertical height as high as 50 μm .
13 Subsequently, surface modification of Pt solutions produced uniformly distributed
14 catalytic Pt micro-nanostructures in a facile method. The efficiency of the grass-like
15 catalysts was demonstrated for the continuous reduction reaction of o-nitrophenol and
16 degradation methylene blue. Reaction rates and yields were significantly enhanced
17 and the catalytic structures were recyclable. The results should be significant upon
18 current microfluidic technologies, and exhibit great potentials in continuous flow
19 reactions.

20 Keywords: capillary microreactor, ultra-long grass-like ZnO arrays, Pt catalysts,
21 reduction of o-nitrophenol

22 1. Introduction

23 Pt is widely used in industry practical application ranging from fuel cells to electronics
24 and environment because of its high catalytic performance and good chemical
25 stability [1] and [2]. Especially in catalytic field, Pt is a necessary catalyst. One of the

most effective measures to control emissions of destructive chemicals and turned them into harmless substances is to use Pt-based catalysts. In a sense, Pt should be considered as an industrial metal more than a precious one [3] and [4]. However, the high economic cost restricts its widely applications. To ameliorate the high economic cost, the catalysts are required to be recycled via various methods but the small size distributions and solution phase restrict the recyclement. For example, they cannot even be completely separated by centrifugation at 12000 rpm [5]. Moreover, nano-sized catalysts tend to aggregate, decreasing the availability of catalytically active centers and thus catalytic efficiency. Therefore, to be effective and stable in catalysis reactions, the catalysts should possess high catalytic rate, physical and chemical stability, and recyclability [6] and [7].

Numerous strategies to achieve the catalysts with high efficiency and good recyclement have been explored. Large reaction area imposes a major influence on catalysis rate [8] and [9]. By changing the shape of carriers, the effective contact area between catalysts and reactants can be increased. Wang et al. [10] developed high efficient photocatalyst films consisting of Pt nanoparticles supported on TiO₂ single crystals for CO₂ photoreduction that provided a large contact surface area between catalyst and gas molecules. Danwittayakul et al. [11] found that ZnO nanorods with a specific surface area of 45 m²g⁻¹ were 13% more catalytically active than those with lower surface areas. Meanwhile, Aijaz and coworkers [12] successfully immobilized Pt nanoparticles inside the pores of a metal-organic framework. And uniform distribution of Pt nanoparticles without aggregation after catalysis exhibit excellent

48 catalytic performances for reactions in all phases of liquid, solid and gas. Although
49 these systems do show high catalytic performance, simply loading Pt onto carriers
50 makes recovery difficult. Therefore, the fabrication of complex, well-designed
51 microreactors has been explored to realize high catalytic activity, recyclability and
52 stability [13] [14][15] and [16].

53 Microchannels are an important component of microreactors that are initially the
54 native surface of the microreactor. For a microfluidic device to become functional, the
55 microchannels need to possess micro-nanostructure. Present physical methodologies
56 to fabricate micro-nanostructures in microchannels are etching, lithography, soft
57 lithography and LIGA (Lithographie, Galvanoformung and Abformung) [17] and [18].

58 These methods are expensive and difficult to apply to slightly larger devices. These
59 limitations have motivated considerable effort to find low-cost technologies.

60 Chemical coating methods such as chemical vapor deposition and layer-by-layer
61 deposition have been used to form functional layers on microchannel devices. For
62 example, Janicke et al. [19] used chemical vapor deposition to obtain a porous
63 alumina coating. A microfluidic chip containing proteins modified with
64 poly(dimethylsiloxane) prepared by layer-by-layer assembly exhibited high separation
65 efficiency [20]. However, these technologies are difficult to use in narrow
66 microchannels. Therefore, considering that sealing an open microchannel will damage
67 micro-nanostructures, it is desirable to fabricate micro-nanostructures directly in
68 closed microchannels. In this vein, particles such as SiO_2 and TiO_2 have been
69 arranged in long capillaries via self-assembly techniques [21] and [22]. With the

development of microreactor technology, 1D materials have been extensively explored as a way to modify the inner wall of capillary microchannels instead of particle arrays. ZnO, a semiconductor oxide with a wide band gap that shows promise as a catalyst to degrade persistent organic pollutants, has been used to fabricate types of micro-nanostructures [23], [24], [25] and [26]. We previously developed a wet chemical route to fabricate 1D ZnO micro-nanostructures inside microchannel [27], [28]. ZnO nanorod arrays were uniformly arranged on the inner wall of capillary microchannels, which suggests that our method could be extended to produce a composite catalyst or device on the inner wall of capillary microchannels. However, 1D ZnO nanostructures such as ZnO nanorods and nanotubes with vertical heights of only 2-5 μm do not make full use of the space inside capillary microchannels [29], [30]. This means there is still considerable room to improve the performance of ZnO/Pt systems. Therefore, we decided to develop an effective microreactor by fabricating a much larger and longer ZnO micro-nanostructure on the inner wall of capillary microchannels than produced previously.

In this work, 3D grass-like ZnO micro-nanostructures are fabricated on a base of ZnO nanorod arrays on the inner wall of capillary microchannels. These double-layer ZnO-modified microchannels are decorated with Pt nanoparticles and then investigated as microreactors using o-nitrophenol and methylene blue as model reactants.

2. Experimental

2.1. Materials

All chemical reagents were of analytical grade and used without further purification. Silica glass capillaries (GL Science, Japan) with an inner diameter of 530 μm were used as the microchannels in this work (Fig. 8a-c). The inner surface of the capillaries was sequentially cleaned with a mixture of concentrated sulfuric acid/peroxide/distilled water (v:v:v = 4:1:20, 80 $^{\circ}\text{C}$), ammonia/peroxide/distilled water (v:v:v = 1:4:20, 80 $^{\circ}\text{C}$) and distilled water, and then dried in an oven at 80 $^{\circ}\text{C}$ for 30 min.

2.2. Preparation of ZnO nanorod arrays

ZnO nanorod arrays were prepared on the inner wall of the capillaries by a reported method [31]. The specific details were showed in supporting information.

2.3. Preparation of double-layer ZnO micro-nanostructure

The procedure used to fabricate 3D grass-like ZnO structure was similar to the preparation of the initial ZnO nanorod arrays except for the solutions. In this step, aqueous solutions of HMTA (0.05 M, 10 mL) and ZnF_2 (0.05 M, 10 mL) were used. ZnF_2 was prepared simply by mixing aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_4F . These two solutions were pumped into the capillary decorated with ZnO nanorod arrays, and then it was heated at 90 $^{\circ}\text{C}$ for 2 h. The capillary was cleaned with distilled water and ethanol, and then dried at 80 $^{\circ}\text{C}$ overnight.

2.4. Preparation of double-layer ZnO micro-nanostructure decorated with PVP-stabilized Pt nanoparticles

The method to prepare the Pt sol used here was reported previously by our group [31]. The specific details were showed in supporting information. Pt sol was pumped into a capillary decorated with double-layer ZnO micro-nanostructure at a rate of 15 $\mu\text{L}/\text{min}$ at 70 $^{\circ}\text{C}$ for 1.5 h. The capillary was then dried at 100 $^{\circ}\text{C}$ for 4 h.

2.5. Characterization

The morphology of ZnO and EDX data were obtained by FE-SEM (S-4800, Hitachi, Japan) and SEM (Phenom G2 pro, Phenom-World, China). HRTEM images were taken by a TEM (JEM-2100F, JEOL, Japan). The effluent was collected and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Prodigy, USA) to determine the durability of the Pt decorated structure. The detection limit of the ICP-AES is 0.01 ppm. The concentration of o-nitrophenol in catalytic experiments was measured on a UV-vis spectrometer (PerkinElmer, USA). X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer.

2.6. Chemical Reduction of o-Nitrophenol by NH_3BH_3 and Degradation of Methylene Blue.

1. The catalytic reduction of o-nitrophenol by the capillary containing Pt-decorated ZnO micro-nanostructure was examined. An ethanol solution (30 mL) of o-nitrophenol (0.01 mmol) and NH_3BH_3 (0.2 mmol) was drawn into the syringes and

then pumped through the capillary. The solutions were collected and the absorption peaks at 273 nm for o-nitrophenol and 287 nm for o-aminophenol were observed by UV-vis spectroscopy. 2. The outer polymer coating was removed from the capillaries containing ZnO/Pt micro-nanostructure grown on their inner walls and then the capillaries were used as microreactors to photo-catalyze the degradation of methylene blue. The capillary microchannels was placed under a medium pressure mercury lamp (GGZ-300, Shanghai Yaming Lighting Co., ltd.) with the central wavelength of 365 nm. An aqueous solution of methylene blue (5 mg/L) was drawn into the syringes, pumped into the capillary microreactor and collected in the dark container.

3. Results and discussion

3.1. Double-layer Grass-like ZnO Micro-nanostructures.

The field-emission scanning electron microscopy (FE-SEM) images in Fig. 1a,b showed that well-aligned single-crystalline hexagonal ZnO nanorod arrays with a typical diameter of 100-500 nm and length of 2-3 μm were formed on the inner wall of the capillary microchannels. The nanorods were oriented perpendicularly to the inner wall of the capillary microchannel and were uniformly arranged. Moreover, the surface of each nanorod was smooth, as shown in Fig. S1c. By adjusting solution composition in the second growth step, grass-like ZnO micro-nanostructure grew in clusters with a height of up to 50 μm on the ZnO nanorod arrays, as shown in Fig. 1c,d. The double-layer structure of the ZnO materials was clearly observed (Fig. S1a-c).

3.2. Formation Mechanism of Double-layer ZnO Structures

The mechanism for the formation of ZnO micro-nanostructures on the inner wall of capillary microchannels was determined by examining their time-dependent FE-SEM images (Fig. 4a-j). The structures formed in four stages; that is, the growth of ZnO nanorod arrays, the growth of the second layer of ZnO, the self-assembly and oriented attachment of ZnO particles and Ostwald ripening [32], [33]. The whole formation process is illustrated in Fig. 4. In the second stage, ZnO grew in the radial direction rather than simply along the vertical direction (Fig. 4a and b). According to Zhang et al. [33], radial ZnO aggregates are the kinetically stable form of wurtzite ZnO. Therefore, it is possible to fabricate a hierarchical structure of ZnO on top of ZnO nanorod arrays. The surface of the initial ZnO nanorods acted as starting points for the growth secondary rod arrays, which tended to grow at an oblique or horizontal angle to the capillary microchannel. The close arrangement of nanorods resulted in the strong interaction between the two layers. Just like the foundation of a building, the lower ZnO nanorods kept the top layer stable. When the capillary was cooled in a closed oven for 2 h after the end of the formation reaction, the nanoparticles need to grow further or aggregate to decrease the total energy of the system to reach thermodynamic equilibrium. Therefore, in the self-assembly stage, ZnO particles were directionally arranged and an ordered self-assembled structure formed, as depicted in Fig. 4c and d. To identify the evolution of morphology in these systems, samples were cooled for different periods. When the cooling time was lengthened to 4 h, ZnO fibers with many large particles on their surface were observed (Fig. 4e and f). When the

capillary was cooled for 6 h, as shown in Fig. 4g and h, ZnO fibers with randomly distributed small particles formed. When the cooling time was further extended to 8 h, the fibers became smooth and narrow (Fig. 4i and j). Both the elongation of the second layer of ZnO and the smoothing of the fibers suggested that Ostwald ripening accompanied the growth process. Based on the above discussion, the conclusion that the formation of double-layer ZnO micro-nanostructures involved a four-stage process is reasonable.

Ammonium fluoride (NH_4F) was used to control the growth of ZnO. ZnO micro-nanostructure tends to become more fibrous as the concentration of F^- increases. Therefore, a series of experiments were carried out using different concentrations of NH_4F . This systematic study indicated that the morphology of ZnO could be modified from nanorod arrays to double-layer structure simply by adjusting the concentration of NH_4F . Fig. 5a-f show typical FE-SEM images of the products obtained using different molar ratios of Zn^{2+} to NH_4F . When the molar ratio of Zn^{2+} to NH_4F was adjusted to 3:2, the ZnO micro-nanostructure became fibrous (Fig. S3).

Because of the intrinsic anisotropic character of hexagonal ZnO, 1D nanostructures like the fibrillar nanocrystals found at room temperature are the preferential crystal forms. The strong interaction between Zn^{2+} and surface-absorbed OH^- induced the aggregation of ZnO particles. The oriented attachment mechanism involves the attachment and coalescence of smaller crystals to form larger ones. The total energy of the system could be decreased by oriented attachment of ZnO nanocrystals. Small crystals dissolve more easily than bigger ones. In addition, aqueous NH_4F solution is

196 acidic, which can markedly accelerate the dissolution of ZnO nanocrystals. Therefore,
197 the surface of the grass-like ZnO structures became smoother as the cooling time
198 lengthened.

199 To prove that oriented attachment and Ostwald ripening occurred during the cooling
200 process, control experiments involving an extra 8 h of reaction time but no cooling
201 were performed. As predicted, compared with the sample reacted for 10 h (Fig. 6a),
202 there was no obvious growth of ZnO during the cooling process (Fig. 6b), which
203 consequently proved the necessity of the cooling process to obtain the grass-like
204 structures. The above results suggest that oriented attachment of ZnO rods could
205 decrease the total energy of the system, making the fusion between ZnO rods
206 energetically favorable, which caused ZnO to form grass-like micro-nanostructure.
207 Moreover, Ostwald ripening occurred simultaneously with oriented attachment to
208 remove defects from the ZnO crystals.

209 The Pt sol used was dark black and the valence state of Pt immobilized on the surface
210 of ZnO was confirmed by X-ray photoelectron spectroscopy (Fig. S5).
211 High-resolution transmission electron microscopy (HRTEM) (Fig. 7) and FE-SEM
212 images (Fig. S2c and d) revealed that the Pt nanoparticles with a size of 3-7 nm were
213 deposited on the surface of ZnO. The lattice spacing between adjacent lattice planes
214 was 0.20 nm, which corresponds well with the characteristic (200) plane of Pt crystals.
215 The additional lattice spacing of 0.28 nm was consistent with the distance between
216 two (100) planes of wurtzite ZnO. A selected-area energy-dispersive X-ray (EDX)

spectrum (Fig. 11a) of the double-layer ZnO/Pt micro-nanostructure confirmed its elemental composition.

3.3 Reduction of O-nitrophenol and Degradation of Methylene Blue

As a hydrogen reservoir, NH_3BH_3 has drawn much attention due to its high hydrogen capacity of 19.5 wt%, strong stability, and nontoxicity [34], [35]. Thus, a new safe hydrogenation reaction, using NH_3BH_3 in the catalytic liquid-phase reduction of o-nitrophenol, has been developed. Fig. 10b–d show the catalytic activity of the capillary microreactor for the reduction of o-nitrophenol. In aqueous solution, NH_3BH_3 will slowly react with ethanol. Therefore, every time the catalytic reaction was performed, a fresh ethanol solution of NH_3BH_3 was prepared. The residence time (RT) in a capillary determines the solid-liquid contact time; i.e., the reaction time of o-nitrophenol with the catalyst. RT is defined by the equation $\text{RT} = V_{(\text{capillary microchannel})} / v$, where $V_{(\text{capillary microchannel})}$ is the total internal volume of the silica capillary microchannel, which can be calculated from the length and diameter of the capillary, and v is twice the set flow rate of the dual-syringe infusion pump. According to the Fig. S6a, as RT increased, the absorption peak of o-nitrophenol shifted from 273 to 286 nm. When $\text{RT} = 25$ s, the peak remained at 286 nm, which means that o-nitrophenol was rapidly reduced in the microreactor. The o-nitrophenol solution became completely transparent when the RT exceeded 10 s.

The performance of the double-layer ZnO/Pt microreactor was analyzed by performing contrast experiments using Microreactor 1 with grass-like ZnO on top of

ZnO nanorod arrays and Microreactor 2 with only ZnO nanorod arrays. The catalytic performance of Microreactor 1 and 2 is presented in Fig. 10b. As expected, Microreactor 1 maintained its high performance even after a recycling time of 30 h while that of Microreactor 2 decreased sharply as the recycling time increased. After continuous catalysis for 20 h, Microreactor 2 had no activity. This difference will now be explained from the viewpoint of fluid mechanics.

To determine the flow state of a fluid in microchannels decorated with ZnO nanorod arrays and grass-like ZnO, respectively, COMSOL Multiphysics modeling software was used. Ultralong ZnO/Pt hierarchical structures had great advantages in the catalytic field. It was also known that during the chemical reaction, adhesion of molecules onto surface of the catalysts is one reason for catalyst deactivation. Simulating results show that turbulent flow state appears in more area inside the microreactor containing ultralong ZnO/Pt hierarchical structures than the microreactor decorated by ZnO/Pt nanorods. Turbulent flow state makes the molecules in the solution move faster. Just because of this, molecules can't collect on the surface of catalysts. Three types of microchannels are shown in Fig. 8 and The modeling results are shown in Fig. 9. In addition, the high surface area of the 3D grass-like morphology of the inner wall of the capillary microchannel also contributed to the higher catalytic activity of the reactor containing them than that of microchannels modified with ZnO nanorod arrays. The grass-like ZnO micro-nanostructure allowed the catalyst particles maximum contact with reactant molecules.

The physical stability of the microreactors was verified by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results obtained from ICP-AES of the microreactors are presented in Table 1. After continuous reaction for 10 h, 20 h and 30 h, the effluent was collected and analyzed by atomic emission spectroscopy to determine the durability of the Pt decorated structure. No signal of Pt was detected suggesting that Pt adheres well to the substrate and is not readily depleted. FE-SEM images of the microreactor before and after use (Fig. S2a and b, respectively) indicated that ZnO structures had not been damaged. In addition, according to some references [36], [37], [38], [39], [40], [41] and [42], we summarized this work and make a comparison among current work, previous work and other microreactors, which were shown in Table 2.

For the ZnO/Pt modified microchannels, owing to the well connectivity between the constructed microstructures and inner wall of glass capillary, it is almost impossible to scrap the microstructures off inner wall to have an accurate calculation. So, the minimum and maximum turnover frequency (TOF) values have been calculated according to the molar value of the Pt sol during the reaction process. The TOF, is given by equation 1:

$$TOF = \frac{n(o-aminophenol)}{t \times n(Pt)}$$

where $n(o-aminophenol)$ is the molar value of o-aminophenol, $n(Pt)$ is the molar value of o-nitrophenol; and t is the reaction time of the 80% conversion. For minimum value, $TOF=0.026$. For maximum, $TOF=0.884$.

In a practical oxygen reduction reaction, the facile dehydrogenation of reductant is necessary. The mechanism accounting for AB dehydrogenation is rather complex, and it is strongly dependent on the catalyst of choice. Some seminal papers have appeared in the literature describing the process, from both an experimental and a theoretical point of view [37] and [38]. NH_2BH_2 and NB will be produced with the catalytic dehydrogenation of NH_3BH_3 . And o-aminophenol, NH_2BH_2 , NB and H_2O are displayed as the final products. The reaction mechanism is shown below:

Methylene blue, a typical nitro compounds to investigate the catalysis performance, has been tested using the Pt microchannels. Fig. 11c shows UV-visible absorption spectra of degradation of methylene blue under different RTs. From Fig. 11b,c and d, two obvious absorption peaks of methylene blue at 291 nm and 664 nm can be observed, and the absorption peak intensity gradually reduce with the increase of RT. When the RT = 120 s, the absorption peak disappeared basically, methylene blue has almost been completely degraded. Using the conventional device, it's 2 h to reach the same catalytic effect [39]. Compared with conventional reaction devices, ZnO/Pt composite arrays modified microreactor exhibited much higher catalysis efficiency. From the inset in Fig. 11b, the color change (from blue to colorless) of methylene blue solution can be observed during photocatalytic degradation process. Methylene blue is steady in the air, and unstable in aqueous solution. Blank tests were carried out in the absence of the ZnO/Pt hierarchical structures. Under the irradiation of

ultraviolet light, about 20% methylene blue was decomposed with a residence time of 180 s. Therefore, by way of contrast, these results can show an appreciable degradation of the methylene solution.

The excellent photocatalytic performance of ZnO/Pt composite arrays microreactor is attributed to the synergism of zinc and platinum. Once Pt was loaded on the surface of ZnO, a new Fermi level was produced between Pt and Zn. When the photon energy on the surface of ZnO is greater than or equal to the width of ZnO band, the valence band electrons will be excited to conduction band, while holes were left in the valence band. The new Fermi level is lower than the energy levels of ZnO semiconductor conduction band, so the electrons will transfer to the Fermi level and then move to Pt nanoparticles. The electrons cannot return to the ZnO semiconductor owing to the existence of Schottky barrier. In brief, quickly transferred electronics improve the photocatalytic performance.

Recyclability and high catalytic rate are usually regarded as advantages of nanoparticle-based catalysts, but the nanoparticles in these catalysts in liquid-phase reactions are still limited by both their low efficiency of separation and degradation of catalytic activity resulting from nanoparticle aggregation. The results in this work reveal that capillary microreactors can solve these problems because our microreactors with double-layer ZnO/Pt micro-nanostructure exhibited high activity and stability in the chemical reduction of o-nitrophenol.

4. Conclusions

A method to fabricate double-layer ZnO micro-nanostructure with a vertical height of up to 50 μm on the inner wall of capillary microchannels was developed. The 3D grass-like micro-nanostructure changed the motion of fluid on the inner wall of the capillary microchannel, inducing fast transfer of reactant molecules. Experimental and theoretical studies revealed that the large effective contact area of this grass-like morphology should promote catalysis. Pt/ZnO hierarchical structures showed high physical and chemical stability and used microreactor can be easily and cheaply recycled. In addition, the technology of wet chemical process is simple. Therefore, our prepared microreactor had practical applications, such as tail gas treatment, degradation of highly toxic substance and synthesis of valuable medicines.

Acknowledgements

We gratefully acknowledge the financial support by NSF of China (No. 51572046, 51503035), MOE of China (No.111-2-04, 2232014A3-06), STC of Shanghai (13JC1400200, 15ZR1401200, 16XD1400100, 15CG33, 16YF1400400), and Eastern Scholar.

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Fig. 1. (a) The FE-SEM images of ZnO nanorod arrays on the inner wall of the capillary; (b) front view of ZnO nanorod arrays; (c) top view of ZnO micro-nanostructure grown on the inner wall of the capillary and (d) corresponding section view of ZnO nanowires.

Fig. 2. The SEM images of Silica glass capillary modified with grass-like ZnO micro-nanostructure grown on the ZnO nanorod arrays:(a) top view of capillary; (b) corresponding highly magnified image.

Fig. 3. (a) schematic diagram of the preparation of the microreactor; (b) Schematic diagrams illustrating the formation of double-layer and 3D grass-like ZnO micro-nanostructure in capillary microchannels.

Fig. 4. FE-SEM images of grass-like ZnO nanowires obtained following cooling for (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, and (e) 8 h. (f), (g), (h), (i), (j) are corresponding high-magnification images.

Fig. 5. FE-SEM images of ZnO produced using different molar ratios of Zn to NH_4F of (a) 5:0, (b) 5:1, (c) 5:2, (d) 5:3, (e) 5:4, and (f) 5:5.

Fig. 6. The morphology of ZnO under different conditions: (a) 10 h reaction time without cooling. (b) 2 h reaction time with 8 h cooling time.

Fig. 7. HRTEM images of Pt catalyst particles on ZnO.

Fig. 8. (a) FE-SEM image of a pristine capillary. (b) and (c) Magnified images of (a). (d) FE-SEM image of a capillary modified with ZnO nanorod arrays. (e) and (f) Magnified images of (d). (g) FE-SEM image of a capillary modified with grass-like ZnO nanowires. (h) and (i) Magnified images of (g).

Fig. 9. (a) and (b): The velocity profile of capillaries respectively decorated by ZnO nanorod arrays and grass-like ZnO micro-nanostructure (velocities increase from blue to red). (c) The schematic diagram of the motion of fluid and reactant molecules in different microchannels.

Fig. 10. (a) UV-vis absorption spectra of o-nitrophenol and o-aminophenol in ethanol. (b) Continuous catalytic performance of two microreactors with RT = 25 s. (c) the solution from Microreactor 2 with RT = 25 s, (d) the solution from Microreactor 1 with RT = 25 s.

Fig. 11. (a) EDX spectrum of grass-like ZnO/Pt micro-nanostructures. (b) UV-vis absorption spectra of Methylene blue before and after degradation. (c) Successive UV-vis absorption spectra showing the degradation of methylene blue. (d) Degradation of methylene blue in the ZnO/Pt microreactor and blank capillary.

517 Table 1. Stability of Pt catalyst and ZnO micro-nanostructure in capillary
518 microreactors during catalytic reaction.
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Exp. No.	Time	Pt element content		Zn element content	
		ZnO/Pt nanorod	grass-like ZnO/Pt	ZnO/Pt nanorod	grass-like ZnO/Pt
		arrays	micro-nanostructure	arrays	micro-nanostructure
1	10 h	Pt: $\leq 0.01 \mu\text{g/mL}$	Pt: $\leq 0.01 \mu\text{g/mL}$	Zn: $0.06 \mu\text{g/mL}$	Zn: $0.70 \mu\text{g/mL}$
2	20 h	Pt: $\leq 0.01 \mu\text{g/mL}$	Pt: $\leq 0.01 \mu\text{g/mL}$	Zn: $0.68 \mu\text{g/mL}$	Zn: $0.87 \mu\text{g/mL}$
3	30 h	Pt: $\leq 0.01 \mu\text{g/mL}$	Pt: $\leq 0.01 \mu\text{g/mL}$	Zn: $\leq 0.01 \mu\text{g/mL}$	Zn: $0.28 \mu\text{g/mL}$

521
522 Table 2. Comparison among current work, previous work and other microreactors.
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Features	Other common microreactors	Previous work:	Current work:
		ZnO/Pt nanorod arrays	Grass-like ZnO/Pt micro-nanostructure
Fabrication technique	Soft lithography [1], CO ₂ laser technique [2], UV lithography [3] and stereo lithography [4]	Simple wet chemical method	Simple wet chemical method
Materials	PMMA [5], PDMS [1], steel plate [2], ceramic [6], glass and silica [7]	Commercial glass capillary	Commercial glass capillary
Layers	-	Single layer	Double layers
Structure	Nano-particles [2] and nano granular films [1], [6]	Vertical arrangement	Radial pattern and grass structure
Vertical height of ZnO	-	2-3 μm	50-60 μm
Fluid movement	-	Laminar flow	Turbulent flow
Catalytic performance	-	There is little effect after continuous reaction for 30 h.	Keep high catalytic performance after continuous reaction for 30 h.

In this work, A method to fabricate **grass-like ZnO micro-nanostructure on the inner wall of capillary microchannels** is presented. These grass-like ZnO-modified microchannels are decorated with Pt nanoparticles and then investigated as microreactors using o-nitrophenol and methylene blue as model reactants.

Double-layer and grass-like ZnO micro-nanostructure

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Ultralong ZnO/Pt Hierarchical Structures for Continuous-Flow Catalytic Reactions