Development and application of a simple capillary-microreactor for oxidation of glucose with a porous gold catalyst†

Chanbasha Basheer,[a] Sindhu Swaminathan,[b] Hian Kee Lee*[a] and Suresh Valiyaveettil*[ab]

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An efficient oxidation of glucose to gluconic acid was performed using a porous gold(0) catalyst in a low-cost microreactor designed from Pyrex glass capillary tubing; compared with the conventional synthesis procedure this novel approach of using a capillary-microreactor offers a convenient and highly efficient means to optimise reaction conditions and catalytic activities.

Miniaturised microreactors have many advantages such as excellent mass and heat transfer properties over conventional large-scale synthetic methodologies.[1,2] Other specific advantages include inherent safety, high efficiency and rate as well as opportunities to discover or optimize new reactions, in particular, reactions which are explosive in nature, and screening of catalysts.[3] The microreactor or lab-on-a-chip technology using photolithographic procedures has been well established for carrying out reactions on a small scale.[1] However, (for heterogeneous catalysis) the technology is still not well developed due to the requirement of catalyst immobilization in the channels (either chemical or mechanical bonding of the catalyst)[4] and it is prone to failure from clogging and solvent incompatibilities.

Ecofriendly catalytic methods for the oxidation of organic molecules are of growing interest to develop eco-sustainable chemical processes.[5] The use of gold as a relatively new catalyst for chemical oxidation is interesting owing to its resistance to oxygen deactivation.[6] Owing to the importance in many applications, oxidation of glucose to gluconic acid using heterogeneous catalysis is important in chemical industries.[7]

In this context, we have designed and developed a new capillary microfluidic system for oxidation of glucose (Fig. 1(a)). Our design is focused on a low-cost disposable glass capillary tube (5 cm × 0.4 mm) reactor with high efficiency for chemical transformations. A porous gold(0) sponge catalyst was synthesized and utilized for the oxidation of D-glucose to D-gluconic acid (Fig. 1(b)) in an aqueous solution at room temperature (ESI†). The reaction yield was compared with a batch scale oxidation procedure.[8]

Metallic foams or metallic sponges possess different properties depending on their manufacturing techniques.[9] Various templating methods are available for the production of macroporous materials, which includes microemulsions and colloidal crystals.[10] Here we employed porous seastar skeleton as a template for fabricating porous (pore diameter of 10–20 μm) gold catalyst. Details on the preparation are provided as ESI.†

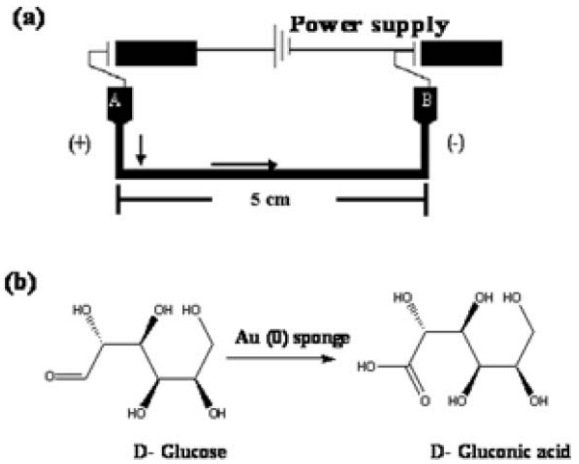

Fig. 1 (a) Schematic design of capillary-microreactor and (b) reaction scheme of D-glucose oxidation to gluconic acid.

Fig. 2 shows the SEM micrographs of the seastar scaffold, the scaffold coated with gold and the porous gold sponge after the removal of natural template. EDAX analysis was performed to confirm the complete removal of scaffold and no calcium existed on the surface (Fig. 2(d)). These freshly prepared thin metallic sponges were used as catalysts for further reaction.

In the capillary-microreactor, the poly(propylene) pipette tips were inserted at both ends of the 5 cm capillary tube and used as reservoirs. The capillary tube (0.4 mm, internal diameter) and reservoirs A and B were filled with phosphate buffer solution (50 mmol, pH 10) mixed with porous Au(0) catalyst. A few pieces

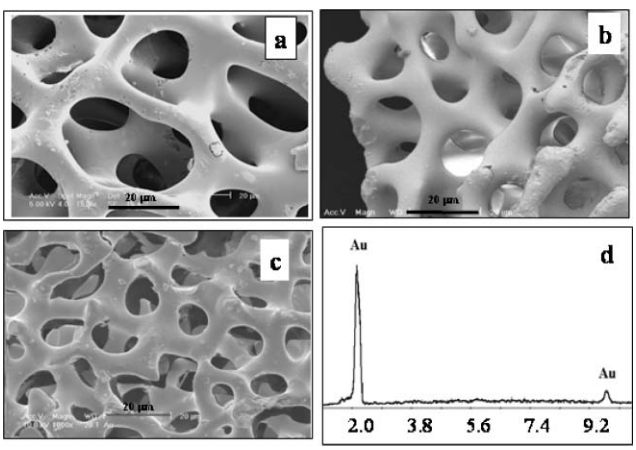

Fig. 2 SEM micrographs of (a) seastar skeleton, (b) gold coated seastar template, (c) porous gold after removal of the template and (d) EDX spectra of the gold sponge.

† Electronic supplementary information (ESI) available: Details on experimental procedures and characterization. See http://www.rsc.org/suppdata/cc/b4/b414429e/

*chmleehk@nus.edu.sg (Hian Kee Lee)
chmsv@nus.edu.sg (Suresh Valiyaveettil)

of the porous and low-density catalysts were introduced into the capillary tube and the reagents were passed through them under an applied potential. Extreme care was taken to ensure that air bubbles were absent inside the capillary tube by applying a constant current. For demonstrating the capability of the reactor, 5 μl (1 mmol) of glucose was introduced in to the reservoir. Platinum wires were used as electrodes and a reaction potential of 5 kV and 100 μA current was applied to reservoir A. Reservoir B was connected to the ground. Glucose was pumped through the channels using electrokinetic pumping.[11] The reaction was monitored for 40 min at room temperature and yields were quantified using HPLC with a refractive index detector. The bulk-scale oxidation of glucose was performed using a previously reported procedure.[8]

Analytical parameters affecting the reaction yield such as reaction time, applied potential and pH were optimized to get a good yield of 99% for the oxidation. Keeping a constant current of 100 μA, the reaction yield was determined with respect to time within the range of 10–50 min. In general, the reaction yield increases with increase in reaction time up to 40 min and no further increase in yield was measured at 50 min (Fig. 3(a)). After optimization of the reaction time, we evaluated the influence of the applied potential (from 1 to 5 kV) on the yield of the oxidation. As can be seen, a maximum product yield was obtained at a potential of 5 kV (Fig. 3(b)).

The influence of pH within the range 2–12 was investigated to maximize the yield of the reaction (Fig. 3(c)). A pH range of 6–10 gave maximum yield of gluconic acid and slightly alkaline pH was suitable to increase the reaction yield and to avoid drastic deactivation of the catalyst and to reduce side reactions.[12,13]

In order to evaluate the stability and reactivity of the catalyst, oxidation was repeated five times with the same catalyst under the optimum reaction conditions (40 min, 5 kV, 100 μA) with 50 mmol phosphate buffer at pH 10. No significant loss of reactivity was observed. Compared with conventional synthesis, the microreactor provided higher reaction yields. The liquid chromatograms of reaction products obtained for the oxidation of glucose using porous Au(0) catalyst in the capillary-microreactor and conventional routes are shown in Fig. 3(d). A reaction yield of 99% was achieved in the capillary-microreactor, whereas the conventional method yielded only 48% of gluconic acid. In the capillary-microreactor, it is believed that active sites were generated on the surface of Au catalyst under an applied voltage and the higher surface area of the porous sponge catalyst also helped to obtain a high reaction yield.[14]

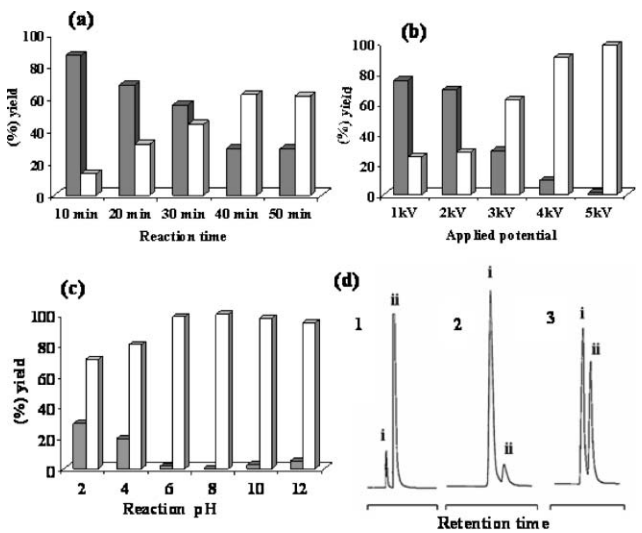

Fig. 3 Effect of (a) reaction time, (b) applied potential and (c) reaction pH on D-glucose oxidation in the capillary-microreactor (■, D-glucose; □, D-gluconic acid), (d) liquid chromatogram of reaction products (1) at 1 kV, (2) 5 kV and (3) bulk scale. Peak identification: (i) D-gluconic acid and (ii) D-glucose.

Oxidation of glucose in our capillary-microreactor has proven to be an attractive alternative to the conventional synthetic procedures.[15] No isomerization of glucose to fructose was observed during the reaction and total selectivity to D-gluconic acid was obtained. Owing to the large size and porous nature of the catalyst, no immobilization of catalyst to the capillary tube is required.

The low cost of fabrication, disposable nature of the capillary tube and availability of a wide range of porous catalysts make our reactor highly efficient, versatile and cost effective. In addition, the observed high reaction yield, ready applicability of external stimuli such as voltage or temperature, and the possibility for scale up, increase the potential of our reactor design.

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Chanbasha Basheer,[a] Sindhu Swaminathan,[b] Hian Kee Lee*[a] and Suresh Valiyaveettil*[ab]
[a]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543. E-mail: chmleehk@nus.edu.sg; chmsv@nus.edu.sg; Fax: 65 6779 1691; Tel: 65 6874 2995*
[b]*NUS-Nanoscience and Nanotechnology Initiative, National University of Singapore, 2 Science Drive 3, Singapore, 117542*

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