STEP organic synthesis: an efficient solar, electrochemical process for the synthesis of benzoic acid†

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This study presents the first demonstration of STEP for organic synthesis. The synthesis of benzoic acid was fully driven by solar energy without the input of any other forms of energy. STEP (the Solar Thermal Electrochemical Process) was established to drive chemical reactions by using solar heat to minimize the energy and maximize the rate of a growing portfolio of electrolysis reactions. The use of solar energy can minimize or eliminate the carbon footprint associated with the production of societal staples. To date this has included STEP chemistries for the high solar efficiency generation of hydrogen fuels, carbon dioxide splitting to generate fuels and graphite, hematite (iron ore) splitting for iron metal, of lime from limestone, and the production of bleach, magnesium and other useful chemistries. Benzoic acid is produced by the electrolysis of toluene. Solar thermal and solar electrical energy synergistically drive the electrolysis; solar thermal decreases the requisite electrolysis voltage, and improves the kinetics, selectivity and yield of the reaction, while solar electrical current drives the electrolysis. The low electrolysis potential inhibits over-oxidation of the product. In this STEP organic synthesis of benzoic acid at an applied photopotential of 3 V the reaction conversion of benzoic acid is 3.9% at a temperature of 30 °C, 12.4% at 60 °C, and 32.0% at 90 °C. The results demonstrate that the STEP is suitable for an efficient synthesis of benzoic acid from toluene.

Introduction

Fossil fuel (coal, oil and natural gas) is the main resource consumed in energy use.[1–3] However, the large amount of carbon dioxide emissions from fossil fuels is linked to the urgent problem of climate change; fossil fuels can cause significant pollution, and their distribution and scarcity constrains economic growth.[4–6] Under these circumstances developing the use of sustainable low carbon footprint non-fossil fuel processes has become an urgent priority. Solar energy is contributing an increasing role to energy production owing to its abundance, increasing cost-competitiveness, and low associated carbon emissions. In the long term solar energy has a potential to largely displace fossil fuels, and the traditional energy structure needs to give way to a renewable, sustainable

economy.[7,8] To date, the principal uses of solar energy fall within two principal categories,[9,10] the first is solar thermal, which is used both as a heat source in solar water heaters, and increasingly in a more centralized fashion in a large energy plant, such as in solar power towers; the second is for solar cells, modules and panels, which have been increasingly deployed in both silicon and various thin film technologies. In addition, related solar technologies such as concentrator multiple bandgap photovoltaics and solar Sterling engines are reaching record high solar to electrical conversion efficiencies.[11]

STEP, the solar thermal electrochemical process, is an alternative solar energy conversion process. STEP uses the full spectrum of sunlight, including the sub-bandgap (IR) spectrum not accessible to solar cells, to lower the energy and facilitate the kinetics of useful endothermic chemical reactions.[12–14] The aim is to focus on the solar production of chemicals, rather than the solar production of electricity, and to improve the conversion of solar energy, reaction efficiency and product selectivity through chemistries, which utilize this synergy between solar energy and chemical reaction. Solar energy in the form of heat diminishes the energy required by endothermic electrochemical splitting. Rather than tuning the bandgap of a semiconductor to match the solar synthetic process, STEP tunes the electrochemical potential, for example

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†Electronic supplementary information (ESI) available: Outdoor and indoor photocurrent configurations, expanded Fig. 3 yield data, summarized spectral data. See DOI: 10.1039/c4gc01448k

by increasing temperature or increasing concentration, to lower that potential and open up a path for the desired electrolysis to occur. STEP originates from theory and experiments derived for a range of endothermic electrolyses including carbon dioxide splitting and useful chemical syntheses (metals, fuels, chlorine, *etc.*).[15–18] STEP is intrinsically more efficient than other solar energy conversion processes as it utilizes not only the visible sunlight used to drive PVs, but also utilizes the usually detrimental (to PVs) thermal component of sunlight for the electrolytic formation of chemicals.[12] Based on matching and coupling the distribution of the solar-to-thermal and solar-to-electrical conversion to the electro-chemistry and thermo-chemistry for a specific molecular reaction, solar chemical processes and systems are synergistically controlled to maximize chemical yield.

Benzoic acid is mainly used as an important intermediate in the synthesis of several compounds, primarily phenol, caprolactam and a variety of pharmaceuticals. It is synthesized industrially by the liquid-phase oxidation of toluene in the presence of cobalt catalysts.[19] Another route to the synthesis of benzoic acid is indirect, in which an oxidant is first produced electrolytically, such as Mn^{3+} through the oxidation of Mn^{2+} at an anode, and toluene is subsequently oxidized by the Mn^{3+} in another reactor, although the process is considered wasteful of energy and polluting.[20] The oxidation of toluene to benzoic acid is endothermic, indicative that increasing temperature will beneficially drive down the energy of formation of benzoic acid.[21] To the best of our knowledge, there is no prior report of the preparation of benzoic acid by the direct anodic electrolytic oxidation of toluene.

Milder organic synthetic reaction conditions can lead to both advantages (higher chemical yield) and disadvantages (unwanted side reactions, and detrimental environmental impacts).[22,23] Electrochemical syntheses open up alternative "green" synthetic routes, which are often efficient,[24,25] but are less useful when the cost and carbon footprint of electricity are high. As shown here, higher temperature and the use of solar energy can negate these disadvantages.

In this study, the STEP approach is applied to the synthesis of organic (benzoic acid) *via* the direct electrochemical oxidation of toluene, that is the reaction is only carried out in one reactor and without any other operations and catalysts. Benzoic acid and alternative products (benzyl alcohol, benzaldehyde, *etc*) were detected. The principal product from toluene is benzoic acid. Product selectivity is improved through the formation of the peroxides of toluene, perbenzoic acid or their intermediate products, in which the oxygen was generated on platinum anode by water electrolysis. An order of magnitude increase in conversion efficiency (from 3.9% to 32.0%) is achieved with a temperature increase from 30 °C to 90 °C using solar thermal energy. The synthesis of benzoic acid is fully driven by solar energy without the input of any other forms of energy. The thermodynamic model and experimental results indicate that STEP is an effective process for organic synthesis. The high conversion and selectivity were achieved by balancing and matching the point of the thermo-
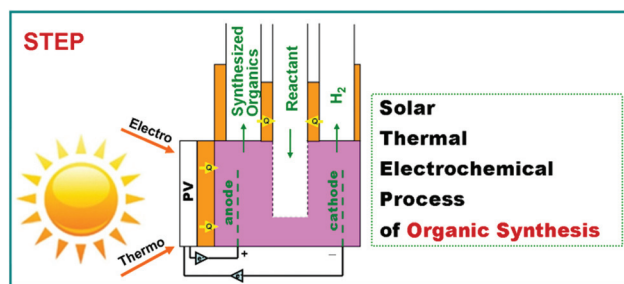
Scheme 1 Schematic overview of STEP organic synthesis (the solar thermal electrochemical process for organic synthesis).

and electro-process of solar energy. As illustrated in Scheme 1 the benzoic acid product is co-produced with the simultaneous generation of hydrogen at the cathode. The hydrogen co-product is a useful fuel.

Results and discussion

Thermodynamic calculation

Overall, toluene (C_7H_8) and water in sulfuric acid are observed to form benzoic acid (C_6H_5COOH) at the anode and hydrogen at the cathode in the electrolysis cell; consistent with half-cell reactions, eqn (1) and (2), and full cell reaction eqn (3) as:

Anode, electrochemical oxidation of toluene to benzoic acid:

$$C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH + 6H^+ + 6e^- \tag{1}$$

Cathode, hydrogen evolution:

$$6H^+ + 6e^- = 3H_2(g) \tag{2}$$
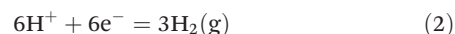
Full cell six electron reaction:

$$C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH + 3H_2\uparrow \tag{3}$$

Sunlight can drive electrochemical oxidation with the release cathodic hydrogen. In the synthesis of benzoic acid, the electrolytic decomposition of the water leads to the simultaneous generation of a co-product H_2, which is useful as a fuel.

Solar heating can decrease the energy to drive endothermic electrolyses. Such processes can be determined by the entropy (S), enthalpy (H), and free-energy (G), and they are identified by the isothermal coefficient of the cell potential as delineated in an earlier article.[13] The relevant thermochemistry of the individual reactant and product species may be calculated from consistent, compiled thermochemical data sets, such as the NIST condensed phase and fluid properties data, including ΔS, ΔH, ΔG as a function of phase and temperature. The electrolysis potentials are then calculated from the thermodynamic free energy components of the reactants and products. At unit activity and at any electrolysis temperature, T_{STEP}, the reaction has electrochemical potential, E_T°.

$$E^\circ = -\frac{\Delta G^\circ}{nF} \quad \text{(for a general cell)} \tag{4}$$

where E_T° is the standard-state cell voltage, n is the number of electrons in the cell reaction equation, and the Faraday constant, $F = 96\,485$ C mol^{-1}.

The thermoneutral potential, $E_{\text{thermoneutral}}$, is given by the enthalpy of a reaction necessary to sustain an electrochemical process without cooling, often $E_{\text{thermoneutral}}$ tends to be nearly temperature independent and is given for products, C_i and reactants, R_j by:

$$E_{\text{thermoneutral}}(T_{\text{STEP}}) = -\Delta H(T)/nF$$

$$\Delta H(T_{\text{STEP}}) = \sum_i c_i H(C_i, T_{\text{STEP}}) - \sum_j r_i H(R_j, T_{\text{STEP}}) \quad (5)$$

The variation of the toluene electrolysis potential with temperature is calculated by eqn (5) and presented in Fig. 1. The oxidation potential of toluene to benzoic acid decreases with increasing temperature, which signifies that the STEP process may be readily applied to synthesize benzoic acid by toluene oxidation. The electrolytic potential of toluene decreases from 0.301 V to 0.287 V with increasing temperature from 298 K through the 395.13 K melting point of benzoic acid. Hence, it is expected that solar thermal heating will decrease the applied voltage required to synthesize benzoic acid from toluene and provides a theoretical basis for this STEP organic synthesis.

Solar thermal energy is collected at an efficiency of η_{thermal} to decrease the energy from $E_{\text{thermoneutral}}$ to $E_{\text{electrolysis}}$, and then electrolysis is driven at a solar electric energy efficiency of $\eta_{\text{solar-electric}}$:[12]

$$\eta_{\text{STEPsolar}} = (\eta_{\text{thermal}}(E_{\text{thermoneutral}} - E_{\text{electrolysis}})$$
$$+ \eta_{\text{solar-electric}} E_{\text{electrolysis}})/E_{\text{electrolysis}} \quad (6)$$

Pt cyclic voltammetry of toluene oxidation

The cyclic voltammetry, CV, of toluene in 2 M sulfuric acid as a function of temperature is presented in Fig. 2. At lower temp-
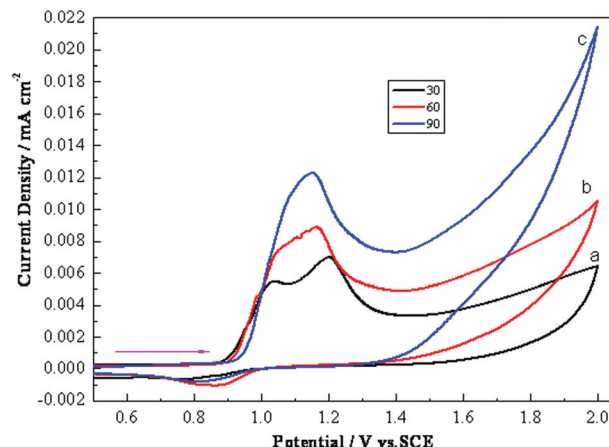

Fig. 2 The cyclic voltammetry of 2500 ppm toluene in 2 M sulfuric acid and 0.01 M surfactant at 50 mV s^{-1} on 1 cm^2 Pt at either: (a) 30 °C, (b) 60 °C, or (c) 90 °C.

erature (30 °C) two oxidative peaks are evident, one peak occurring at 1.20 V and the other peak occurring at 1.04 V. As discussed in a later section, subsequent GC and UV/vis analysis indicates that toluene has been converted to both benzaldehyde and benzoic acid at 30 °C with the co-production of trace benzyl alcohol as a probable related intermediate. When the temperature is subsequently increased to 60 °C and then to 90 °C Fig. 2 anodic peaks appear to merge. At 90 °C a single 1.15 V peak dominates the cyclic voltammetry, which upon subsequent GC, UV/vis and FTIR analysis is consistent with the formation of benzoic acid as the principal product. The decrease in peak oxidation potential from 1.20 to 1.15 V *vs.* SCE is consistent with the synergy of a thermodynamic potential drop with temperature increase in Fig. 1 combined with a kinetic overpotential drop expected with facilitated electron transfer at higher temperatures.

In Fig. 2(a–c), the corresponding reverse cathodic peaks are not observed, or are very small relative to the anodic significant, suggesting an electron transfer followed by subsequent chemical rearrangement.[26,27] The above characteristics illustrate that the enhancement of the rate and selectivity of the electrolytic synthetic conversion of toluene to benzoic acid with increase of temperature. This condition is conducive to the inclusion of solar thermal energy to improve the efficiency and decrease the energy for the (STEP) electrolytic production of benzoic acid from toluene.

Conversion and selectivity of benzoic acid and benzaldehyde

STEP conversion of toluene. Fig. 3 presents the conversion of benzoic acid and intermediates (benzaldehyde and benzyl alcohol) at different temperatures generated in the STEP electrolysis of toluene. As expected from the CV results in Fig. 2 and the thermodynamic calculations in Fig. 1, solar thermal heat is beneficial to the oxidation of toluene to benzoic acid. The conversion rate to benzoic acid increased with temperature and electrolysis potential. Solar energy can supply
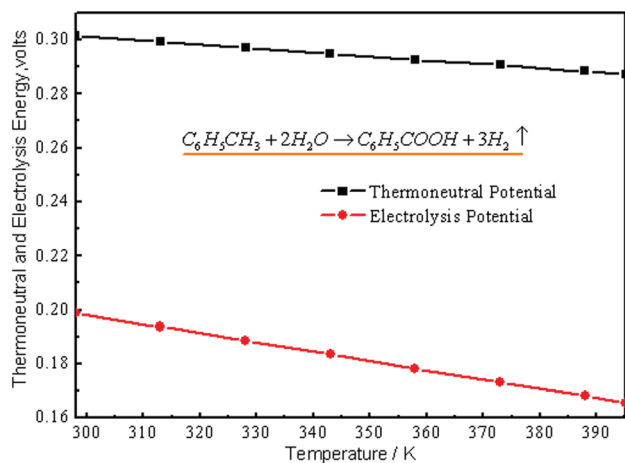

Fig. 1 Theoretical, thermoneutral and dynamic calculation of the electrochemical potential of toluene oxidation.
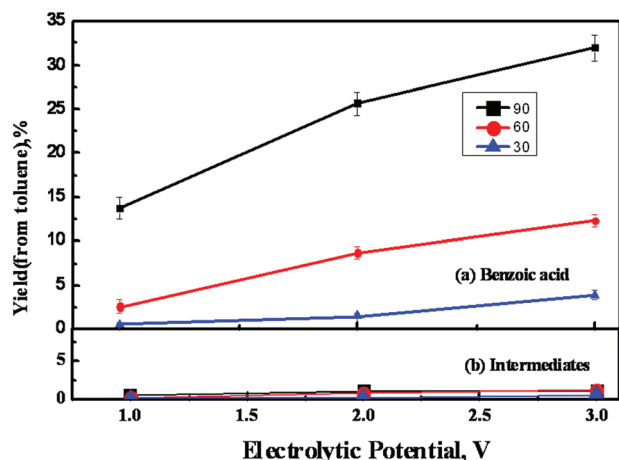
Fig. 3 The STEP electrolytic yield of 200 ppm toluene in 100 mL of 2 M sulfuric acid (with 0.001 M surfactant) to (a) benzoic acid and (b) intermediates (sum of benzaldehyde and benzyl alcohol) at: 30 °C, 60 °C, 90 °C, and as measured at the indicated photopotential during electrolysis to a tenth of current. Individual benzaldehyde and benzyl alcohol yields are delineated in the ESI.†

sufficient thermal and electric energy for synthesis of benzoic acid.

In order to determine compositional analysis in the product of benzyl alcohol, benzaldehyde and benzoic acid, the synthesized product was collected and analyzed using a gas chromatograph (GC-14C) installed with a flame ionization detector and a 30 m × 0.25 mm × 0.33 μm FFAP capillary column, the toluene remainder also can be checked. At 30 °C, the yield of benzoic acid increased with electrolyzed potential, but only increases to a maximum of 3.9 mol% at the maximum applied 3 V potential. However this increases with temperature, and the yield of benzoic acid is 12.4% of 60 °C and 32.0% of 90 °C, as shown in Fig. 3(a). As seen in Fig. 3(a) at an applied potential of 1.0 V the variation of benzoic acid yield with temperature at 30, 60, 90 °C is 1.1, 3.3 and 13.1%, respectively. In Fig. 3(b), it can be seen the yield of intermediates remains very low at all applied potentials and temperatures.

Selectivity for benzoic acid in the electrochemical oxidation of toluene. The selectivity of benzoic acid (in percent) compared to the combined yield of all products (benzyl alcohol, benzaldehyde and benzoic acid) during the toluene electrolysis is summarized in Table 1. The amount of intermediates stays

nearly invariant, but the amount of benzoic acid increased with temperature. The selectivity of toluene to benzoic acid increased with temperature and electrolytic potential, and reaches a maximum value both at the highest temperature (90 °C) and highest applied electrolysis potential (3.0 V). The reason for this is the synergistic effect of the solar thermal and solar electricity. By utilizing both high temperature (solar thermal) and high electrolysis (solar electronic) potential, a high conversion and selectivity can be achieved. In this STEP organic synthesis, the highest observed conversion of benzoic acid was 32.0% at temperature of 90 °C, 3 V, and the selectivity achieved 96.85%.

Analysis of the STEP toluene reaction product†

Infrared analysis. Spectral analysis of the product has been probed. As shown in Fig. 4, the FT-IR spectrum of the STEP synthesized toluene product(s) was carried out between 4000 and 400 cm⁻¹. The strong 1660 cm⁻¹ peak can be assigned to the C=O stretching vibration band of carboxyl (typically occurring at 1760–1660 cm⁻¹), and the broad band between 3200 and 3542 cm⁻¹ can be attributed to the O–H stretching bonds of –COOH and at 2079 cm⁻¹ to the combination bands of stretching and bending vibration of O–H.[28]

The typical absorption bands of benzaldehyde are the C=O stretching vibration at 1660 nm and absorbance bands at 2720 cm⁻¹ denote the C–H stretch of –CHO, the band at 2385 cm⁻¹ is related to the unsymmetrical C–H deformation stretch of –CHO; the peak at 957 cm⁻¹ assigned to the C–OH out-of-plane bending vibrations of benzyl alcohol,[29] these weak bands indicate that the amount of benzaldehyde and benzyl alcohol is trace and nearly negligible. In addition, 1207 cm⁻¹ is the C–O peak of carboxyl, the peaks that appear at 1117 cm⁻¹ and 1054 cm⁻¹ are attributable to the bending stretching of C–H. The peak at 705 cm⁻¹ is assigned to the out of plane deviational vibration of –COOH and 667 cm⁻¹ assigned to deformation of C–H on mono-substituted benzene
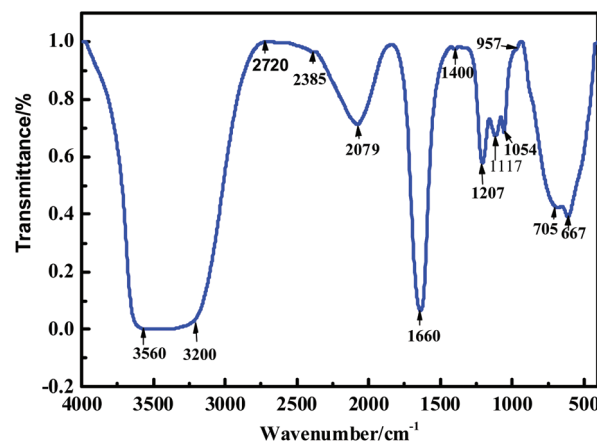
Table 1 Selectivity of benzoic acid compared to intermediates (including benzoic acid, benzyl alcohol and benzaldehyde) as the toluene electrolysis product (%)

Temperature (°C)	Electrolysis potential (V)		
	1.0 V	2.0 V	3.0 V
90	96.07	96.29	96.85
60	91.55	91.67	91.79
30	81.96	84.27	84.97

Fig. 4 FT-IR spectra of the synthesized sample, electrolysis conditions: 90 °C, 3 V, 200 ppm toluene in 100 ml 2 M sulfuric acid−0.001 M surfactant solution.

ring. The small peak at 1400 cm^{-1} denotes the symmetric carboxyl (–COOH) stretching vibration.[30] Together these provide evidence that the principal product of the synthesis is benzoic acid.

UV absorption spectrum analysis. Every chemicals has the typical absorption bands on its UV-vis absorption spectra of standard solution. It has been shown that the typical absorption bands are 230, 256 and 213.5 nm for benzoic acid, benzaldehyde and benzyl alcohol respectively, and 195–210 nm for toluene.[31]

Fig. 5 presents the UV-vis absorption spectra of the synthesized samples under different temperatures (30 °C, 60 °C, 90 °C). In Fig. 5(a), there are two apparent peaks, one is at 195 nm due to the high content of toluene which remains in the solution, the other is at 213.5 nm for the absorbance of benzyl alcohol. In Fig. 5(b) and (c), the absorbance at 195 nm and 213.5 nm is less at higher temperature because a greater fraction of the toluene was consumed during the electrolysis and the concentration of the intermediate benzyl alcohol decreased with the increase of temperature. At the same time, the peaks at 230 and 256 nm increased with temperature for the formation of more benzoic acid and intermediate benzaldehyde. Moreover, two new peaks appear at 224 and 244 nm. These are respectively the typical absorbance peaks of –COO$^-$ (ref. 32) and –CHO [33] substitutes on benzene, which is also evidence of the formation of carboxyl group and aldehyde group at benzene ring. This absorbance increased with temperature indicating more products.[34] All of these are consistent with benzyl alcohol as the principal product of toluene electro-oxidation at low temperature. However with temperature increase the benzaldehyde and benzoic acid products are increasingly formed. Benzaldehyde is also an intermediate that will convert to benzoic acid at higher temperature, it can be identified by the yield reported in the toluene reaction yield product section.
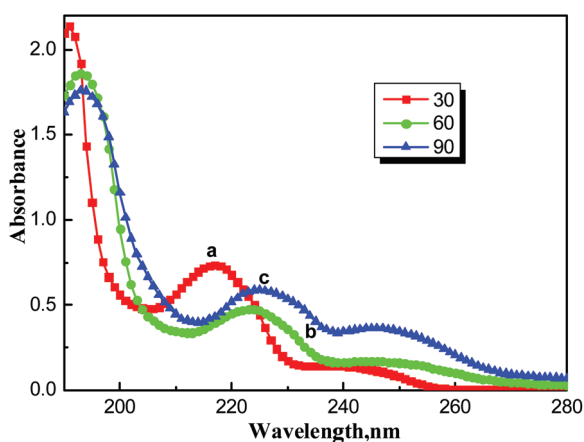

Fig. 5 The spectra of the synthesis samples (the background spectra of 2 M sulfuric acid & surfactant has been subtracted) at the temperature of: (a) 30 °C, (b) 60 °C, (c) 90 °C at voltage of 3 volts, 200 mg L^{-1} toluene in 100 ml 2 M sulfuric acid and 0.001 M surfactant solution.

Description of alternative mechanistic pathways of toluene oxidation to benzoic acid

As shown in Scheme 3, and as evidenced by the measured cyclic voltammetry there are two distinct reaction routes for the electrolysis of toluene in sulfuric acid. The first route shown leads from top left moving to the right side of the scheme in which toluene (A) oxidation undergoes three stages to benzyl alcohol (B), benzaldehyde (C) and eventually benzoic acid (D) at potentials E1, E2 and E3, respectively. The second route leads from the top left moving down the left side to the right hand bottom corner and is the fast electrochemical and chemical step coupled thermo-electrochemical route, which is observed at higher temperatures and improves the yield of the solar thermal (enhanced) electrolysis for the oxidation of toluene. In this second route, the toluene molecule gains thermal energy from solar heat for the activation and formation of the activated states (O), including three active states similar to toluene (a), benzyl alcohol (b) and benzaldehyde (c), they are the activation centers of the whole reaction, which make the reaction conducive to the generation of benzoic acid. As this second path can occur at lower overpotential, the E4 (overoxidation) stage to carbon dioxide is impossible (it can be identified that there is no oxidation peak of the produced benzoic acid in CV). Most important of all, energy of the whole process is derived from the sun, and as shown in the selectivity of benzoic acid section the reaction occurs at high selectivity and conversion of benzoic acid. The scheme focuses on the anode processes and not the concurrent cathodic electrolytic decomposition of the water eqn (3) and the simultaneous generation of a co-product H$_2$, which is useful as a fuel. Other anodic oxidation reactions that also generate hydrogen at the cathode have been noted.[35]

A consistent mechanism is that the toluene oxidation is initiated by an anodic electron transfer, and through the formation of the radical cations the reactions proceed *via* radical intermediates. This is shown in Fig. 6 with the rapid transfer of six electrons proceeding *via* three subsequent EC transformations.[36] The challenge of a six electron transfer for the oxidation of toluene to benzoic acid is overcome by thermal activation and electrons provided by the full spectrum uses of sunlight by the
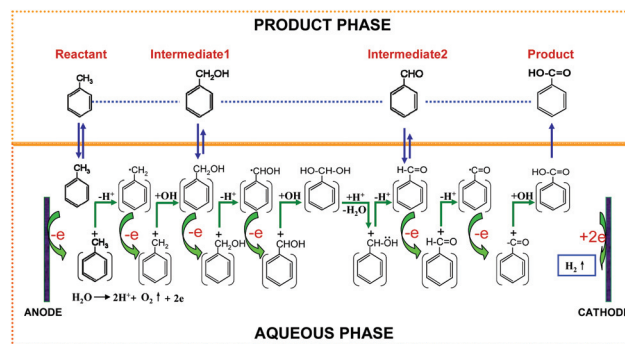

Fig. 6 A possible mechanism of the electro-synthesized benzoic acid from toluene in STEP mode.

STEP mode. When the reaction is heated by solar thermal and matching with solar electricity the rates of the individual steps (such as (a) to (b) and (b) to (c)) increases. This will be a challenge to carry out in the general case without the input of solar energy to overcome the energy barriers associated with the more difficult oxidation steps later in the overall transformation.

Benzyl radicals can be generated from toluene by anodic electron transfer as shown in eqn (7). Simultaneously, the electrolysis of water can generate oxygen at the anode as described in eqn (8).

$$PhCH_3 \xrightarrow{-e} PhCH_2^{\bullet} + H^+ \tag{7}$$

$$2H_2O \xrightarrow{-4e} 4H^+ + O_2 \tag{8}$$
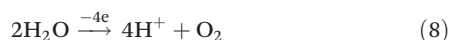
Peroxides in general are considered as the source of radical initiation.[37] As reported in the literature,[38] such mechanisms comprise a diffusion controlled oxygen-coupling reaction with benzyl radical to form a peroxy radical, as shown in eqn (9).

$$PhCH_2^{\bullet} + O_2 \rightarrow PhCH_2OO^{\bullet} \tag{9}$$
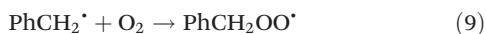
This peroxy radical can remove hydrogen from a suitable substrate, most often from toluene or benzaldehyde (eqn (10) and (11)).

$$PhCH_2OO^{\bullet} + PhCH_3 \rightarrow PhCH_2OOH + PhCH_2^{\bullet} \tag{10}$$

$$PhCH_2OO^{\bullet} + PhCH(O) \rightarrow PhCH_2OOH + PhC^{\bullet}(O) \tag{11}$$

$$2PhCH_2OO^{\bullet} \rightarrow PhCH(O) + PhCH_2OH + O_2 \tag{12}$$

$$PhC^{\bullet}(O) + O_2 \rightarrow PhC(O)OO^{\bullet} \tag{13}$$

The formed perbenzoic acid takes part in the oxidation of benzaldehyde to benzoic acid. Perbenzoic acid can also be decomposed to benzoic acid by

$$PhC(O)OOH + 2H^+ \xrightarrow{-2e} PhC(O)OH + H_2O \tag{14}$$

$$PhCH_2OH + O_2 \rightarrow PhCOOH \tag{15}$$

The oxidation of benzaldehyde to benzoic acid is a Baeyer–Villiger type reaction, perbenzoic acid oxidizes benzaldehyde to form two benzoic acid equivalents,[39] as shown in eqn (16).

$$\tag{16}$$
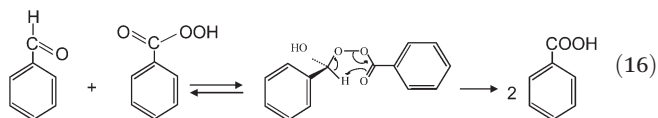
Using the sub-bandgap (IR) spectrum not accessible to solar cells, it not only can lower the energy for the reaction but also facilitates the kinetics of useful endothermic chemical reactions to preferred products. At higher temperature we observe an improvement in the product selectivity for toluene electrooxidation to benzoic acid (compared to benzaldehyde or alternative toluene electrooxidation products). The relative extent of the contribution to this improved selectivity from eqn (16), compared to peroxyl radical, and peroxide and other reactions to the observed improved selectivity for benzoic acid will be of interest in future studies.

Scheme 4 compares the room temperature electronic to the alternative combined electronic/thermal pathways of the synthesis of benzoic acid. STEP enhances energy conversion, reaction efficiency and product selectivity of endothermic reactions by tuning of the electrolysis potential, coupling solar-to-thermal and solar-to-electricity conversion, and driving the synthesis by solar energy without the input of any other energies. As represented in Scheme 4 on the left, the oxidation of toluene at room temperature, without solar thermal or other heat source, can comprise a series of three sequential processes, from toluene to benzyl alcohol with corresponding potential $E1$, benzaldehyde, $E2$, and benzoic acid, $E3$, respectively, the product is the mixture of the compounds mentioned. In the synthesis of benzoic acid by STEP, as shown on the right side, in combination with the electronic energy, the solar thermal energy heats the electrolyte and forms activated states. In this circumstance, at the higher temperature, a relatively small potential opens the pathway in which toluene oxidation occurs to the preferred benzoic acid product rather than to the two intermediates (benzyl alcohol, benzaldehyde), it is also benefit to improve the utilization rate of solar energy.

Conclusions

This paper presents the first application of solar thermal electrochemical process to the synthesis of a useful organic reagent (benzoic acid from toluene). The solar process is endothermic; the highest conversion yield of toluene was 32.0%, which occurs when solar thermal energy heats the electrolysis chamber. The electrolysis appears to occur *via* electron transfer followed by subsequent chemical rearrangement (EC transformation), and the peroxides that can initiates the radical in the reaction becoming the key factor in formation of products. The primary component formed at high conversion is benzoic acid. The synthesis of benzoic acid was fully driven by solar energy without the input of any other forms of energy. With temperature increase (solar thermal heating) there is a decrease in the requisite calculated and observed toluene potential. The current density of toluene oxidation and product (benzoic acid) selectivity are also significantly enhanced by solar thermal heating, and the formation of competing side-products (benzyl alcohol, benzaldehyde) is inhibited, and as evidenced by the order magnitude increase of yield at 90 °C compared to 30 °C of the targeted benzoic acid product.

Results demonstrated that the STEP is suitable for the efficient synthesis of benzoic acid from toluene. In this STEP of the organic synthesis, the reaction conversion of benzoic acid gained 3.9% of 3 V at temperature of 30 °C, 12.4% at 60 °C, and 32.0% at 90 °C.

Experimental

Chemicals and reagents

All aqueous solutions were prepared with distilled double-deionized water. While insoluble in water, toluene is soluble in sul-

furic acid.[40] Benzoic acid (C_6H_5COOH, ZT Co., LTD, 99.5%), toluene ($C_6H_5CH_3$, YX Chemical Co., LTD, 99.5%), Benzaldehyde (C_6H_5CHO, CL Co., LTD, 98.5%), Sodium dodecyl benzene sulfonate ($C_{18}H_{29}NaO_3S$, XW Co., LTD), Sodium hydroxide (NaOH, PK Chemical Co., LTD, 99.5%) and Sulfuric acid (H_2SO_4, LT Chemical Co., LTD, 98%) were used in the solutions.

Cyclic voltammetry

Cyclic voltammetry (CV) experiments were performed with BAS Epsilon-EC electrochemical workstation at a sweep rate of 50 mV s^{-1}. A conventional three-electrode system was used with a Pt anode (10 mm × 10 mm) working electrode, a Pt cathode (10 mm × 10 mm) counter electrode, and a SCE reference electrode. Cyclic voltammetry measurements utilized platinum to ensure that the observed oxidation peaks were not related to electrode corrosion.

CV measurements were performed with a high concentration of toluene (2500 ppm), to distinguish the peaks, (a higher concentration for the apparent peaks) in a 2 M sulfuric acid solution containing 0.01 M sodium dodecyl benzene sulfonate as a surfactant. No peaks are observed during CV measurement in the toluene-free electrolyte (2 M sulfuric acid solution containing only the 0.01 M $C_{12}H_{25}C_6H_4SO_3Na$).

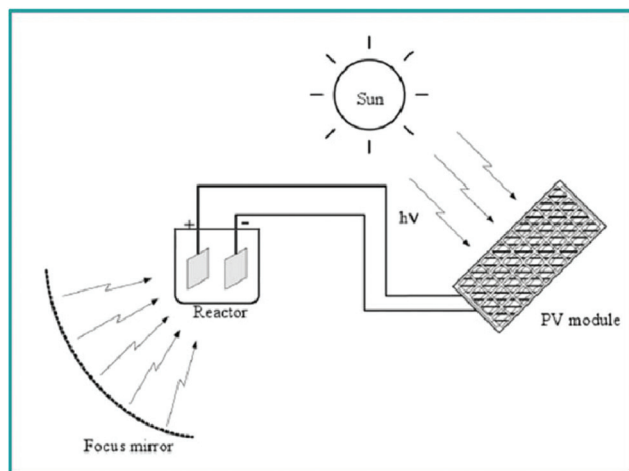## Synthesis of benzoic acid by solar thermal and electrochemical process

The synthesis of benzoic acid was experimentally characterized in a STEP mode,[12] which incorporates a mirror to focus sunlight to heat the electrolyte, in an electrolysis reactor up to a 100 °C maximum temperature. A polycrystalline silicon PV module was used to generate 18 V at the maximum power point. As shown in Scheme 2, this STEP mode directs all concentrated solar energy to the electrolyte. In our indoor lab, a concentrator photovoltaic (CPV) provides more efficient solar
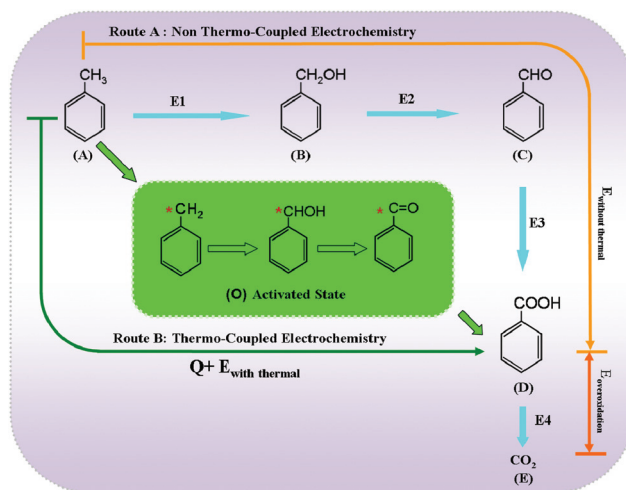
Scheme 3 Reaction routes of the synthesized benzoic acid from toluene by STEP.
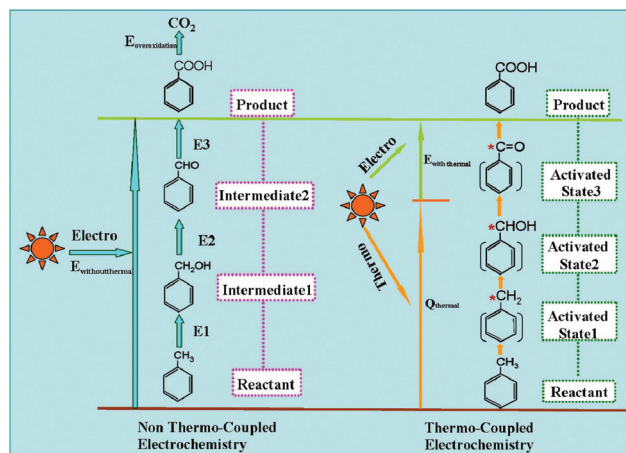
Scheme 4 Comparison of solar energy utilization STEP implementations of the solar thermal electrochemical process for benzoic acid.

photocurrent (∼39% efficiency under 550 suns) under a 1 kW Xenon, daylight colour (5600 K) AM1 (air mass) illumination. The indoor and outdoor photocurrent modes are compared in the ESI.†

The electrolyzer configuration has been detailed in our previous article.[41] The electrolyzer contains two-electrodes, both are 1.0 cm^2 platinum. In a typical procedure, 100 ml solution of the 2 M sulfuric acid and 0.001 M surfactant is placed into the electrolysis cell, and then 200 ppm toluene is added to this reaction chamber, the relatively low toluene concentration for synthesis, rather than CV, is for the kinetic and chemical control of the reaction. The temperature is controlled by tuning the tracking control system to use solar thermal heat. The reactor was centred at the focal point of a parabolic solar concentrator (diameter = 1.5 m), and then defocused to generate benzoic acid at different temperatures (30 °C, 60 °C, or 90 °C). The PV module output is applied to the electrolysis cell

Scheme 2 STEP synthesis experiments, in which the full solar spectrum is applied to electrolysis heating, and electrolysis charge is generated by a PV.

with the photovoltage controlled by a regulator. The reaction lasted 2–6 hours, and the (constant photopotential) electrolysis was terminated and as the electrolysis reaction progresses and toluene is consumed the photocurrent decreases tenfold. After completion of the reaction, the cell was placed in the air and cooled to room temperature. The products can be isolated. Any precipitated solid formed during the reaction was collected by filtration, and both the precipitate and filtrate were analyzed. The solubilized crude product was separated by alkali-solution and acid-isolation,[42] the analysis of the mixture of the products was conducted at room temperature.

Product analysis

Subsequent to STEP electrolysis the products were identified by UV/Vis and FTIR and the content of product and intermediates (benzyl alcohol, benzaldehyde) determined quantitatively by Gas Chromatograph. IR-spectra were measured in KBr pellets from 4000–400 cm^{-1} using a Tensor 27 FTIR Spectrometer.[43] UV-Vis Spectra samples were measured in sulfuric acid using a 1 cm path length quartz cell at room temperature with a UV-1700 Shimadzu Spectrophotometer using Cary Win UV Scan software. The reaction yield (in percent) was calculated by comparing the initial moles of toluene to the measured moles of either benzoic acid or intermediates produced in the electrolysis. After a stabilization period of 2 h, liquid products were collected and analyzed using a gas chromatograph (GC-14C Shimadzu) installed with a flame ionization detector and a 30 m × 0.25 mm × 0.33 μm FFAP capillary column. The selectivity of benzoic acid (in percent) was determined by comparing the moles of benzoic acid produced to total moles (of intermediates and benzoic acid) produced.

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