FOCUS ARTICLE

ChemComm www.rsc.org/chemcomm

New chemistry on old CDs

Hua-Zhong Yu

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6. E-mail: hzyu@sfu.ca; Fax: +1-604-291-3765; Tel: +1-604-291-5601

First published as an Advance Article on the web 29th October 2004

Old compact discs (CDs) have been found to be useful for modern chemical research. Their metal reflective film is suitable for the preparation of high-quality self-assembled monolayers (SAMs) and for electrochemical analysis; pre-grooved polycarbonate base is ideal for the "customized" fabrication of material micro/nanostructures; and the immobilization of biomolecules on CDs, in conjunction with a conventional CD drive, promises to be an inexpensive tool for point-of-care biomedical diagnosis and gene analysis.

Introduction

Compact disc recordables (CD-Rs) and analogs are the most popular portable media for data storage today. Meanwhile, CD players (including CD readers and writers) rapidly became common and inexpensive electronic devices at home and in office. As shown in Fig. 1, a regular CD-R consists of four layers of materials: a polycarbonate base, an organic dye layer, a metal reflective film, and a protective polymer coating at the very top.[1] The CD-R is read by an optical drive that measures the changes in the reflection of a polarized laser ($\lambda = 780$ nm).[2] During the recording process, the CD writer focuses the laser beam on the dye layer. The dye layer absorbs the laser light and darkens, blocking the reflective layer from the visible laser light. During the last few years, chemists have developed many novel applications of CD-Rs (and CD drives) beyond their conventional functions (to store documents, images, and music permanently); even old CD-Rs can be utilized in modern research rather than simply serving as coasters for hot drinks.

Surface chemistry on CD-Rs: Beyond self-assembly

The metal reflective layer of the CD-R is essential for writing/reading information from and to a computer as shown in Fig. 1. For some brands of high-quality CD-Rs (including Kodak and Mitsui), this film is made of pure gold due to its high stability and ideal optical performance (other popular choices are aluminium and silver). We have investigated CD-Rs as an inexpensive source of gold substrates for the fabrication of self-assembled monolayers (SAMs).[3]

SAMs, as molecularly tunable organic materials, have shown great potential in technological applications such as corrosion prevention, wear protection, and biosensing devices, as well as in the study of long-range electron transfer kinetics. Typically, researchers produce these monolayers with evaporated gold substrates that require cleaning in a dangerous bath of H_2SO_4 and H_2O_2 (so-called "Piranha" solution). We have shown that a three- to five-minute surface treatment (etching) of gold CD-R pieces with nitric acid exposes the 50 nm thick gold film that is ready for self-assembly of alkanethiols (Fig. 2). Contact angle measurements and electrochemical examinations showed no significant differences between commercially available gold substrates (*i.e.*, glass slides coated with a 100 nm thick gold film) and those produced from CD-Rs. The structures and molecular conformations of the alkanethiolate SAMs formed on both types of substrates are also very similar, as confirmed by Fourier transform infrared spectroscopy.[3]

In fact, the etching step can be successful even with an entire disc (Figs. 3A and 3B).

Hua-Zhong (Hogan) Yu received his BSc (1991) and MSc (1994) degrees from Shandong University (Ji'nan) and his PhD (1997) from Peking University (Beijing) in China. He then worked as a postdoctoral scholar with Fred C. Anson and Ahmed H. Zewail (1999 Nobel Laureate in Chemistry) at the California Institute of Technology (Pasadena, USA). Upon moving to Canada in 1999, Yu joined the NRC's Steacie Institute of Molecular Sciences as an NSERC fellow (working with Danial D. M. Wayner). Since 2001 he has been a faculty member in the Chemistry Department of Simon Fraser University in Burnaby, BC. Yu's current research is focused on DNA surface chemistry, CD-R based biosensing devices, and molecular modification of semiconductors. In May 2004, he won the Fred Beamish Award of the Canadian Society for Chemistry for his demonstrated innovations in analytical chemistry.

DOI: 10.1039/b412784f

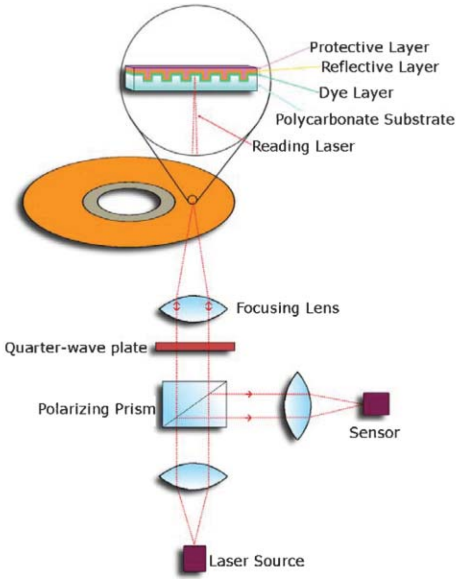

Fig. 1 Schematic illustration of the construction of a compact disc recordable (CD-R) and the optical reading/writing system.

The gold substrate prepared from CD-Rs actually has a slightly flatter morphology than commercial gold slides prepared by evaporation. Examination of the surface by atomic force microscopy (AFM) shows the designed "track-trails" (for data recording/reading) that are typically 800 nm apart (Fig. 3C). The zoom-in picture (Fig. 3D) reveals that these polycrystalline substrates have a rolling-hill topology with an average grain size of 20–40 nm and typical height differences of 3–4 nm. This assures their suitability for surface chemistry studies such as electrochemistry, wetting, and infrared spectroscopy.

Beyond the self-assembly of simple alkanethiols, we have extended our "new chemistry" on CD-Rs to kinetic study of surface reactions. For example, when titanium(IV) isopropoxide molecules are attached to dithiothreitol monolayers on gold, the contact angle of a sessile water droplet on the titanium-coordinated surface decreases significantly as a function of time.[4] This indicates that the surface becomes more hydrophilic as a result of the hydrolysis of titanium(IV) isopropoxide. We evaluated the kinetic parameters of this surface reaction and obtained comparable results on both commercial and CD-R gold substrates.

We also used these gold substrates to prepare mixed SAMs (from a solution of decanethiol and 11-mercaptoundecanol) for the study of water evaporation, a ubiquitous phenomenon in nature. Our investigation confirmed that the evaporation of water microdroplets follows an exclusive trend from constant contact area mode to constant contact angle mode (from pinning to shrinking), irrespective of the wettability or polarity of the surface.[5] This correlates well with the wetting hysteresis that is controlled by the substrate topography.

CDtrodes for electroanalytical chemistry

Following a similar surface etching procedure as illustrated in Fig. 2, gold electrodes (named "CDtrodes") of different sizes and shapes can be made and used for a variety of electroanalytical experiments. Angnes and co-workers have pioneered the use of such CDtrodes in the last few years.[6] They compared the performance of planar CDtrodes with that of commercial gold electrodes (Metrohm Model 6.1204.140) in dilute sulfuric acid,[6a] and examined their application in stationary cells for the detection of copper and mercury by potentiometric stripping analysis.[6a,b] They also used them for the construction of band nanoelectrodes (80 nm width × 8 mm length)[6a] and of thin-layer flow cells for mercury quantification in natural waters.[6c] For the amperometric determination of ascorbic acid in pharmaceutical formulations, they modified the gold CDtrodes with platinum.[6d]

Daniel and Gutz have fabricated long-path thin-layer spectroelectrochemical cells from the same type of CDtrodes for in-situ UV/visible measurements.[7a] Recently, they described a quick procedure for the preparation of gold electrode sets or arrays and of microfluidic flow cells on CDs.[7b] Independently, Westbroek *et al.* have constructed flow-through cells using CDtrodes for the on-line amperometric determination of Ce(IV) during polymerization reactions.[8]

With the recent progress made on the construction of silver electrodes,[9] old CD-Rs are becoming even more appealing as a convenient resource of disposable metal electrodes.

Fabrication of material micro/nanostructures

The simple preparation of material micro- to nanostructures is essential to their potential applications in modern technology. The ability to pattern functional inorganic thin films into useful device architectures is of primary importance in electrochromics, photocatalysis, and batteries/fuel cells. As shown in Fig. 3C, gold substrates prepared from CD-Rs possess the pre-grooved feature that consists of uniform mountain-valley strips ("track and trails") at the micrometer level. This offers a micro-patterned conductive substrate that is simple, inexpensive and convenient for the study of selective crystal growth and of the electrodeposition of metal oxide films.

For example, we deposited zirconia thin films electrochemically on both "flat" (commercial gold slides) and CD-R gold substrates (both are modified with 11-mercaptoundecanol SAMs), in an aqueous electrolyte of $ZrOCl_2$ by cycling the electrode potentials.[10] Unlike the "cracked-mud" appearance of the zirconia thin films on flat gold (Fig. 4A), distinct differences in surface coverage, nucleation, and particle growth were noticed on the samples made on CD-R gold substrates (Fig. 4B–D). At a fast scan rate (50 mV s^{-1}, Fig. 4B), the sample had an almost uniform film formed on the mountains of the CD-Rs′ track trails,

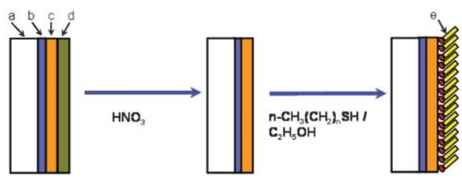

Fig. 2 Self-assembly of alkanethiols onto gold substrates prepared from CD-Rs. (a) polycarbonate base; (b) dye-photosensitive layer; (c) gold reflective layer; (d) protective polymer film; and (e) self-assembled monolayer (SAM).

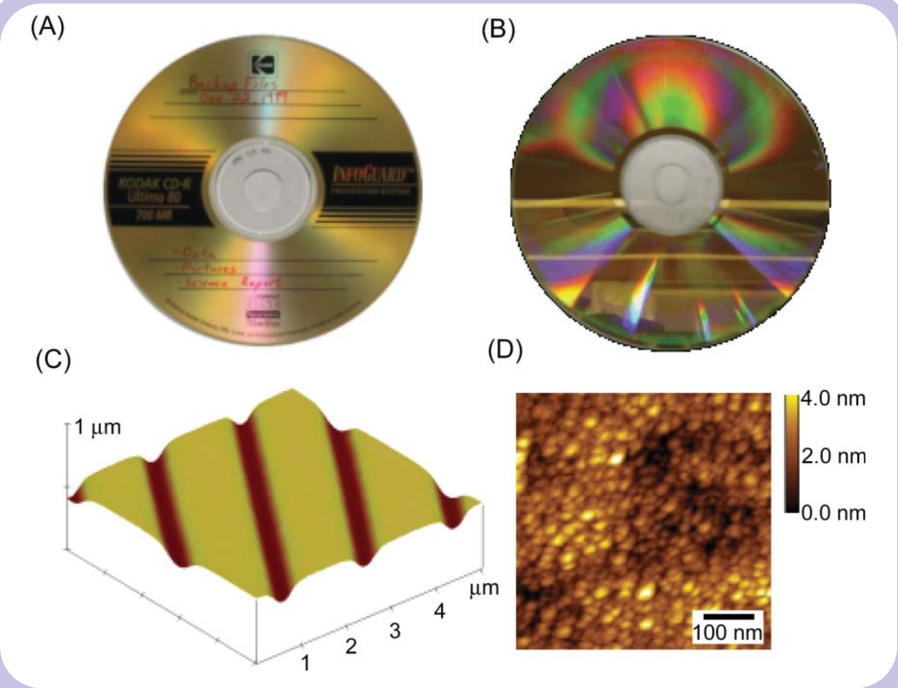

Fig. 3 Photos of CD-Rs before (**A**) and after (**B**) removal of the polymer layer, and atomic force microscope (AFM) images of the CD-R gold substrates ($5 \times 5\ \mu m^2$, **C**, and $500 \times 500\ nm^2$, **D**).

which was less pronounced in the valleys. At a medium scan rate ($20\ mV\ s^{-1}$, Fig. 4C), distinct ZrO_2 particle islands were visible only on the mountains of the substrate. These particles had diameters in the range of a few hundred nanometers and maintained uniform alignment along the mountains to form oriented zirconia "microstrips". The particles were of different shapes, and their placement in the strips appeared largely random. The sample cycled at a low scan rate ($10\ mV\ s^{-1}$, Fig. 4D) showed another type of thin film possessing a much larger, amorphous cluster-like growth and nucleation pattern on top of, or spawning from, the smaller particles without clear confinement to the mountains. These observations demonstrate the potential of using CD-R substrates in conjunction with a simple electrochemical control to tune the formation and features of inorganic material microstructures.

Other examples include the work by Drain *et al.* on the development of a bench-top method for the fabrication and patterning of nanostructures on polymers.[11] Delaminated ("naked") CD-R polycarbonate substrates were used as polymeric stamps to direct the formation of metal nanostructures. Chattopadhyay *et al.* used them as molds to create parallel lines and cross patterns and to fabricate plastic thin-film fluidic devices.[12]

Biomedical sensing on CDs

Early studies have focused on the fabrication of biosensing devices on plastic disks (not conventional CDs),[13] integrating a number of microfluidic functions with the CD technology, such as the fluid transfer control by spinning the disk and sample analysis with optical detection systems. Several companies, including Burstein Technologies, Gyros AB and Tecan, have been working on their commercialization; the Swedish firm Åmic AB provides special disk fabrication services, *i.e.*, the preparation of high-precision masks and development of replication techniques.[14]

We find the idea of using a conventional CD drive to detect biorecognition reactions on a regular CD-R particularly appealing. This idea can be traced back to the concept of Hammock and co-workers.[15] Remacle *et al.*[16] created unique bio-CDs, with both numeric and genomic information, as DNA microarray platforms for genomic analysis. A double-sided CD reader (a modified CD drive) was specially developed to simultaneously read both arrays and numerical data. La Clair and Burkart went one step further by using conventional CD-R technology to screen the molecular recognition of proteins by surface-attached ligands.[17] The binding of proteins to selected ligands was detected by an error determination routine of the CD-R reading mechanism. We contributed to this new field *via* the development of simple attachment strategies (surface reaction) for biomolecules on CD polycarbonate substrates. In addition, we demonstrated that different patterns or arrays can be created by using a conventional CD printer (Fig. 5), *i.e.*, by printing water-resistant ink onto the gold CD-R substrate and subsequent treatment with aqueous gold-etching reagent. The delivery of terminal-derivatized DNA strands by the same technique produces microarrays with a resolution down to the 10 µm range. These pioneering results may lead to powerful biomedical diagnostic tools based on readily available CD-Rs and CD players.[16,17] In comparison to the technology currently used, including fluorescence spectroscopy

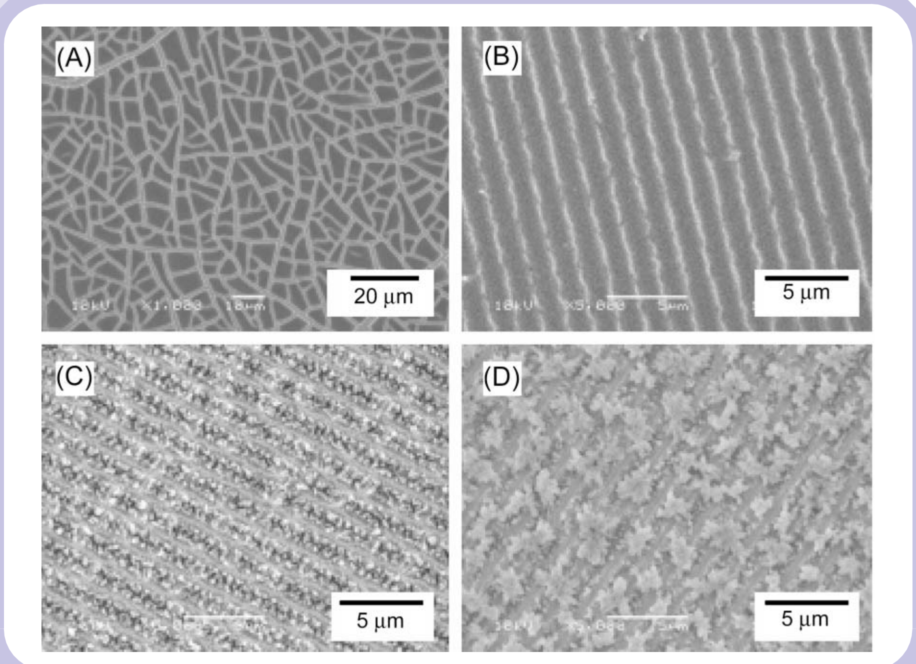

Fig. 4 Scanning Electron Microscopy (SEM) images of zirconia thin films formed on "flat" (**A**) and CD-R (**B–D**) gold substrates *via* electrochemical deposition. The gold surfaces were modified with 11-mercaptoundecanol SAMs, and the scan rates were 50, 20, and $10\ mV\ s^{-1}$ for (**B**), (**C**), and (**D**), respectively. The accelerating voltage of the electron beam for SEM imaging was 10 kV.

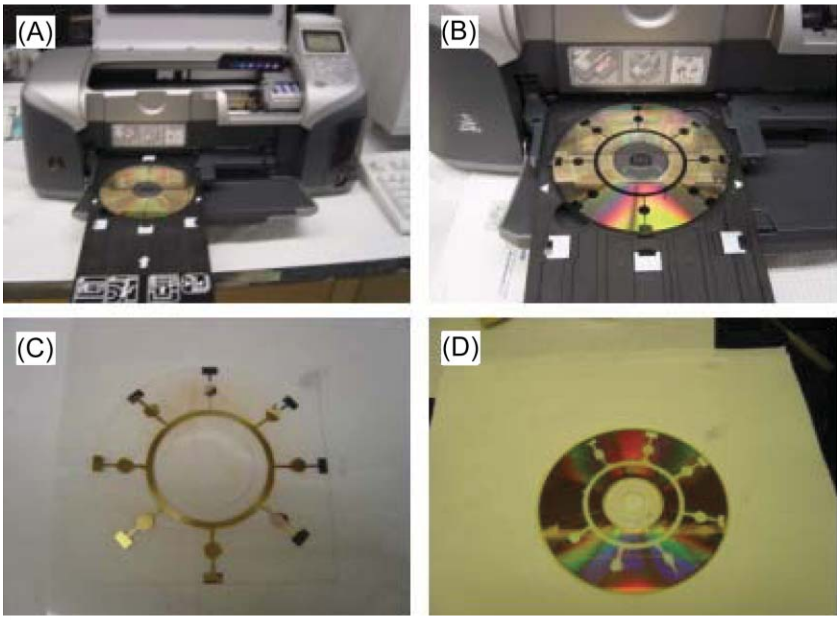

Fig. 5 Fabrication of sensor arrays *via* direct ink-jet printing on gold CD-Rs. (A) and (B) show the loading and printing of designed patterns on the CDs; (C) shows the patterned surface after etching, and (D) the pattern after the transparent film has been peeled off.

and mass spectrometry, the instrumentation is by far simpler and cheaper.

Concluding remarks

Compact discs are indispensable for modern research in material science, surface chemistry, and biomedical diagnosis. A wide range of innovative experiments can be carried out on CDs: from the preparation of self-assembled monolayers (SAMs) and the "customized" fabrication of material micro/nanostructures, to the immobilization of biomolecules and exploration of the potential application of conventional CD drives for biomedical diagnosis and gene analysis.

Acknowledgements

I am unable to provide more details of the relevant research of many colleagues because of space limitation. I hope all those who have contributed to make "chemistry on CDs" exciting will accept a collective acknowledgment. My research has been financially supported by the Natural Science and Engineering Research Council (Canada), Simon Fraser University, and the World Gold Council (UK). Dr. Eberhard Kiehlmann was awarded a Beck's beer for reading the manuscript.

Notes and references

1 D. Birkett, *J. Chem. Educ.*, 2002, **79**, 1081 and references cited therein.
2 J. D. Lenk, *Complete guide to compact disc (CD) player: troubleshooting and repair*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1986.
3 H. Z. Yu, *Anal. Chem.*, 2001, **73**, 4743.
4 J. T. Banks, T. T. Yu and H. Z. Yu, *J. Phys. Chem. B*, 2002, **106**, 3538.
5 H. Z. Yu, D. M. Soolaman, A. W. Rowe and J. T. Banks, *ChemPhysChem*, 2004, **5**, 1035.
6 (*a*) L. Angnes, E. M. Richter, M. A. Augelli and G. H. Kume, *Anal. Chem.*, 2000, **72**, 5503; (*b*) E. M. Richter, M. A. Augelli, S. Magarotto and L. Angnes, *Electroanalysis*, 2001, **13**, 760; (*c*) E. M. Richter, G. H. Kume, R. N. Mioshi, L. Angnes and M. A. Augelli, *Fresenius J. Anal. Chem.*, 2000, **366**, 444; (*d*) R. A. A. Muñoz, R. C. Matos and L. Angnes, *Talanta*, 2001, **55**, 855.
7 (*a*) D. Daniel and I. G. R. Gutz, *Electroanalysis*, 2001, **13**, 681; (*b*) D. Daniel and I. G. R. Gutz, *Electrochem. Commun.*, 2003, **5**, 782.
8 P. Westbroek, J. De Strycker, P. Dubruel, E. Temmerman and E. H. Schacht, *Anal. Chem.*, 2002, **74**, 915.
9 E. M. Richter, D. P. de Jesus, C. A. Neves, C. L. do Lago and L. Angnes, *Quim. Nova*, 2003, **26**, 839.
10 H. Z. Yu, A. W. Rowe and D. M. Waugh, *Anal. Chem.*, 2002, **74**, 5742.
11 J. M. Helt, C. M. Drain and J. D. Batteas, *J. Am. Chem. Soc.*, 2004, **126**, 628.
12 P. Hazarika, D. Chowdhury and A. Chattopadhyay, *Lab on a Chip*, 2003, **3**, 128.
13 (*a*) M. J. Madou, L. J. Lee, S. Daunert, S. Lai and C. H. Shih, *Biomed. Microdevices*, 2001, **3**, 245; (*b*) S. Lai, S. Wang, J. Luo, L. J. Lee, S. T. Yang and M. J. Madou, *Anal. Chem.*, 2004, **76**, 1832 and references cited therein.
14 http://www.amic.se/, accessed on August 15, 2004.
15 H. Kido, A. Maquieira and B. D. Hammock, *Anal. Chim. Acta*, 2000, **411**, 1.
16 I. Alexandre, Y. Houbion, J. Collet, S. Hamels, J. Demarteau, J.-L. Gala and J. Remacle, *BioTechniques*, 2002, **33**, 435.
17 J. J. La Clair and M. D. Burkart, *Org. Biomol. Chem.*, 2003, **1**, 3244.