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Photocatalytic reaction using novel inorganic polymer derived packed bed microreactor with modified TiO_2 microbeads

Tae-Ho Yoon [a], Lan-Young Hong [a], Dong-Pyo Kim [a,b,*]

[a] Center of Applied Microfluidic Chemistry, Chungnam National University, Daejeon 305-764, South Korea
[b] Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 305-764, South Korea

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ABSTRACT

We report that glass like microreactor fabricated with inorganic polymer, allylhydridopolycarbosilane, having optical transparency and solvent resistance, *via* economic microimprinting process, was evaluated for photocatalytic degradation of 4-chlrophenol with TiO_2 photocatalysts. In comparison with commercial microreactor made of glass, inorganic polymer reactor packed with TiO_2 photocatalyst nanoparticles showed only 6% lower photochemical reaction performance. To enhance the catalytic effectiveness of microreactor than those of glass or film type microreactors coated with TiO_2 nanoparticles, we prepared packed bed type microreactor with TiO_2 coated microbeads that have high mechanical stability and surface area through sol–gel reaction to get uniformity. Eventually the performance of the fabricated inorganic microreactors, was investigated in a comparative manner to that of glass-based microreactor. The sterilization performance of *Escherichia coli* was demonstrated with inorganic polymer microreactor which was packed with TiO_2 microbeads. It is for the first time, that the surface modified TiO_2 beads packed bed inorganic polymer-based microreactors fabricated *via* a cheap and simple technique demonstrated the reliable microchemical performance, which is very promising for developing an integrated microfluidics by taking advantage of available microstructuring techniques of the polymers.

1. Introduction

Titanium dioxide is widely used as a photocatalyst which degrades hydrocarbon under the existence of ultraviolet or increase of hydrophilicity of surface for self-cleaning effect in the fields of surface chemistry as bulk film coating [1,2]. By taking advantage of those unique properties, it is extended to microfluidics for the modification of microchannel surface by growth with TiO_2 nanopillar or coating of particles. Because it has high surface to volume ratio, diffusion dominated mass transfer effect and easy controlling of fierce reaction [3,4]. In case of microfluidics, most of cases are glass or quartz based microreactor owing to its optical transparency and mechanical stability [5]. According to previous work, the simplest way is to use aqueous dispersed form of Degussa P25, TiO_2 nanoparticles as a starting material, by washing and drying the glass or quartz derived micro channel repeatedly which is called 'wash coat' [6]. And sol–gel process with TiO_2 precursor, $TiOCl_2$ or titanium tetraisopropoxide has been applied frequently to form ultra thin film inside the glass microchannel [7]. In these cases, the fabrication processes including photolithography, etching and bonding of glass or quartz were very expensive, time and labor consuming, and only surface coated area participated in reaction out of channel owing to its existence of extremely small amount on channel surface. Therefore, we report the feasible chip preparation process and performance evaluation of inorganic polymer derived microreactor having optically transparent, facile fabrication capability by imprinting lithography, as photocatalytic microreactor. We evaluated the photocatalytic performance by comparison with commercial glass microreactor and inorganic derived microreactor using Degussa P25, TiO_2 nanoparticles as photocatalysts under identical conditions. Furthermore, we prepared packed bed type of microreactor with TiO_2 coated beads *via* sol–gel process and they are packed in microchannel in monolayer to enhance the photonic efficiency. To evaluate the photocatalytic performance of packed bed microreactor, live cell count of *Escherichia coli* was used as a reporting system for the evaluation of sterilization performance.

2. Materials and methods

The inorganic polymer microreactor was fabricated by UV-imprinting lithography with stamp prepared by conventional photolithography by using PDMS (Sylgard 184, Dow Corning, USA), and allylhydridopolycarbosilane (AHPCS, SMP-10 matrix®) mixed

* Corresponding author at: Cooperation Center for Industry (W1) 318, Chungnam National University, Gung-dong, Yusung-gu, Daejeon 305-764, South Korea.
Tel.: +82 42 821 8920; fax: +82 42 823 6665.
E-mail addresses: dpkim@cnu.ac.kr, thyoon@cnu.ac.kr (D.-P. Kim).

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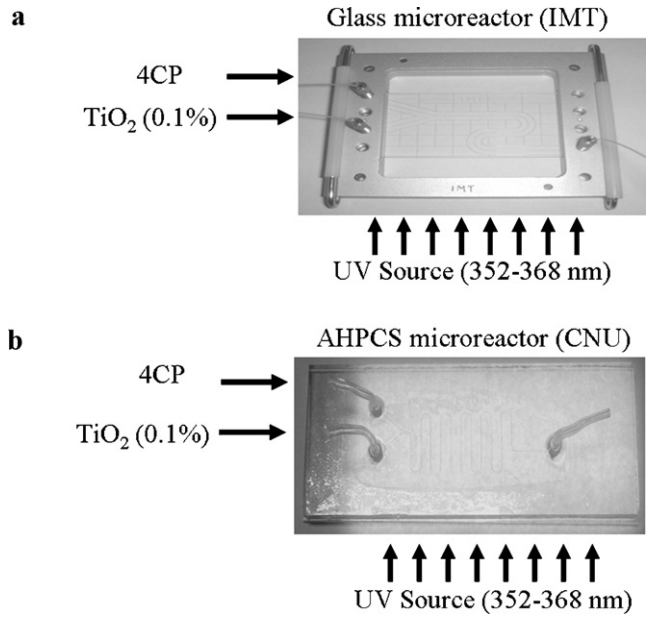

Fig. 1. Images of commercial glass microreactor (top) and in-house AHPCS inorganic polymer microreactor for photocatalytic chemistry (bottom).

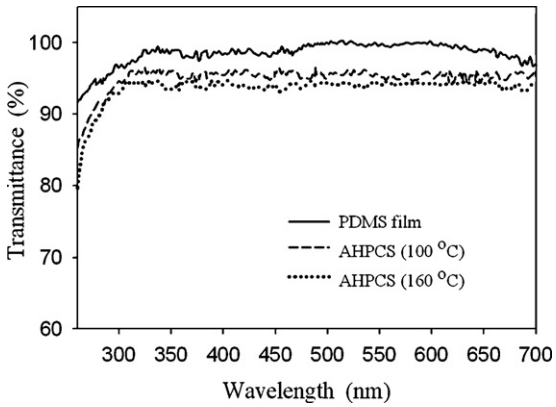

Fig. 2. Comparative UV–vis transmittance of PDMS and inorganic polymer AHPCS cured at different temperatures.

with 2 wt% of dicumylperoxide (Sigma–Aldrich, USA), and Irgacure 500 (Ciba Specialty, Japan) as a thermal and a photo initiator, respectively, were used as a structural material on glass substrate [8]. Glass microreactor (ICC-DY10, IMT, Japan) with the identical dimensions was used as a reference (Fig. 1). Two kinds of TiO_2 photocatalysts were prepared for this work, the one is Degussa P25 TiO_2 nanoparticles (Degussa AG Company, Germany) which are a fine crystalline powder with a surface area of $55 \pm 15\ m^2\ g^{-1}$ and particle size in the range 20–200 nm. It is mostly anatase (ca. 80% anatase and 20% rutile), that favors applications in photocatalysis [9]. Degussa P25 nanoparticles were mixed in 0.1 mg/μl of concentration in water as a slurry type for degradation of 4-chlorophenol (CP) with different concentrations (0.1–6.0 mM) [3]. And the other is TiO_2 coated glass microbeads prepared by sol–gel method with $TiCl_4$ 0.7 ml in H_2O 5 g for 3 h by dipping and thermally annealed at 550 °C under air atmosphere for sterilization of microorganism, *E. coli* (ATCC W3110, KRIBB, Korea). It was cultured in Luria–Bertani media for 8 h until exponential growth phase was reached. All feeds were injected by a syringe pump (PHD 2000, Harvard Apparatus, USA) with 5 μl/min to 20 μl/min of flow rate. UV source was black-light blue lamp (F4T5 BLB, Sankyo, Japan) emitting 352–368 nm of max peaks. The residual 4-CP concentration in samples was analyzed by HPLC system (Younglin M-930 pump) with a Zorbax Eclipse XDB-C18 column (4.6 mm × 150 mm × 5 μm) by measuring UV absorbance at 254 nm. To calculate the number of live bacteria in eluted sample from microreactor, single colonies were counted on 2% of agar plate media cultured for 24 h after stretching. For the

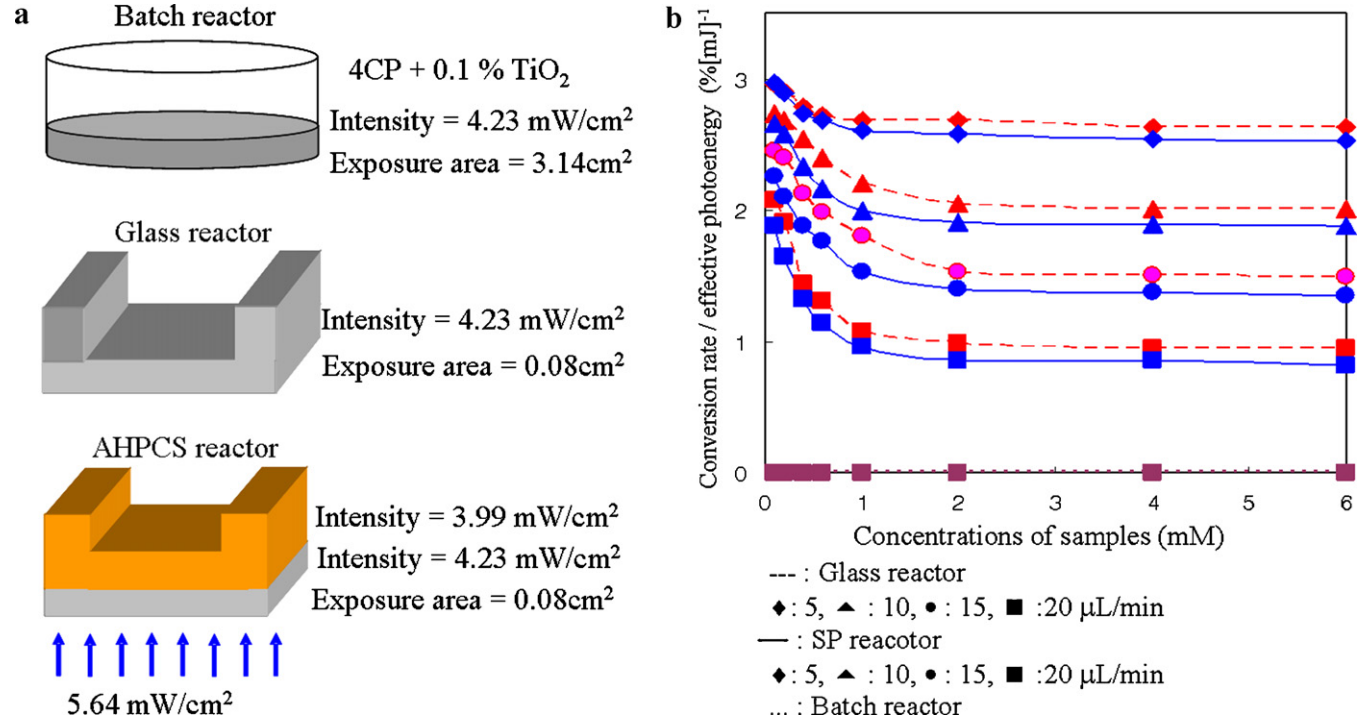

Fig. 3. (a) Schemes of measurement of effective photonic energy for photocatalytic reaction; left-up = batch reactor, middle = glass rector and inorganic polymer reactor, and (b) comparative degradation rate of 4-chlorophenol in two types of microreactors (- - -: glass based, —: inorganic polymer base, flow rate ♦: 5 μl/min, ▲: 10 μl/min, ●: 15 μl/min and ■:20 μl/min).

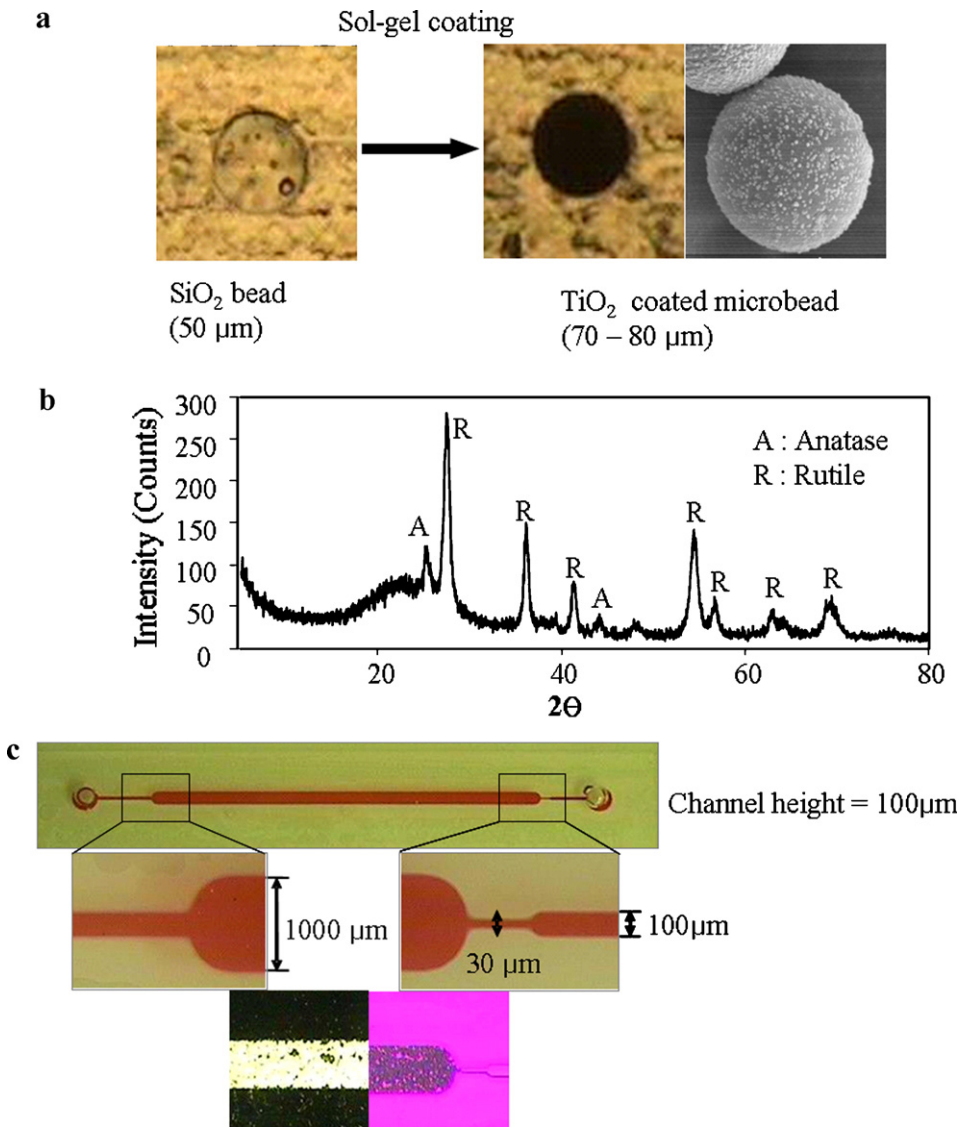

Fig. 4. (a) Microscopic and SEM images of SiO_2 and TiO_2 coated microbead after sol–gel process, (b) characterization of rutile and anatase TiO_2 by XRD analysis and (c) optical images of TiO_2 packed bed microreactor and magnified image of throat barrier structure at the end of microchannel.

optical transmittance with UV–vis spectrophotometer (Avantes, Netherland), the AHPCS films were spin-coated at 1300 rpm on glass slides with 100 μm thickness and cured at 100 °C and 160 °C in nitrogen atmosphere. In addition, PDMS films were prepared by spin-coating at 1000 rpm and those having the same thickness was used as a reference sample [10].

3. Results and discussion

The optical transmittance of the inorganic polymers coated on glass substrates was measured across the UV–visible range under different curing temperatures (100 °C and 160 °C). As shown in Fig. 2, cured AHPCS showed a high transmittance (over 90%) from 300 to 700 nm of wavelength range, which is close to that of PDMS sample having the same thickness. It was observed that the AHPCS samples cured at a higher temperature (160 °C) showed a slightly lower transmittance which was attributed to their color change from transparent to yellow tinge. It was supposed that higher crosslinkage degree is achieved in higher curing temperature. Nevertheless, the optical transparence of AHPCS is promising for their applications in the fabrication of microreactors, in particular when incorporating photo-induced chemistry or optical detections.

For the comparison of the photocatalytic performance of AHPCS microreactor, glass microreactor and batch reactor, effective photonic energy (UV intensity × exposure area × time) inflicted on reaction site is an important factor; therefore, the energies of batch, glass and AHPCS microreactor were investigated based on the effective exposed area as shown in Fig. 3(a). Measured UV intensity from light source beneath the reactor bottom was 5.64 mW cm^{-2} and depended on the material and thickness of layer. In case of batch reactor, UV exposed area was 3.14 cm^2 and intensity was 4.23 mW cm^{-2} after passing 1 mm thickness of glass plate. And commercial glass microreactor received same UV intensity, 4.23 mW cm^{-2} with 0.08 cm^2 channel bottom area, meanwhile measured UV intensity of the AHPCS microreactor coated with 100 μm thickness of inorganic polymer was 3.99 mW cm^{-2}. The specific degradation rates of 4-CP in the presence of TiO_2 nanoparticles per unit photonic energy at various conditions were illustrated with different concentrations and injection flow rates of 4-CP solution. Based on this intensity, effective photonic energy was calculated by multiplying UV intensity, exposure area and retention time for each case as listed in Table 1. Generally, AHPCS microreactor showed 95% of conversion rate at various flow rates compared with glass microreactor, which is consistent with the similar optical

Table 1
Effective photonic energy at different reactors and retention times.

Type	Intensity (mW cm^{-2})	Effective area (cm^2)	Absorbed UV (mW)	Flow rate (μl/min) [retention time (s)]	Dose (mJ)
Batch reactor	4.23	3.14	13.2822	20 [20]	265.6
				15 [27]	358.6
				10 [40]	531.3
				5 [80]	1062.6
Glass reactor	4.23	0.08	0.3384	20 [20]	6.8
				15 [27]	9.1
				10 [40]	13.5
				5 [80]	27.1
AHPCS reactor	3.99	0.08	0.3192	20 [20]	6.4
				15 [27]	8.6
				10 [40]	12.8
				5 [80]	25.5

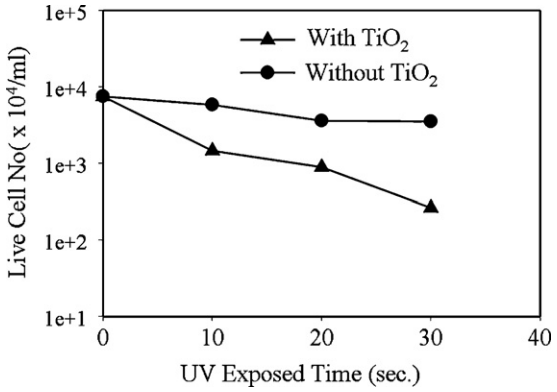

Fig. 5. Comparative photocatalytic sterilization effect of plain and TiO_2 packed bed microreactor.

transparency of both microreactors. Deviation between glass and AHPCS microreactors is supposedly by the loss of photonic energy that occurred by the scattering of UV at the microchannel. In the range of 4-CP concentration below 2 mM, degradation rates were highly dependent on concentration above 2 mM, it became constant at each flow rate, by reaching the saturation stage of injected TiO_2 amount.

To increase the photocatalytic efficiency, alternative TiO_2 packed bed photocatalytic microreactor was prepared by packing TiO_2 coated silica bead into the chamber (100 μm of height and 1000 μm of width, and throat barrier of 30 μm width) of AHPCS microchannel for higher capacity and immobilization of photocatalysts. As shown in Fig. 4(a), 50 μm diameter of silica bead increased to 70–80 μm after coating and turned to opaque owing to TiO_2 shell. In addition, TiO_2 nanoparticles in the range 300–500 nm were crystallized on the surface of the beads. For identification of TiO_2 species for photocatalytic activity, a rutile and an anatase TiO_2 were confirmed by XRD (Fig. 4(b)) [11].

Because microbeads were packed in monolayer in microchannel, facile flow with low pressure drop were generated, and microbeads were captured by mouth–throat structure at the end of micro channel as shown in Fig. 4(c). As a photocatalytic performance indicator, *E. coli* was prepared. When *E. coli* broth was injected into TiO_2 packed bed photocatalytic microreactor showed sterilization effect by decreasing the numbers of live *E. coli* to 110 from 9500 in 4.2 μl/min of flow rate, which was verified by 24 h incubation on a nutrient agar plate with eluted sample from microreactor as shown in Fig. 5. It is originated that the electrons which have strong deoxidization ability produce oxidized free radicals anion and oxyhydrogen free radicals after reacting with H_2O and O_2 dissolved in water. They have strong oxidation ability, and affected cell membrane and DNAs. In contrast, plain microchannel with no TiO_2 beads was infused with broth containing *E. coli* at the same flow rate and then exposed to UV radiation, there was slight sterilization effect of *E. coli*, which occurred by UV irradiation. Eventually, it demonstrated that optically transparent AHPCS derived microchannel was very useful as a photocatalytic microreactor by decomposition photochemistry and sterilization effect of *E. coli*. And it is plausible that inorganic polymer based microchannel is very useful as a photochemical microreactor with high optical transparency and excellent stability, which cannot be realized in the plastic or polymer derived microreactors.

4. Conclusion

It is evaluated that optically transparent inorganic polymer derived microchannel showed good performance for photocatalytic microreaction by decomposition of 4-chlorophenol by photochemistry as much as commercial glass derived microreactor. In addition, microreactor packed with TiO_2 microbeads is effective for photocatalytic reaction by demonstration of sterilization of *E. coli*. Finally, it is plausible that inorganic polymer based microchannel fabricated facile UV imprinting process is very useful as a photochemical microreactor with high optical transparency and excellent stability.

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