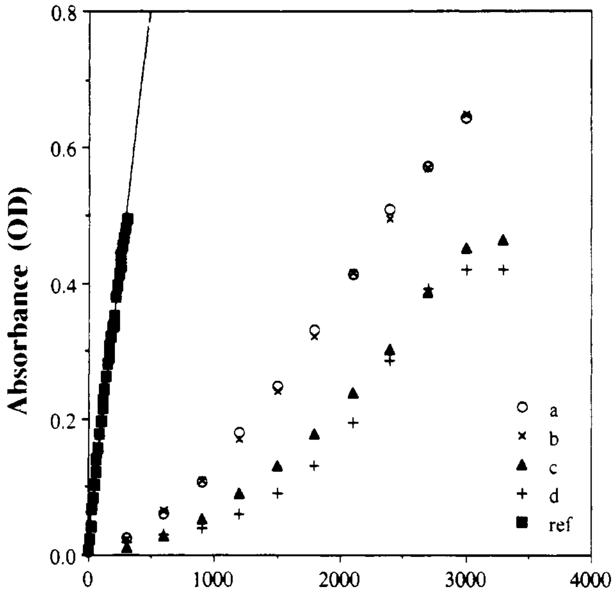

Figure 2. Plots of the absorbance as a function of the time in which glass samples containing glucose oxidase and peroxidase were exposed to a solution of glucose, 4-aminoantipyrine, and *p*-hydroxybenzene sulfonate. Sample (a) was aged 2 weeks, (b) was aged 3 weeks, (c) was aged 2 weeks and dried 1 week, and (d) was dried 2 weeks (no aging). The squares connected by the straight line are the results from the reference solution containing 3 mL of the enzyme mixture and 9.0 mL of sodium phosphate buffer pH 6.

constant for the enzyme, i.e., K_m, is 2-fold higher than that of the enzyme in solution indicating that binding of the substrate is weaker. The lower apparent activity found for the mixed enzyme system with dyes (see Figure 2) is not due to a slower turnover number for glucose oxidase. The difference in the relative rate may be influenced by the diffusion of both of the dye components and glucose into the gel structure in order to reach the enzymes, and the diffusion of the products back into solution to be measured.

In summary, optically transparent silica glass containing the active enzymes glucose oxidase and peroxidase was synthesized by the sol-gel method. The enzymes were immobilized, but small molecules such as glucose diffused readily through the porous glass. The enzymatic reactions that occur normally in solution were readily carried out in the pores of the glass matrix. When all of the enzymes and colorimetric precursors were encapsulated and the glass was exposed to glucose solutions, the colored products which were formed in the glass produced a colored glass which is suitable for use as the active element in a solid-state optically based detector. The turnover number for encapsulated glucose oxidase with β-D-glucose is the same in the glass and in solution. The results show not only that the enzymes retain similar activities when immobilized in an inorganic matrix but also that optically transparent biochemically active glasses can be synthesized.

Acknowledgment. This work was made possible by grants from the National Science Foundation (DMR90-03080 to B.D. and J.I.Z. and CHE91-06545 to J.S.V.). C.R.N. is a predoctoral trainee supported in part by USHHS National Institutional Research Award (T32 GM-08375).

Registry No. Glucose oxidase, 9001-37-0; peroxidase, 9003-99-0; β-D-glucose, 492-61-5.

Preparation of Titanium Diboride from Titanium Alkoxides and Boron Powder

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The high chemical and thermal stability of TiB$_2$, along with its low electrical resistivity and high thermal conductivity, has made it a very interesting engineering ceramic material.[1] An important element controlling the commercial success of TiB$_2$ as an engineered ceramic material is the availability of pure, submicron TiB$_2$ powders at low processing temperatures. The methods most often used for preparing TiB$_2$ powders include the direct reaction between Ti and B[2] and the reduction of TiO$_2$ and B$_2$O$_3$ (or B$_4$C) by carbon.[3,4] These methods generally require high temperatures (around 2000 °C) and yield TiB$_2$ powders with low purity and large particle sizes (5-30 μm). High-purity TiB$_2$ powders have been prepared by a gas-phase reaction[5] or from organometallic precursors.[6,7]

This communication reports our results on the preparation of highly crystalline TiB$_2$ powders with small particle sizes (0.3-0.4 μm), by pyrolyzing mixtures of boron and a polymeric precursor. It is well-known that thermal decomposition of furfuryl alcohol (FuOH) and hydrolysis of Ti(OBu)$_4$ produces carbon[8] and TiO$_2$,[9] respectively. Therefore, heating a mixture of boron, titanium butoxide, and furfuryl alcohol should result in the generation of carbon and titanium oxide. As the temperature is increased, the carbon causes the reduction of TiO$_2$, forming TiB$_2$ as the final product as indicated by reaction 1.

$$2C + 2B + TiO_2 = TiB_2 + 2CO \qquad (1)$$

The amorphous boron powder used in the present study had an average size of 0.22 μm, based on a centrifugal particle size analysis and SEM micrograph (Figure 1a). The elemental analysis of the powder indicated that it contained 94.06% B; oxygen was assumed to be the major impurity due to surface oxidation. The precursor with a nominal composition of 2.1B/[(FuO)$_{0.63}$(BuO)$_{0.37}$TiO$_{1.5}$] was

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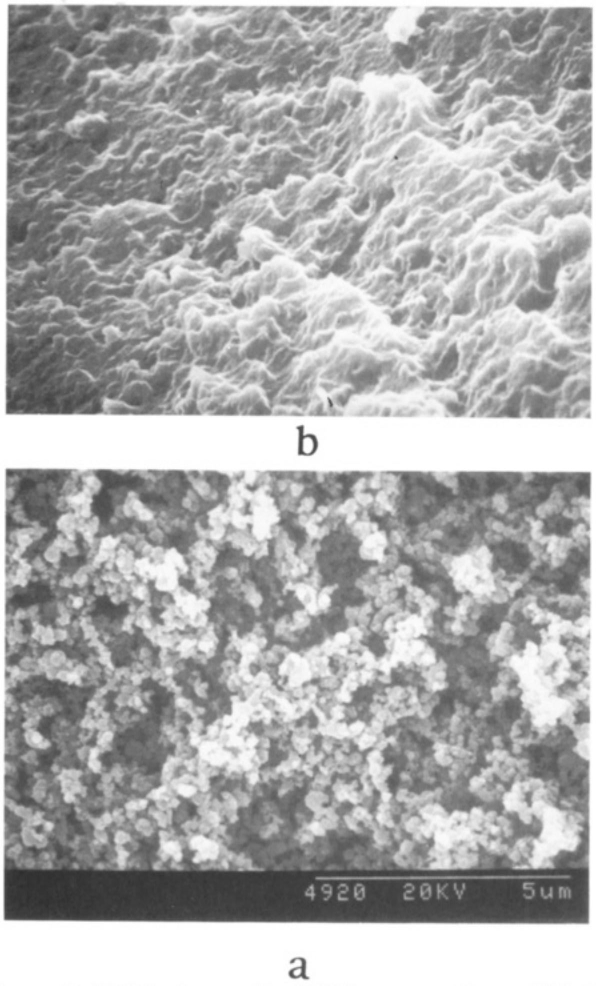

Figure 1. SEM micrographs of (a) boron powder and (b) the as-synthesized precursor.

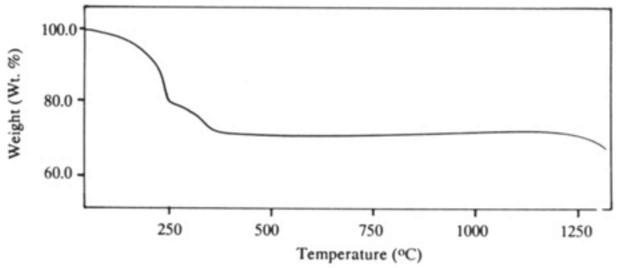

Figure 2. TGA curve of the precursor under a flow of argon.

prepared by hydrolyzing titanium butoxide and subsequently mixing it with boron powder.[10] The solid precursor obtained consisted of large (30–200 μm), dark and irregularly shaped pieces. An SEM micrograph (Figure 1b) of the pieces revealed that the boron particles were well dispersed in the polymer, and the pieces were devoid of visible pores.

The FT-IR spectrum of the as-synthesized precursor is similar to the spectra previously reported[11] and indicates the existence of both furfuryl alcohol groups (3118 cm^{-1}, C–H stretching vibration of the olefinic H on the furan rings; 1718 and 1596 cm^{-1}, C=C stretching vibrations of the furan rings) and –OBu groups (2960, 2929, and 2870 cm^{-1}, C–H stretching; 1461 and 1375 cm^{-1}, C–H bending). In addition, two broad bands (one below 900 cm^{-1} and the other around 3500 cm^{-1}) are observed in the spectrum, and they are attributed to the polymeric Ti–O units and the OH stretching vibration, respectively.

Table I. Weight Losses of the Precursor with a B:Ti Ratio of 2.1:1.0 Heated at Various Temperatures

temp, °C	700[a]	900[a]	900[b]	1100[a]	1300[a]	1500[a]
time, h	6	6		6	6	6
wt loss, wt %	30.70	30.98	29.50	37.23	53.77	66.60

[a] Based on weight loss of sample heated in furnace. [b] The weight loss at 900 °C on the TGA curve.

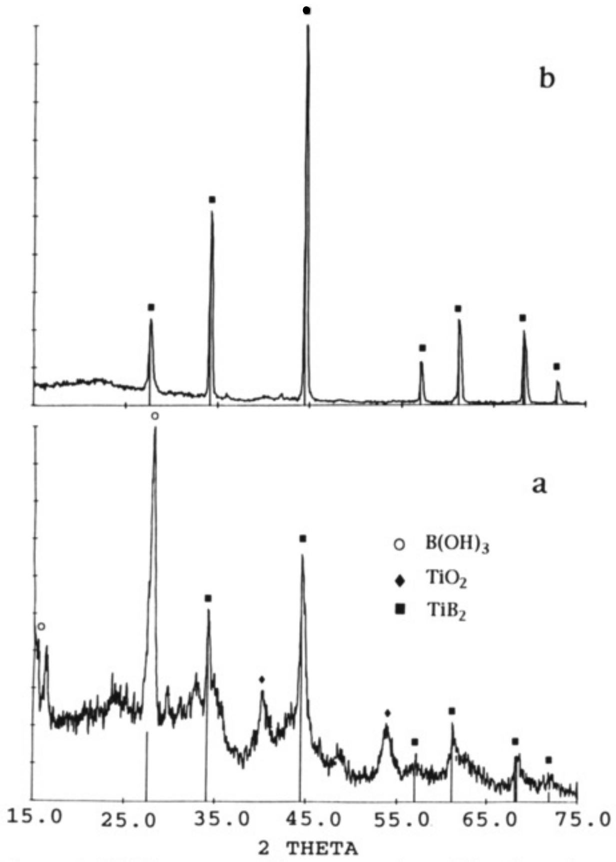

Figure 3. XRD patterns of the precursor heated in a flow of argon at (a) 700 °C for 6 h and (b) 1300 °C for 6 h.

Figure 2 shows the TGA curve obtained for the precursor when heated under a flow of argon. The TGA curve indicates that decomposition occurs in three steps between 50 and 1320 °C. The first weight loss occurs between 120 and 260 °C and was attributed to the decomposition of –OBu groups; the second one occurs between 260 and 450 °C and corresponds to the decomposition of –OFu groups and polyfurfuryl alcohol, which will lead to the formation of carbon. All the organics are removed by 450 °C, and no additional weight loss is observed until 1200 °C, where the third weight loss begins, which was attributed to the beginning of the carbothermic reduction reactions.

Weight losses were also determined by weighing samples after heating them in a carbon furnace, with a heating rate of 3.3 °C/min under a flow of argon. Table I shows the weight losses of the precursor between 700 and 1500 °C;

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(10) A solution of 0.32 g of 1 N H_2SO_4 in 20 mL of THF was added dropwise to 30 mL of a THF solution containing 4.00 g of titanium butoxide and 0.73 g of furfuryl alcohol, under vigorous stirring. The resulting yellow solution was then mixed with 0.284 g of boron powder, yielding a dark suspension of boron powder in the THF solution of furfuryl alcohol–$(BuO)TiO_{1.5}$ (the B:Ti:FuOH:H_2O molar ratio in the starting material is 2.1:1.0:0.63:1.5). After this suspension was stirred at room temperature for 2 h, the volatile components (THF and *n*-butyl alcohol) were removed by distillation at 150 °C under vacuum, leaving a dark solid (2.2 g) which was insoluble in hydrocarbon solvents. This precursor has a nominal composition of $2.1B/[(FuO)_{0.63}(BuO)_{0.37}TiO_{1.5}]_n$.

(11) Jiang, Z.; Rhine, W. E. *Chem. Mater.* **1991**, *3*, 1132.

these weight losses agree with those observed in the TGA at 900 °C (29.50%). When the precursor is heated at 1100 °C for 6 h, a 37.27% weight loss is observed, suggesting that carbothermic reduction has begun. Further heating the precursor to 1300 °C resulted in more weight loss, and an additional 12.7% weight loss occurred between 1300 and 1500 °C.

The evolution of crystalline phases during the decomposition of $2.1B/[(FuO)_{0.63}(BuO)_{0.37}TiO_{1.5}]_n$ was determined from the XRD patterns of the pyrolysis intermediates. Figure 3a shows the XRD pattern of the pyrolysis product heated at 700 °C for 6 h. The peaks marked with ■ are attributed to TiB_2; the peak at 44° (labeled as ○) is assigned to TiO_2. The peaks labeled as ◆ match very well with the XRD pattern of boric acid, $(B(OH)_3)$; however, the IR spectrum of this product indicates that B_2O_3 is the actual intermediate. The boric acid detected by XRD probably was produced by the hydrolysis of B_2O_3 during the XRD experiment.[12] After the precursor was heated at 900 °C for 6 h, the XRD pattern of the resulting product showed an X-ray diffraction pattern similar to that of the sample heated to 700 °C, except that the relative intensity of the TiO_2 peak had greatly decreased relative to the TiB_2 peaks. On the basis of the above observations, B_2O_3 is one of the products, and since no weight loss was observed below 900 °C by TGA, carbon is not involved in the formation of TiB_2 below this temperature. Evidently, at these temperatures TiB_2 is formed by the borothermic reduction of TiO_2 through the following reaction:

$$10B + 3TiO_2 = 3TiB_2 + 2B_2O_3 \qquad (2)$$

The borothermic reduction of TiO_2 is known and has been studied as a method for preparing TiB_2.[13-15] Barton et al.[13] studied the reaction between boron and TiO_2 under vacuum; their study indicated that B_2O_2, rather than B_2O_3, was one of the products:

$$TiO_2 + 4B = TiB_2 + B_2O_2 \qquad (3)$$

However, they found that B_2O_2 decomposed to B and B_2O_3 above 450 °C in a nitrogen atmosphere through the following disproportionation reaction:

$$3B_2O_2 = 2B + 2B_2O_3 \qquad (4)$$

Therefore, under the present experimental conditions, TiB_2 is assumed to form through reaction 2, which is the combination of reactions 3 and 4. Walker[14] has also reported the formation of TiB_2 at similar temperatures and with no weight loss when he used B_4C as the boron source.

Heating the precursor to 1100 °C results in additional weight loss and, according to the XRD pattern, leads to the formation of TiC in addition to TiB_2 and B_2O_3. The TiC is presumably formed by the following reaction:[11]

$$TiO_2 + 3C = TiC + 2CO \qquad (5)$$

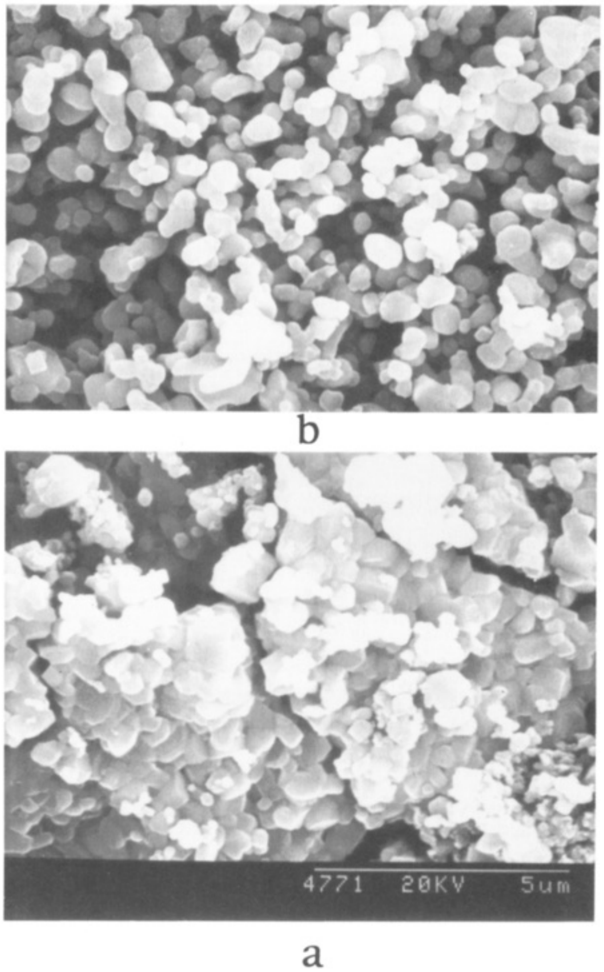

Figure 4. SEM micrographs of the precursor heated in a flow of argon at (a) 1300 °C for 6 h and (b) 1500 °C for 6 h.

Table II. Elemental Analyses (wt %) of the Precursor and Pyrolysis Products under Argon

B/Ti[a]	T, °C	Ti	B	C	H	B/Ti[b]
2.1/1	as prepared	26.69	12.58	26.59	4.55	2.08
2.1/1	1500 (6 h)	70.67	27.49	0.37	0.22	1.77
2.3/1	1500 (6 h)	65.27	30.58	2.57	1.00	2.08

[a] Molar ratio as prepared. [b] Molar ratio analyzed.

The weight loss observed in the samples heated to 1100 °C in the furnace (Table I) and in the TGA beginning at 1200 °C (Figure 2) is attributed to the evolution of CO and is evidence that the carbothermic reduction reaction begins above 1000 °C. The XRD pattern (Figure 3b) of the precursor heated at 1300 °C for 6 h shows that crystalline TiC and B_2O_3 phases have disappeared, and TiB_2 is the only crystalline phase remaining. This fact suggests that TiB_2 may also be formed between 1100 and 1300 °C, as illustrated by the following reaction:

$$TiC + B_2O_3 + 2C = TiB_2 + 3CO \qquad (6)$$

The XRD pattern of the precursor heated to 1500 °C is similar to the XRD obtained after heating the precursor to 1300 °C (Figure 3b), except that the diffraction peaks are sharper.

Figure 4a shows the SEM micrograph of the pyrolysis product heated at 1300 °C for 6 h, and it indicates that some liquid phase was present in the product, which is presumably B_2O_3. On the basis of the results in Table I, we know that the carbothermic reduction 6 was not complete by 1300 °C. Evidently, the particles obtained at 1300 °C still contain B_2O_3, and/or TiC, which continue to react

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(12) The XRD sample for Figure 3a was prepared by grinding the sample in air, dispersing the fine powder on a piece of glass slide with colloidion, and drying the slide in an oven. The samples prepared in this way experienced severe hydrolysis. For example, commercial B_2O_3 showed a XRD spectrum similar to that of $B(OH)_3$ based on this procedure. The IR sample of the pyrolysis product obtained at 700 °C was prepared by mixing the pyrolysis product with dry KBr in a drybox. The ground mixture was transferred into the IR sample cell in a glovebox and quickly transferred to the IR spectrometer's sample chamber, which was flushed with N_2 for a minimum 10 min before data collection. In this way, the hydrolysis of B_2O_3 can be avoided as indicated by the absence of the BO–H absorptions (3200 and 1200 cm^{-1}) in the IR spectrum. However, when the IR sample was ground in air, the BO–H absorptions were observed in the IR spectrum.

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to form the final TiB_2 particles. An SEM micrograph (Figure 4b) of the product heated to 1500 °C clearly shows the morphology of the TiB_2 particles obtained. The particle size distribution measurement (with centrifugal technique) indicates that the particle sizes are between 0.05 and 1 μm. The average particle size based on the above distribution was 0.30 μm.

The elemental analyses of the precursor and the pyrolysis product at 1500 °C (Table II) indicates that some boron was lost during the heat treatment, which subsequently led to a Ti:B ratio of 1:1.78 in the final product. This loss of boron is not surprising, since boron oxide is known to be volatile above 1300 °C. In addition, this B_2O_3 loss could be partially responsible for the weight loss between 1300 and 1500 °C. The pyrolytic yield (weight of residue) of product after heating to 1500 °C was 33.40% and is 92.3% of the amount expected based on Ti(O–*n*-Bu)$_4$.

To prepare TiB_2 with a 1:2 Ti/B ratio in the final product, a precursor was synthesized which contained more boron and carbon and had a nominal composition of $2.3B/[(BuO)_{0.31}(FuO)_{0.69}TiO_{1.5}]_n$. After pyrolysis at 1500 °C for 6 h, the elemental analyses (Table II) of the resulting pyrolysis product indicated that it had a Ti:B ratio of 1:2.08 but still contained 2.57% C and 1.00% H. The oxygen content in this product was estimated to be less than 0.6%, based on the combined percentages (99.42%) of Ti, B, C, and H. The average particle size of the product was found to be 0.38 μm. The low oxygen content of this product indicates that the carbothermic reduction of B_2O_3 is nearly complete at 1500 °C, a condition also observed in the borothermic/carbothermic reduction of TiO_2 with B_4C.[14]

On the basis of the above observations, pure TiB_2 powders with submicron sizes can be prepared with this procedure at 1500 °C if the quantities of the starting materials are carefully controlled. Furthermore, we found that the pyrolysis process did not follow reaction 1 but proceeded by a combination of borothermic and carbothermic reduction reactions in agreement with the results obtained by Walker.[14] However, reaction 1 still can be used to describe the overall reaction, since it is obtained by combining reactions 3–6.

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Registry No. TiB_2, 12045-63-5.

Nanoparticles of Anatase by Electrostatic Spraying of an Alkoxide Solution

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Much effort has been directed toward the synthesis of submicron particles with a narrow size distribution for the preparation of nanophase ceramic materials[1–3] that have improved properties.[4] This is done by consolidating and sintering nanometer-sized particles, often called nanoparticles.[5] In most cases, the nanoparticles are synthesized in vacuum or at low pressure by evaporation of a bulk source material. Synthesis of nanocomposite materials in solution is limited by aggregation; although additives help keep particles dispersed in solution, they have to be removed before a pure, nanophase solid can be formed.[6] Because condensation reactions are enhanced during the drying stage of the sol–gel process, particles of gel-forming compounds become larger than those produced by gas-phase methods.[7] Titania particles have been made from metal–organic compounds by reactions in aerosols.[8,9] Particles smaller than 100 nm were made by thermal decomposition of titanium alkoxides.[10] These methods, however, can be applied only to volatile compounds.

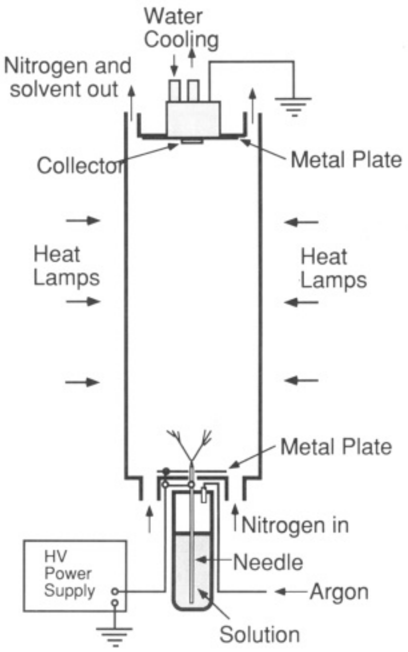

Figure 1. Schematic diagram of the setup used for the fabrication of TiO_2 nanoparticles.

When a liquid droplet, under the influence of an intense electric field, acquires charge density above the Rayleigh limit, the droplet becomes unstable and breaks up into numerous, charged small droplets; the liquid emanating from a tube forms either a single jet or a multiple jet depending on the electric field strength.[11,12] Many practical applications of this phenomenon have been de-

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