〔 高度技術教育研究センター 〕

〔区　分　A〕

Modification of Phosphatidylcholine Liposomes with Poly(ethylene oxide)- Substituted Lipid

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Modification of egg phosphatidylcholine (eggPC) and dimyristoylphosphatidylcholine liposomes with poly(ethylene oxide)-substituted lipids [PEO-lipid(*m*,*n*); *m* and *n* mean, respectively, the chain length of alkyl group and the number of PEO segments]. Morphologies of these supermolecules were investigated by means of laser dynamic light scattering and transmission electron microscopy. Reconstitution of the PEO-lipid to eggPC liposome was possible below 40-50 mol% of total lipids for PEO-lipid(12, 5), and 30-40 mol% for PEO-lipid(12, 13) and PEO-lipid(12, 31). Effective encapsulation of FITC-dextran (1.96 kDa) into the liposome was obtained using the eggPC liposome modified with PEO-lipid. This PEO-modified liposome showed sufficient barrier function to water-soluble polymers such and dextran. Through various studied, it was found that PEO-lipid (12, 13) is relatively compatible for modifying conventional eggPC liposome.

Mobility of Poly(ethylene oxide) Segments on Surface of Lecithin Liposomes

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J. Bioact. Comat. Polym.,, 194-205 (2001)

To better understand the dynamics of PEO-lipid-modified phosphatidylcholine liposomes ("fusogenic liposomes"), the mobility of the PEO segment on the liposomal surface and the fluidity of the bilayer were investigated by measuring the spin-lattice relaxation time (T_1) by ^{13}C-NMR spectroscopy and by fluorescence depolarization. ^{13}C-NMR studies revealed that the PEO-lipids in this work exhibit similar behavior on liposomal surfaces irrespective of the PEO chain length. Furthermore, with regard to the relationship between morphology and dynamics of the PEO-lipid and phosphatidylcholine mixture, it was found that the mobility of PEO segments are altered by the morphology; liposome ＜ aqueous micelle ＜ monomeric dispersion in organic solution. Fluorescence depolarization studies revealed that liposomal membranes were tighter with the addition of PEO-lipid(12. a31) than with the addition of PEO-lipid(12, a13). In contrast, the reconstitution of PEO-lipid(12, a5) into liposomes increased membrane fluidity.

Mid-Membrane Photolabeling of the Transmembrane Domain of Gylcophorin A in Phospolipid Vesicles

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The center of the transmembrane domain of a protein has been selectively functionalized. Although *photoaffinity-labeling* methods have been successfully employed to determine receptor-ligand binding sites, there has been no success so far in the siteselective photolabeling of proteins within phospholipid bilayers. Despite the limitation cited above for the use of our probe, this method could be useful for the study of transmembrane domains of other proteins.

DEVELOPMENT OF AN ECO - FRIENDLY SENSOR ELEMENT - (OPTICAL HCl DETECTION USING COMPOSITE FILMS OF TETRAPHENYLPORPHYRIN - BIODEGRADABLE POLYMER)

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Chemical Sensors, Vol. 17, Supplement B, pp 484-486 (2001).

Composite films of 5,10,15,20-tetraphenylporphyrin($TPPH_2$) embedded in various biodegradable polymer matrices(BPM) were prepared and their optical response to HCl gas were examined in comparison with nonbiodegradable polymer matrices(NBPM). The absorbance of the Soret and Q-bands for BPM composite films are reversibly, more sensitive to low ppm levels of HCl gas than for NBPM composite films. High sensitivity to low ppm levels of HCl gas was achieved by using a $TPPH_2$-poly(butylene succinate adipate)composite film.

Optochemical Sensor for HCl Gas Based on tetraalkoxyphenylporphyrin Dispersed in an Acrylate Polymer Matrix

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Sensors and Materials, Vol. 13, pp 359-371 (2001).

Tetraalkoxyphenylporphyrin-polymer composite films were prepared and examined for the detection of HCl gas. The sensing process is characterized by the following steps; the sorption of HCl to the polymer metrix ($HCl_{gas}\cdot HCl_{film}$), and the disprotonation of the porphyrin ($TPPH_2 + 2HCl_{film} \rightleftarrows TPPH_4{}^{2+}\cdot 2Cl^-$). Based on the lmax of the Q band of the dicationic form of the porphyrin in acrylate polymers, the equilibrium constants of the diprotonation for all tetraalkoxyphenylporphyrins uses are expected to be almost the same, i.e., the effect of the alkyl chani of the substituent is not observed, and those values are matrix and is of the order of butyl methacrylate ＞ hexyl methacrylate ＞ hexyl acrylate. A faster response to an increase in HCl was observed for the composite made from a polymer with a lower glass transition temperature, but the sensitivity decreased.

Optochemical HCl gas detection using mono-substituted tetraphenylporphin-polymer composite films

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Sensors and Actuators B, Vol. 76, pp 36-41 (2001).

Hydroxy-／alkoxy-substituted tetraphenylporphin were synthesized and their Soret- and Q-bands'changes with HCl gas in ppm levels were examined. Both the bands were influenced by HCl gas concentration and their changes in sub-ppm levels of HCl were decreased with an increase in the alkoxy chain length. The changes of the absorbance of the Soret- and Q(0, 0)-bands were enhanced by replacing ethylcellulose with polyhexyl methacrylate as a matrix while the recovery times prolonged. The introductions of electron donating substituents to p-phenyl positions of the porphin ring result in the basicity of pyrrole nitrogens.

$LaFeO_3$ perovskite-type oxides prepared by oxide-mixing, coprecipitation and complex synthesis methods

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Journal of Materials Science, Vol.36 (2001), p.5643-5648.

The perovskite oxide, $LaFeO_3$, was synthesized by three different preparation methods i.e., the calcination of a mixture of La_2O_3 and Fe_2O_3 (La-Fe-O), a co-precipitated precursor (La-Fe-OH), $La(OH)_3$ and $Fe(OH)_3$, and a heteronuclear complex (La-Fe-CN), $La[Fe(CN)_6]\cdot 5H_2O$. The obtained powders were characterized by thermogravimetric analysis, powder X-ray diffraction, electron microprobe analysis, specific surface area measurment and scanning electron microscopy. The formation of $LaFeO_3$ is clearly recognized for La-Fe-O, La-Fe-OH and La-Fe-CN at calcining temperatures above 1000, 800 and 600°C, respectively. The mean particle diameter of La-Fe-CN calcined at 600°C for 2 hours was 30 nm. The $LaFeO_3$ perovskite oxide powder obtained by the thermal decomposition of La-Fe-CN was most uniform on an atomic level and the nanosized $LaFeO_3$ powder was obtained at low temperatures. Furthermore, the sinterability was good.

Preparation of $(Li_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ (RE＝Sm, Gd, Dy, Ho, Y, Er and Yb) glasses and their electrical properties

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Journal of the Ceramic Society of Japan, Vol.110 (2002), p.200-203.

Lithium rare-earth silicate glasses, $(Li_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ (RE＝Sm, Gd, Dy, Ho, Y, Er and Yb), were prepared by melting a mixture of Li_2CO_3, RE_2O_3 and SiO_2 under the composition ratio of each component. The density was increased with increasing the atomic weight of RE. Three differential thermal analysis (DTA) exothermic peaks (Tc(Ⅰ), Tc(Ⅱ) and Tc(Ⅲ)), attributed to crystallization, were observed in the temperature range of 650 to 880°C. The powder X-ray diffraction analysis indicated that Li_2SiO_3, (Li_2SO_3＋$RE_2Si_2O_7$＋RE_2SiO_5) and (Li_2SO_3＋$RE_2Si_2O_7$) formed around Tc(Ⅰ), Tc(Ⅱ) and Tc(Ⅲ), respectively. The conductivity of $(Li_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ glass was found to increase about two orders of magnitude over that of the corresponding $Li_5YSi_4O_{12}$ ceramic.

固相反応法、共沈法による前駆物質の熱分解法または複核錯体の熱分解法により調製されたペロブスカイト型酸化物 $LaCoO_3$

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日本化学会誌、2002、p.485-488.

ペロブスカイト型酸化物 $LaCoO_3$ を３つの異なる調製法から作製した。La_2O_3 と CoO との混合物を仮焼したもの (La-Co-O)、$La_2(C_2O_4)_3 \cdot xH_2O + CoC_2O_4 \cdot yH_2O$ 共沈前駆体の熱分解物 (La-Co-ox) 及び異核錯体 $La[Co(CN)_6] \cdot 5H_2O$ の熱分解物 (La-Co-CN) である。調製した各前駆体の特性を、熱重量測定、赤外吸収スペクトル測定、粉末 X 線回折測定、走査型電子顕微鏡観察及び比表面積測定などによって検討した。$LaCoO_3$ 単相の生成は、La-Co-O が 1000℃以上、La-Co-ox が 1200℃以上、La-Co-CN が 600℃以上で認められた。La-Co-CN の熱分解によって、低温でナノサイズの $LaCoO_3$ 粉末が得られた。600℃で２時間熱処理された La-Co-CN の結晶粒子径は 72nm であった。

〔区分B〕

Application to Cancer Chemotherapy of Supramolecular System

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"Biomedical Polymers and Polymers Therapeutics" ed. By E. Chiellini, J. Sunamoto, C. Migliaresi, R. M. Ottenbrite and D. Cohn, KA／PP, New York, Chapter 3, 33-36 (2001).

Cholesterol conjugated pullulan (CHP) allows drug carriers to easily conjugate with galactose moiety, thus resulting in the effective and selective targeting of anti-tumor drugs against cancer lesion.

A Novel Hydrophobized Polysaccharide／oncoprotein Copmlex Vaccine for HER2 Gene Expressing Cancer

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"Biomedical Polymers and Polymers Therapeutics" ed. By E. Chiellini, J. Sunamoto, C. Migliaresi, R. M. Ottenbrite and D. Cohn, KA／PP, New York, Chapter 25, 331-337 (2001).

We investigated whether or not the HER2 protein alone or complexed with CHM or CHP can induce responses by CD^{8+} CTLs and tumor rejection specific for HER2 expressing tumor cells. The humoral immune response against HER2 generated by this novel vaccine was investigated. Its usefulness for the prevention against tumor growth and the therapy of established tumors was evaluated.

〔区分E〕

Simple, Small-Sized, Lock-in Light Detection System Using a Gated Si Avalanche Photodiode

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Optical Engineering for Sensing and Nanotechnology (ICOSN2001)

We have constructed a simple, small-sized, lock-in light detection system using a gated Si avalanche photodiode (APD). The gate mode operation of the APD was achieved by a transistor-transistor-logic (TTL) signal superimposed on a direct-current (dc) bias not exceeding the breakdown voltage of the APD. The attainable gain was thirty times larger than that obtained by the normal dc-biased APD. The APD is operated at a frequency of 2f (＝ 20 kHz) and its output signal is fed into a compact, laboratory-made lock-in amplifier that works in synchronous with the gated APD at a frequency f (＝ 10 kHz). The system is useful for detecting a weak signal light superimposed on a large background.

種々のアルコキシル基を含むテトラフェニルポルフィリン誘導体を用いたオプティカル HCl ガスセンサ素子の特性(6)

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日本化学会中国四国九州合同大会（島根大学、松江市）、平成 13 年 10 月 27 日

環境汚染物質である HCl ガスをサブ-ppm レベルで検出するため本研究では、5，10，15，20-テトラフェニルポルフィリン（$TPPH_2$）のフェニル基のパラ位に電子供与性及び電子吸引性置換基を導入したポルフィリンをセンサ素子材とし、ppm レベルの HCl ガスに対する吸光度の変化量と置換基（R）のハメットσ値を用いてプロットすると、アルコキシル基と水酸基のσ値において最大を示す結果が得られた。

Ｎ－混乱ポルフィリンのオプティカルセンサ素子への応用（１）

堀川晃玄*[1]・帆谷依美*[2]・中川克彦*[1]・堤　主計*[1]・古田弘幸*[3]

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日本化学会中国四国九州合同大会（島根大学、松江市）、平成 13 年 10 月 27 日

本研究では、通常のポルフィリンの４つのピロール環の内、１つのピロール環が反転したＮ－混乱ポルフィリン(N-Confused Porphyrin：NC-P)のセンサ材料としての工学的応用を目的とし、NC-P のクロロホルム溶液をシリカゲルプレート上に塗布した素子の反射 UV スペクトルの変化を測定した後、N,N-ジメチルホルムアミド(DMF)の室温中における蒸気を暴露すると、NC-P の反射 UV スペクトルは、シリカゲルプレート上ではモノカチオン構造($NC\text{-}PH^+$)から中性構造である(NC-P 3H)へ変化した。一方、$TPPH_2$, $TP(BuO)PH_2$ は、シリカゲルプレート上において中性構造であり、DMF 蒸気を暴露後のスペクトルにおいても変化は見られない。以上の結果より、NC-P の外周部窒素が、通常のポルフィリンと比べてプロトン化され易いことが分かった。

環境にやさしいオプティカルガスセンサ素子の開発(1)

大杉隆史*[1]、帆谷依美*[2]、中川克彦*[1]、堤　主計*[1]、ヘルスプリヤトノ*[3]、定岡芳彦*[3]

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日本化学会中国四国九州合同大会（島根大学、松江市）、平成 13 年 10 月 27 日

本研究では、ポリマー・マトリックスとして環境共生型である生分解性ポリマーに $TPPH_2$ を分散した複合膜をセンサ素子材に用い、ppm レベルの HCl ガスに対する感度･応答速度等のセンサ特性に及ぼすポリマー・マトリックス効果について検討した。

DEVELOPMENT OF AN ECO-FRIENDLY SENSOR ELEMENT-(OPTICAL HCl DETECTION USING COMPOSITE FILMS OF TETRAPHENYLPORPHYRIN-BIODEGRADABLE POLYMER)

Katsuhiko NAKAGAWA*[1], Emi HOTANI*[1], Chikara TSUTSUMI*[1], Nobuki HAYASE*[1], Michiaki MABUCHI*[1], Heru Supriyatno*[2], and Yoshihiko SADAOKA*[2].

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第５回東アジア化学センサ国際会議（日本・佐世保）、平成 13 年 12 月 6 日

Spectral changes of $TPPH_2$ dispersed in polymer matrices such as synthetic polymers and biodegradable polymers were examined. Absorbance of the Soret- and Q- bands was sensitive to HCl gas at ppm levels except for $TPPH_2$-PLA composite film. For the $TPPH_2$-PBSA film, the HCl concentration dependence of log(I_0／I) at the Soret band was significantly enhanced in comparison with other $TPPH_2$-polymer films. Interestingly the maximum sensitivity was at Tg＝-45°C of PBSA. And the most response upon switching from N_2 to 11ppm HCl gas was $TPPH_2$-PBST which included phenyl group in the main chain of polymer. On the other hand, the rate of enzymatic degradation of TPPH2-biodegradable polymer composite films is in the order of PBAT, PBS ＜＜ PBSA ＜ PCL. This result suggests that a phenyl group acts as a retardant.

Ｎ－混乱ポルフィリンのオプティカルセンサ素子への応用(2)

堀川晃玄[*1]、帆谷依美[*2]、中川克彦[*1]、堤　主計[*1]、間淵道昭[*1]、古田弘幸[*3]

[*1]新居浜工業高等専門学校生物応用化学科、[*2]新居浜工業高等専門学校生産工学専攻、[*3]京大院理

日本化学会　第81回春季年会（早稲田大学、東京都西新宿)、平成14年3月26日

本研究では、通常のポルフィリンの４つのピロール環の内、１つのピロール環が反転したＮ－混乱ポルフィリン(N-Confused Porphyrin：NC-P)のセンサ材料としての工学的応用を目的とし、NC-P をシリカゲル、アルミナおよびポリマーの各種マトリックスに分散した素子の有機溶媒の極性変化による NH 互変異性化に対するセンサ特性についてテトラフェニルポルフィリン($TPPH_2$)誘導体と比較検討すると、非水素供与性極性溶媒である N,N- ジメチルホルムアミド(DMF)を検出するオプティカルセンサ素子の開発に世界で初めて成功した。

環境にやさしいオプティカルガスセンサ素子の開発(3)

大杉隆史[*1]、帆谷依美[*2]、中川克彦[*1]、堤　主計[*1]、間淵道昭[*1]、ヘルスプリヤトノ[*3]、青野宏通[*3]、定岡芳彦[*3]

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日本化学会　第81回春季年会（早稲田大学、東京都西新宿)、平成14年3月26日

本研究では、ポリマー・マトリックスとして環境共生型である生分解性ポリマーに $TPPH_2$ を分散した複合膜をセンサ素子材に用い、ppm レベルの HCl ガスに対する感度･応答速度等のセンサ特性に及ぼすポリマー・マトリックス効果について、これまで最も高感度であったビニルポリマーでるポリアクリル酸エステルと比較検討すると、Tg 値が -60°Cから高くなると共にセンサ感度も高くなり、PBS (Tg＝-35.0°C)の時センサ感度が極大値を示した。この理由として、１）ビニル系エステルポリマーと縮合系ポリエステルの Tg 以上における主鎖運動と側鎖運動の差異　２）縮合系ポリエステルの結晶度の差異によるものと考えている。さらに、センサ素子材の酵素による生分解性についても検討した。

希土類含有アルカリシリケートガラスの作製と電気特性評価

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第８回ヤングセラミスト・ミーティング in 中四国　2001年

出発組成が $(M_2O)_{35.7}(RE_2O_3)_{7.2}(SiO_2)_{57.1}$ (M＝Li、Na、K：RE＝Sm、Gd、Dy、Y、Ho、Er、Yb) からなるガラスを作製し、そのアルカリ金属イオン導電性と希土類元素のイオン半径の関係についての検討を行った。Na 系と K 系では、導電率は希土類元素のイオン半径が大きくなるに従い低くなる傾向が得られたが、Li 系では高くなる傾向が得られた。また、K 系の導電率は Li 系と Na 系の導電率に較べ約 0.5 桁程度低かった。

Polymer film produced by marine bacterium, *Alteromonas* sp. SHY1-1

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Fourth International Symposium on Frontiers in Biomedical Polymers, Williamsburg, Virginiae, USA.
May 16-19, 2001

Alteromonas sp. SHY1-1 was isolated from the suspended solution of Biojelly, which was fouling-free natural film. Strain SHY1-1 secreted water-soluble polymeric materials and water-insoluble polymer film in natural seawater medium supplemented with yeast extract and glucose. In order to investigate the chemical structure of naturally occurring Biojelly® and the polymer film produced by strain SHY1-1, these polymeric materials were analyzed by FTIR and TLC. These results indicated that these polymeric materials were mucopolysaccharides consisting of amino sugars. The chemical structure of Biojelly® and the polymer film was almost same. The antifouling effect of the polymer film was also investigated obtained in this work with the barnacle attachment. The attachment of barnacle larvae decreased on the polymer film compared with that on glass surface.

〔区　分　G〕

バイオゼリー産生微生物

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微生物を含有する塗膜を水中構造体上に形成させた場合に、水中にて、バイオゼリーを産生し、大型水棲生物に対する防汚効果を発揮する微生物を提供する。