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Colloidal semiconductor nanocrystals, a new material class for printed photonics

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Over the last 30 years, colloidal semiconductor nanocrystals or quantum dots (QDs) have emerged as a new opto-electronic material. Bolstered by highly precise synthesis methods, QDs stand out by offering tunable properties and a suitability for solution-based processing. This unique combination has resulted in a shift of research focus from the understanding of fundamental aspects of nanophysics and nanochemistry to the development of QD technology as enabler for printed photonics. This talk will first provide a basic description of QD properties as basis to discuss the principle of several QD applications, such as lighting and lasing, and display and imaging. Next, we highlight recent progress in QD research to overcome the restrictions on Cd-based materials. Focusing on InP QDs as a Cd-free alternative, we introduce the use of aminophosphines as a low-cost, easy-to-handle phosphorous precursor. We show how size-tuning-at-full-yield strategies can be implemented by means of this precursor, and we demonstrate that an understanding of the reaction chemistry enables us to extend the synthetic approach to different III-V QDs. In addition, we highlight the intrinsic quality of the resulting InP/ZnSe core/shell QDs by means of single dot photoluminescence microscopy and we show the principle of shell-enhanced absorption as a way to further optimize InP-based QDs for lighting and display applications. Building on these results, the talk ends by giving an outlook on the promises and remaining challenges for QD-based lighting.

Mixed Ionic Electronic Conductors for High Temperature Electrochemical Devices

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Introduction

High temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, have been under development for application in clean energy systems for many years. Although acceptable performance can be achieved, the requirements of low cost and high durability have been a major hurdle to commercialization. This has necessitated a lowering of operating temperatures from circa 800-900°C, to temperatures in the region 5-600°C, with a consequent loss of electrochemical activity of the electrodes, particularly the cathode. Key to optimizing the performance of these devices is gaining an understanding of the gas/solid interface of the Mixed Ionic Electronic Conducting (MIEC) cathodes and how the structure, composition and activity evolves with time.

Results and Discussion

We have used a multifaceted approach to probe the surfaces of ceramic mixed conductors, after treatment at temperature. This involved using ion beam based techniques such as Low Energy Ion Scattering (LEIS) to sample the composition of the outermost atomic layers. Figure 1 shows the typical surface termination and subsurface restructuring of an A' substituted ABO₃ perovskite-based MIEC material found using LEIS analysis [1]. We have used the knowledge gained from experiment to investigate the exchange of molecular oxygen with typical surfaces

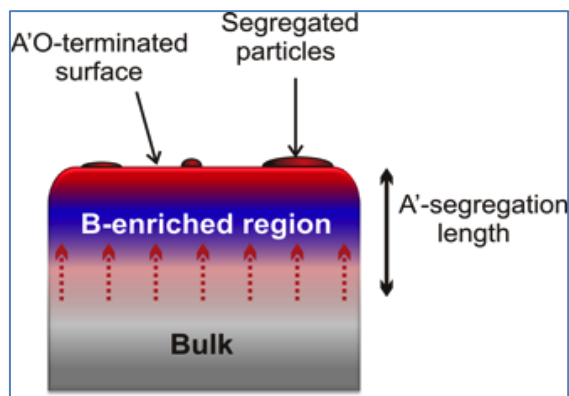


Figure 1: Representation of the surface of a perovskite material after high temperature exposure in an oxidising atmosphere.

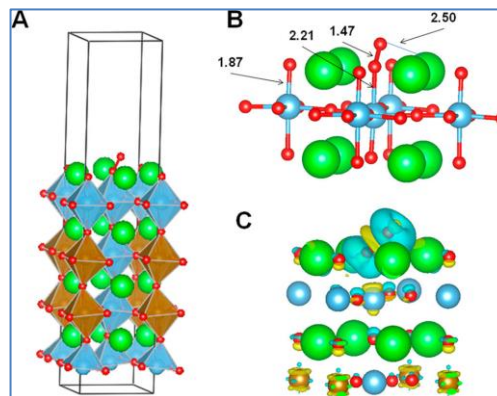


Figure 2: Results of DFT simulation of the interaction of an oxygen molecule with an SrO terminated surface with a single oxygen vacancy.

found experimentally, to aid in the optimization of candidate cathode materials. This theoretical study was done using Density Functional Theory (DFT) to simulate the interaction of an oxygen molecule with a representative segregated surface using Fe doped SrTiO₃ as a model material. Figure 2 shows an SrO terminated surface with an oxygen vacancy showing (a) the overall structure, (b) the internuclear distances (c) the changes in electron density. The perfect SrO surface was found to be unreactive, but the presence of a surface oxygen vacancy was found to promote the adsorption and subsequent dissociation of the oxygen molecule facilitating the

oxygen exchange process [2]. We have extended this study to the LaO surface and found that in contrast to the SrO surface the perfect Lao surface can promote the adsorption and dissociation of the oxygen molecule. This is attributed to the weak transition metal nature of the La cation [3].

Conclusions

We have determined the surface termination of a number of perovskite and perovskite related MIEC materials and found that the AO surface dominates. This has been used to aid in DFT modelling of the interaction of the oxygen molecule with practical MIEC surfaces.

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Recent outline of cement industry in Japan

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Statistics

The transition of amount of production, domestic sales, export and other use are shown in Figure 1. The peak of production and domestic sales was 99.267 million tons and 81.929 million tons in FY 1996. And, these have been in a protracted declining trend. But, the consumption per capita was 369kg in Japan and 154-361kg in European countries at 2013.

On the other hand, the amount of “Other use” has increased year by year. The cement of “Other use” is almost used as a constituent of “cementitious soil stabilizer”. It has been known that the soil stabilization is very effective in earthquake in Japan. So, it is considered that the demand of cementitious soil stabilizer will increase.

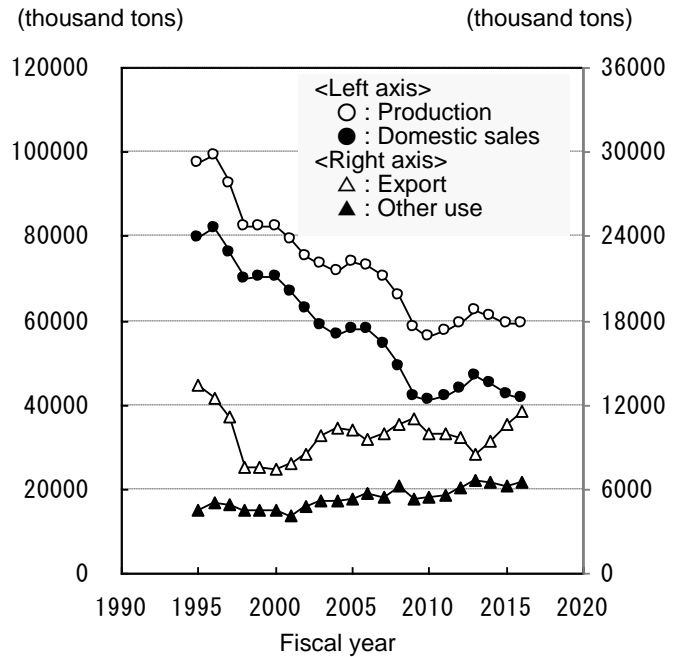


Figure 1 : Transition of the amount of production, domestic sales, export and other use

Use of wastes on manufacturing cement clinker

The cement industry in Japan has used a lot of various wastes and by-products. The kinds and main purposes to use of wastes and by-products are shown in Table 1.

The transition of the specific amount of wastes as alternative raw materials of cement clinker is shown in Figure 2. It has increased year by year. The maximum was 322.8(kg/t-clinker) between 1990 and 2016. But, the range of the specific amount of wastes as alternative raw materials between 2010 and 2016 was 20.9(kg/t-clinker). This shows that the use of wastes as raw materials is approaching the limit.

The transition of the specific amount of wastes as alternative heat energy is shown in Figure 3. It has increased year

Table 1 : The kinds and main purpose of wastes and by-products

Main purpose	Kind
Alternative raw materials of cement clinker	- Coal ash
	- Sludge
	- Waste soil from construction
	- Incineration ash
	- Non-ferrous slag
	- Foundry sand
	- Steel slag
	- Waste white clay
Alternative heat energy	- Glass cullet
	- Waste plastic
	- Wood chips
	- Waste oil
	- Recycled oil
	- Waste tire
	- Coal mining waste
- Meat-and-bone meal	
Admixture	- Blast furnace slag
Additive	- By-product gypsum

by year, too. This shows a possibility that the specific amount of wastes as heat energy will increase.

The use of wastes and by-products leads to decrease the amount of final disposal. The amount of wastes as raw materials was 16446 thousand tons in FY 2014. The amount of landfill of industrial wastes was 10399 thousand tons in same year. This shows that the use of wastes in cement industry has an important role in prolonging of the life of final disposal places.

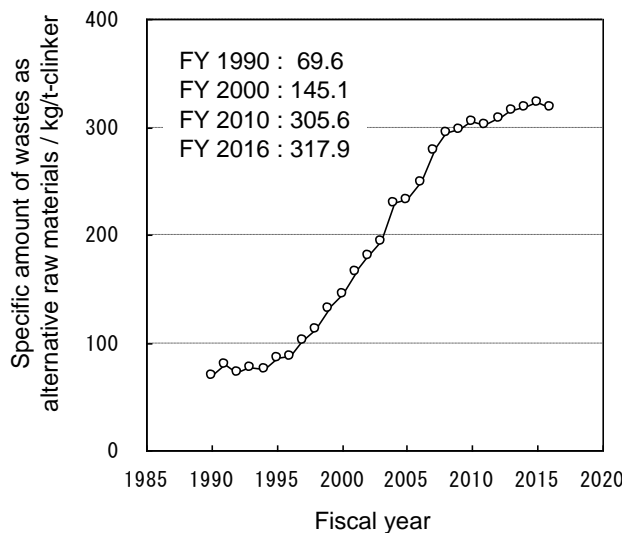


Figure 2 : Transition of the specific amount of wastes used as alterative raw materials

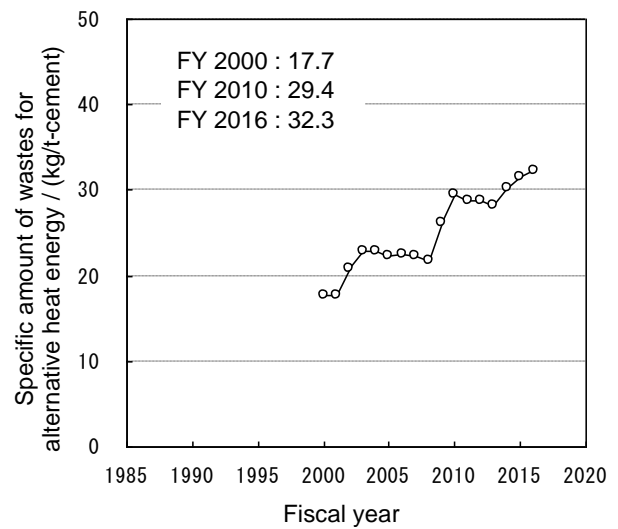


Figure 3 : Transition of the specific amount of wastes used as alternative heat energy

Developing the concrete for pavement

The percentage of concrete pavement of highway is shown in Table 2. The percentage of Japan is almost 6 percent, and it is very small as compared with other countries. Therefore the cement industry of Japan has investigated various properties of concrete pavement. An example is the life cycle cost including durability.

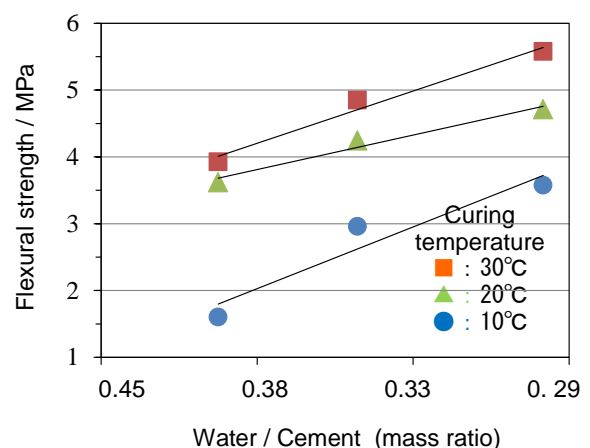
On the other hand, the concrete for pavement called “ONE DAY PAVE” has been developed for some years ahead. The target flexural strength is more than 4.5MPa at 1 day.

The example of flexural strength of concrete is shown in Figure 4. Used cement was high early strength Portland cement. When water/cement (mass ratio) was 0.35 and curing temperature was 30°C, the flexural strength of concrete at 1 day was more 4.5MPa. This result shows that “ONE DAY PAVE” can be applied to repair various pavement within 1 day.

Figure 4 : Relationship between water/cement and flexural strength at 1 day. (used cement : high early strength Portland cement)

Table 2 : The percentage of concrete pavement of highway

Country (year)	Percentage of concrete pavement
USA (2008) * National highway system	15
UK (1990)	20
Germany (2007)	25
French (1992)	15
Belgium (2007)	40
Korea (2009)	63
Japan (2009)	6



The Catalytic Production of Chemicals from Waste Bio - Oils

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Introduction

As oil supplies dwindle and the price increases, it is essential to find new ways of making the many chemicals on which the quality of our lives depends. One approach is to use renewable resources which can be grown. However, there is a tension between using land for fuel or chemicals production and the need to use land to produce food for the rapidly increasing world population. One possible solution is to use waste products for the manufacture of chemicals. In this presentation, we shall discuss the conversion of methyl oleate and oleic acid, a major component of *Tall Oil*, a waste from wood processing, into polymer precursors. We shall also discuss the synthesis of a range of important chemicals from cashew nut shell liquid (CNSL), a waste from cashew nut processing.

Results and Discussion

We shall show how homogeneous carbonylation,^[1, 2] metathesis, and reductive amination^[3] can be used to make difunctional esters acids, alcohols, amines^[1, 4-6] and for polymer formation^[7, 8] from unpurified natural containing oleate residues (Figure 1). We shall also describe the formation of *N*-heterocycles by hydrogenation of diesters in the presence of amines.^[9]

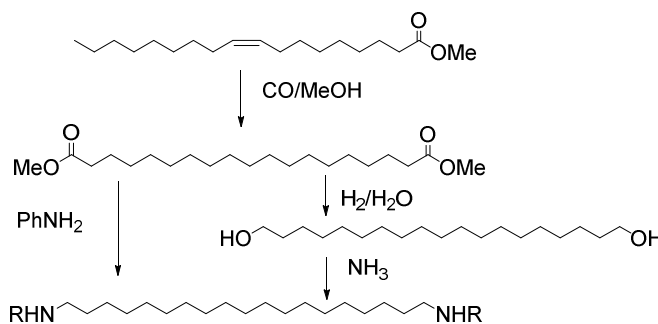


Fig 1 Diesters, diols and diamines from methyl oleate.

Since homogeneous catalysts suffer the potential difficulty of product-catalyst separation, we shall show how supported ionic liquid phase SILP catalysts with carbon dioxide flow (see Figure 1) allow the ready separation of the products from the catalyst, thus overcoming one of the major difficulties associated with scaling up and using homogeneous catalysts commercially. We shall describe our developments on metathesis^[10] and other reactions using these systems.

Cashew nut shell liquid contains interesting phenols *meta* substituted with an unsaturated C₁₅ chain. We shall describe how it can be used to synthesise tse-tse fly attractants, potentially safe detergents, polymer additives, monomers for polymerisation, large ring macrocyclic lactones and pharmaceuticals.^[11-14] (Figure 2). These transformations can be carried out

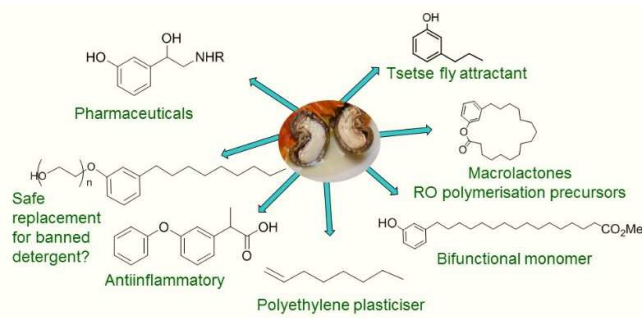


Fig. 2 Chemicals from cashew nut shell liquid

using homogeneous catalytic reactions such as isomerising methoxycarbonylation, cross metathesis, isomerising metathesis and hydroxyamination.

Finally, we shall describe process for the synthesis of a pure single enantiomer of a product by asymmetric hydrogenation under mild conditions in a flow system.^[15]

Conclusions

Several high added value chemicals for use as polymer or detergent precursors, insect attractants and pharmaceuticals can be synthesised in high yield from readily available waste bio-oils.

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