Discovery of a New Catalyst for Photocatalytic Hydrogen Production: Parallel Ink-jet Printing Synthesis of Multicomponent Mesoporous Metal Oxides Library

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Abstract

We introduce an ink-jet printing technique for fabricating Multicomponent Mesoporous Metal Oxides (MMMOs). The properties of the precursors and organic templates, and sol–gel/mesostructure co-assembly process can be controlled to meet the demand of ink-jet printing synthesis onto different solid surfaces (such as ceramic, glass, quartz, paper, and cloth). Parallel syntheses of MMMOs libraries achieve greater stability, precision, highly dispersion, and uniformity. MMMOs libraries with varied composition, stoichiometries and self-assembled nanostructures can be prepared by ejecting precursors microdroplets via nozzles with the aid of a computer specification design file and software (>104 samples/day). This approach provide an efficient way to search through the largely unexplored universe of MMMOs with binary, ternary, and higher order for the discovery and optimization of better catalysts for photocatalytic hydrogen production by liquid-phase reforming of formaldehyde-water solution.

Introduction

Mesoporous metal oxides with varied advanced features such as high surface areas, crystallinity and uniform pore size have been widely used as desirable catalysts or support materials in heterogeneous catalysis. [1-4]An efficient strategy that can parallel synthesis and high-throughput screening of single- and multi-component mesoporous metal oxides (MMMOs) will be useful to expedite searching of catalytic materials from large databases in the catalysis industry. Previous development of catalysts has largely relied on trial-and-error methods, which remains as a time-consuming and unpredictable process.[5] Pioneered by the drug discovery process in the pharmaceutical industry, combinatorial approach is introduced as a high-throughput methodology to speed up the pace for searching catalysts. [6-8] The promising route of combinatorial catalysis is enable to intelligent planning and execution execute of highly parallel synthesis, process and test large-scale solid materials in a high-throughput fashion with minimal human intervention. This progress has been developed for metal oxides catalysts.[9-13] When extending such methodology to the development of MMMOs catalysts, there are two formidable tasks: parallel synthesized of diverse structural and composition MMMOs libraries and rapid high-effective screening strategy of the catalytic activity for large-scale libraries.

Guided by our previously studies of the sol–gel/mesostructure co-assembly process in AcHE system [14]and by understanding of ink-jet printing technique[15], we prepare to parallel synthesize a series of MMMOs (10,000 samples/day) with different compositions and stoichiometries. Ink jet printing (IJP) is distinguished in the high-throughput parallel synthesis by the size of the working area, the flexibility with respect to jet volume range from the microliter to several milliliters, and the support in programming the robots for catalysts, organic device combinations, and biomaterials.[16-18] Although the surfactant-templated silica mesoporous materials has been synthesized by IJP technique, [19-21] high-throughput parallel synthesis of non-silica MMMOs libraries has not been reported yet. This is highly attractive and is easy to image. However, there are three synthetic challenges to take on. First, the dissimilar chemistry properties of the precursors and organic templates lead to clog printer head that disrupts the co-assembly process and affects the real composition of libraries. Second, the computer specification design file and software to ensure the stability, precision, highly dispersion, and uniformity of the libraries. Third, redox reactions, phase transformations, and crystallization question the stability of the printing films at elevated temperatures. Our approach is to adjust the composition of acetic acid, aqueous HCl, ethanol, and different metal alkoxides for satisfying the performances of ink-jet printing.

On the other hand, the rapid high-effective screening strategy of the catalytic activity for large-scale libraries is another key factor that affects the discovery and development of new catalysts. Facing tens of thousands of combinatorial MMMOs libraries synthesized by IJP, it is impractical to analyze each combination individually using most popular combinatorial searching methods. Thus, the critical issue should be to build an available strategy. If we considered the catalytic activity depending on the variables as a 'signal' in the combinatorial space, wavelet analysis can be recommended for finding the feature of the unknown signal effectively. Basing on wavelet analysis, we can decompose the given signal into several groups of coefficients which contain information about catalysis characteristics of the sequence at different scales. Instead of searching the whole space, the decomposition enables us to search the subspace of the libraries iteratively. Furthermore, we can reduce the size of the search space and move forward promising regions of the space in each iteration. Wavelet analysis has been applied to a large variety of biomedical signals. [22] However, so far there have not reports on combinatorial screening materials for catalysis application yet.

Photocatalytic hydrogen production from water is considered as one of the most important transformations to solve the development of renewable energy resources. Thus, we herein report the realization of rapid parallel ink-jet printing synthesize and wavelet analysis screening for combinatorial development of MMMOs catalyst in the photocatalytic hydrogen production by

liquid-phase reforming of formaldehyde-water solution. The meosoporous Cu-TiOx materials is capable of high efficient hydrogen generation which is comparable to that of noble metal loaded TiO_2. The model system demonstrates the full power of our strategy. The advantages of high-throughput parallel synthesis and wavelet analysis screening make this strategy promising for other combinatorial catalysis fields, which could serve as a guide to find the most promising catalyst candidates.

Parallel MMMOs library synthesis with ink-jet printing technique

The power of the synthesis with IJP parallel produces 10^2 samples per second with up to *8* different element components and 10^2 different compositions. It can be used to effectively discovery/optimize materials. The properties of the precursors and organic templates, and sol-gel/mesostructure co-assembly process can be controlled to meet the demand of IJP synthesis onto different solid surfaces (such as glass, filter paper, and cloth) according to previously reported AcHE method. The printing patterns consists of $N \times N$ array, which is created with Adobe Photoshop™ in CMYK (cyan, magenta, yellow and black) mode on an Epson Stylus Photo 4880 ink-jet printer at a resolution of 360dpi. *N* is the total number of combinations. In order to "force" the printers to print "virtual pattern", new printing software "IPrint" are developed to control the information output.

MMMOs libraries with varied composition, stoichiometries and self-assembled nanostructures can be produced by ejecting precursors' microdroplets via the nozzles. Parallel syntheses of the libraries achieve greater stability, precision, highly dispersion, and uniformity. Fig.1a is a macroscopic optical image of Cu-mTiO_2 library with different Cu/Ti ratio formed in several seconds by print copper nitrate and titanium butoxides precursors. Transmission electron microscopy (TEM) shows the wormhole structure characteristic of the calcined Cu-mTiO_2 mesophase formed by IJP (Fig.1c). The inset in Fig.1c shows the high-resolution TEM (HRTEM) image of Cu-mTiO_2, demonstrating the channel walls consist of nano-sized anatase crystals (d_{101}=3.3Å), which are good agree with the wide-angle X-ray diffraction (WXRD) results (d_{101}=3.46Å, Fig.1b). A detailed energy dispersive X-ray (EDX) element mapping measurement of Cu-mTiO_2 at a resolution of ~10 nm shows uniform X-ray intensity of Cu, Ti and O signals throughout the mesoporous particles—revealing the existence of a homogeneous distribution of copper oxide and titania components (Fig.1e). Elemental analysis conducted for verifying the content of Cu and Ti in the Cu-mTiO_2 synthesized by IJP technique. Scanning electron microscopy coupled with EDX analysis indicates that the printing synthesize ratios of Cu/Ti are agree well with the theoretically design ratios aided by a computer specification design file and software (Fig.1d).

Photocatalytic hydrogen production by liquid-phase reforming of formaldehyde-water solution

To illustrate the strategy based on the wavelet analysis for identification and optimization of catalysts, the photocatalytic hydrogen production is used as a model reaction. Taking into account of previously research work on TiO_2,[23] which is one of

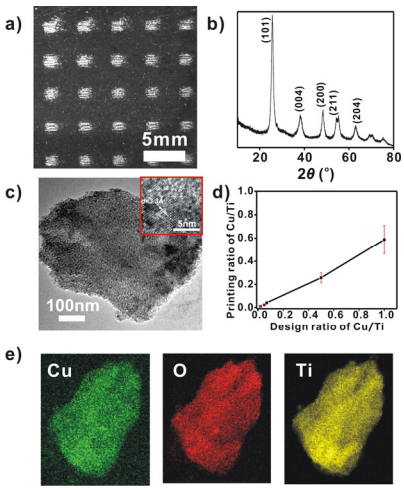

Figure 2. *IJP synthesized MMMOs library calcined at 350°C in air. a) Optical micrograph of Cu-mTiO_2 array with different Cu/Ti ratio created by Epson Stylus Photo 4880 ink-jet printer at a resolution of 360dpi. b) Wide-angle X-ray diffraction patterns of Cu-mTiO_2. c) TEM and HRTEM (inset) micrograph of Cu-mTiO2. d) EDX analysis of Cu and Ti elements in Cu-mTiO_2. e) Element mapping of a single Cu-mTiO_2 particle.*

the most available photocatalysts, we investigate the compositions containing primary Ti with added amount of other transition metal elements. V, Fe, Co, Cr, Mn and Cu are used as candidate components because of their cheap, variable valence than noble metal elements for improve the photocatalysis activity.[24-28] Each *10×10* diverse binary MMMOs library is generated rapidly by IJP, and then divided into 4 subspaces. The photocatalytic hydrogen production reactions of the catalyst subspaces by liquid-phase reforming of formaldehyde-water solution are carried out under 300W high-pressure Hg lamp irradiation at 25°C. The average value of the hydrogen generation amounts (*Avg. HA*) of different subspaces is analyzed by gas-chromatograph (GC). Fig. 2a shows the amounts of hydrogen production obtained from the fourth hours after irradiation for *24* catalyst subspaces with *6* different binary components and *6×10×10* different compositions. The H_2 production efficiency of Cu-mTiO_2 is about 10-fold as high as that of other catalyst libraries. The maximum H_2 evolution of 1247μmol/h·g^{-1} is observed for the Cu-mTiO_2 with Cu/Ti ratio in the range of 0~0.2 (defined as subspace *A*). According to wavelet analysis strategy, this optimal subspace of Cu-mTiO_2 catalyst libraries will be reserved for next iteration. After calculating the difference between the maximum H_2 evolution and other results, we find that the difference value is exceed a given threshold value *500*μmol/h·g^{-1}. Thus, the corresponding other *23* catalyst subspaces will be neglected.

In the second iteration, the Cu-mTiO_2 subspace *A* also follows the same screening strategy. A *10×10* diverse Cu-mTiO_2 library with Cu/Ti ratio in the range of *0~0.2* is printed to synthesis, and then also divided into 4 subspaces (*Aa*, *Ab*, *Ac*, and *Ad*) and employed for hydrogen production, individually. Obvious different of subspace *Aa* is observed as compared with that of other subspaces (Fig.2b). The best hydrogen production is obtained with Cu-mTiO_2 based on Cu/Ti ratio in the range of *0~0.05*, 1437μmol/h·g^{-1}. After wavelet analysis strategy, the optimal subspace *Aa* will be reserved for next iteration. New

subspaces (*Aaa*, *Aab*, *Aac*, and *Aad*) are evaluated individually with the same scheme under identical conditions for hydrogen production. Fig.2c shows that the subspace *Aad* with Cu/Ti ratio in the range of 0.0375~0.05 displays the highest amount of hydrogen generation, 1692μmol/h·g^{-1}. We also calculate the difference between the maximum H_2 evolution subspace *Aad* and other subspaces. Although the difference is still more than 500μmol/h·g-1, the size of the subspace is small enough. According to the strategy, we end the iteration search. In this model reaction, the optimal catalyst is 4.4% Cu-mTiO_2 calculated by the average of the two endpoints (0.0375, 0.05) of the desired subspace *Aad*. After three iterations, we reduce the number of catalyst evaluations for 1000-library to a total of 36 reactions and improve the subspace precision to one thousandth level.

Catalytic Activity of catalysts

Fig.2d shows the photocatalytic hydrogen generation efficiency for mTiO_2, 1wt% Ag-mTiO_2 and optimal catalyst 4.4% Cu-mTiO_2 screened by wavelet analysis strategy as a function of irradiation time at room temperature. Pure mTiO_2 shows less activity for hydrogen production by liquid-phase reforming of formaldehyde-water solution. However, compared with mTiO2, the 4.4% Cu-mTiO_2 shows 20 times higher activity for hydrogen evolution. After 4h irradiation, the amount of hydrogen generation is nearly 10,900umol/g, which is comparable to that of noble metal modified mTiO_2 (Ag@mTiO_2, 1.0wt%, 9,343umol/g). This observation implies that parallel synthesize and wavelet analysis strategy can lead to identification of the optimal catalysts.

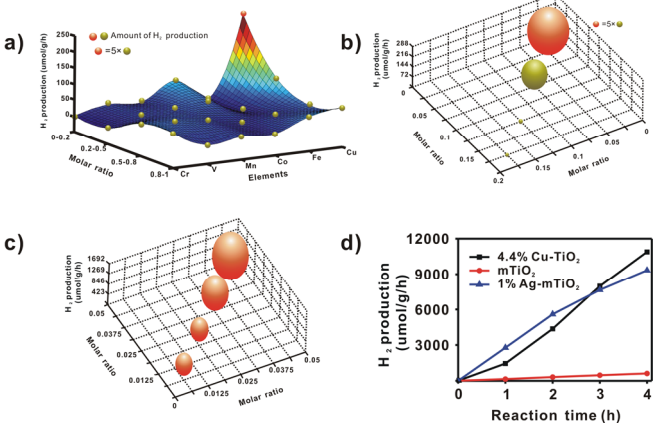

Figure 3. *Identify the most active catalyst combinations for hydrogen production. a, Assay results of total number of chemical species within first iteration. Cu was the only candidate element for modified mTiO2 selected. b, Assay results of second iteration, optimal subgroup with Cu/Ti ratio=0~0.05 is reserved. c, The optimal catalyst is discovered in this iteration process (Cu/Ti ratio=0.0375~0.05). d, Photocatalytic hydrogen production by liquid-phase reforming of formaldehyde-water solution versus irradiation time over mTiO2, 1wt% Ag-mTiO2 and optimal catalyst 4.4% Cu-TiO2.*

Conclusion

In this work, we use ink-jet printer as a tool to synthesize large-scale multi-component mesoporous metal oxides with varied composition, stoichiometries and self-assembled nanostructures under control. Wavelet analysis is introduced here for the first time to accelerate the evaluation speed of large-scale catalyst library by reducing the number of reactions and analysis, and improving the precision unlimitedly. This strategy has proven effective in optimizing the components and compositions for photocatalytic hydrogen production by liquid-phase reforming of formaldehyde-water solution. We find that the mTiO_2 with doped Cu element can lead to improve catalytic activity, which similar to that of the noble metal. This suggests that the strategy is an efficient and systematic way to search large unexplored space of novel multi-component compounds for catalysis and other wide applications.

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References

[1] Taguchi, A. & Schuth, F. Ordered mesoporous materials in catalysis. *Microporous Mesoporous Mat.* **77**, 1-45 (2005).

[2] Yu, C.Z., Tian, B.Z. & Zhao, D.Y. Recent advances in the synthesis of non-siliceous mesoporous materials. *Curr. Opin. Solid State Mat. Sci.* **7**, 191-197 (2003).

[3] Antonelli, D.M. & Ying, J.Y. Mesoporous materials. *Curr. Opin. Colloid Interface Sci.* **1**, 523-529 (1996).

[4] Schuth, F. Non-siliceous mesostructured and mesoporous materials. *Chem. Mat.* **13**, 3184-3195 (2001).

[5] Merrifield, R.B. Solid Phase Peptide Synthesis .1. Synthesis of a Tetrapeptide. *J. Am. Chem. Soc.* **85**, 2149-& (1963).

[6] Senkan, S. Combinatorial heterogeneous catalysis - A new path in an old field. *Angewandte Chemie-International Edition* **40**, 312-329 (2001).

[7] Koinuma, H. & Takeuchi, I. Combinatorial solid-state chemistry of inorganic materials. *Nat. Mater.* **3**, 429-438 (2004).

[8] Reetz, M.T. Combinatorial and evolution-based methods in the creation of enantioselective catalysts. *Angewandte Chemie-International Edition* **40**, 284-310 (2001).

[9] Danielson, E. *et al.* A combinatorial approach to the discovery and optimization of luminescent materials. *Nature* **389**, 944-948 (1997).

[10] Jandeleit, B., Schaefer, D.J., Powers, T.S., Turner, H.W. & Weinberg, W.H. Combinatorial materials science and catalysis. *Angewandte Chemie-International Edition* **38**, 2495-2532 (1999).

[11] Corma, A., Serra, J.M., Argente, E., Botti, V. & Valero, S. Application of artificial neural networks to combinatorial catalysis: Modeling and predicting ODHE catalysts. *ChemPhysChem* **3**, 939-945 (2002).

[12] Hoffmann, C., Wolf, A. & Schuth, F. Parallel synthesis and testing of catalysts under nearly conventional testing conditions. *Angewandte Chemie-International Edition* **38**, 2800-2803 (1999).

[13] Holzwarth, A., Schmidt, P.W. & Maier, W.E. Detection of catalytic activity in combinatorial libraries of heterogeneous catalysts by IR thermography. *Angewandte Chemie-International Edition* **37**, 2644-2647 (1998).

[14] Fan, J., Boettcher, S.W. & Stucky, G.D. Nanoparticle assembly of ordered multicomponent mesostructured metal oxides via a versatile sol-gel process. *Chem. Mat.* **18**, 6391-6396 (2006).
[15] Liu, X.N., Fan, J., Liu, Y.L., Zang, Y.H. & Liu, Z. Evaluation of printing fidelity of ink-jet paper based on measure theory and fuzzy logic. *Nord. Pulp Paper Res. J.* **24**, 239-243 (2009).
[16] Calvert, P. Inkjet printing for materials and devices. *Chem. Mat.* **13**, 3299-3305 (2001).
[17] Evans, J.R.G., Edirisinghe, M.J., Coveney, P.V. & Eames, J. Combinatorial searches of inorganic materials using the ink jet printer: science, philosophy and technology. *J. Eur. Ceram. Soc.* **21**, 2291-2299 (2001).
[18] Woodhouse, M., Herman, G.S. & Parkinson, B.A. Combinatorial approach to identification of catalysts for the photoelectrolysis of water. *Chem. Mat.* **17**, 4318-4324 (2005).
[19] Fan, H.Y. *et al.* Rapid prototyping of patterned functional nanostructures. *Nature* **405**, 56-60 (2000).
[20] Mougenot, M. *et al.* Ink jet printing of microdot arrays of mesostructured silica. *J. Am. Ceram. Soc.* **89**, 1876-1882 (2006).
[21] Fan, H.Y. *et al.* Hierarchically structured functional porous silica and composite produced by evaporation-induced self-assembly. *Microporous Mesoporous Mat.* **44**, 625-637 (2001).
[22] Akay, M. Wavelets in Biomedical-Engineering. *Ann. Biomed. Eng.* **23**, 531-542 (1995).
[23] Linsebigler, A.L., Lu, G.Q. & Yates, J.T. Photocatalysis on Tio2 Surfaces - Principles, Mechanisms, and Selected Results. *Chemical Reviews* **95**, 735-758 (1995).
[24] Liu, B.S. *et al.* Low temperature fabrication of V-doped TiO2 nanoparticles, structure and photocatalytic studies. *Journal of Hazardous Materials* **169**, 1112-1118 (2009).
[25] Neatu, S. *et al.* M/TiO2/SiO2 (M = Fe, Mn, and V) catalysts in photo-decomposition of sulfur mustard. *Applied Catalysis B-Environmental* **91**, 546-553 (2009).
[26] Meichtry, J.M., Brusa, M., Mailhot, G., Grela, M.A. & Litter, M.I. Heterogeneous photocatalysis of Cr(VI) in the presence of citric acid over TiO2 particles: Relevance of Cr(V)-citrate complexes. *Applied Catalysis B-Environmental* **71**, 101-107 (2007).
[27] Hegde, M.S., Nagaveni, K. & Roy, S. Synthesis, structure and photocatalytic activity of nano TiO2 and nano Ti1-xMxO2-delta (M = Cu, Fe, Pt, Pd, V, W, Ce, Zr). *Pramana-Journal of Physics* **65**, 641-645 (2005).
[28] Wei, H.Y., Wu, Y.S., Lun, N. & Zhao, F. Preparation and photocatalysis of TiO2 nanoparticles co-doped with nitrogen and lanthanum. *Journal of Materials Science* **39**, 1305-1308 (2004).

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