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PEPTIDE FORMATION FROM AMINO ACID WITH PARTICULATE SEMICONDUCTOR PHOTOCATALYSTS

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Peptides of diglycine to pentaglycine are formed from glycine under irradiation in the presence of particulate semiconductor photocatalysts such as TiO_2, CdS, CdSe, MoS_2, In_2O_3, and GaP, with and without Pt deposition. Platinization of the semiconductors efficiently enhanced the yield of the peptides.

Peptide synthesis is one of the most important subjects in organic chemistry, and variety of peptides have been hitherto synthesized from amino acid. In organic chemistry, peptides have been synthesized in nonaqueous solvents by introducing various kinds of protecting groups into the amino acid.[1,2] We report here that the formation of oligoglycine from glycine is achieved in aqueous solution at room temperature under irradiation by taking advantage of the strong redox power of particulate semiconductor photocatalysts such as TiO_2, CdS, CdSe, MoS_2, In_2O_3, and GaP, with and without Pt deposition. Platinization of each photocatalyst, moderate pH condition, and a longer irradiation time led to the higher yield of the peptides.

Compounds examined as photocatalysts are TiO_2 (Rutile; >99% pure), CdS (mixture of cubic and hexagonal), CdSe (hexagonal; >99.99% pure), MoS_2 ($2H_1$-hexagonal;>99% pure), In_2O_3 (cubic; >99.9% pure), and GaP (cubic; >99.999% pure). Platinized photocatalysts were prepared by mixing the compound with powdered Pt black (Nippon Engelhard) in an agate mortar.[3] A 10 mmol of glycine (Wako Pure Chemical) and 300 mg of the photocatalyst powder in water (30 ml or 3 ml) were irradiated with a 500 W Xe lamp under deaerated condition. Products in the solution were analyzed with HPLC (Shimadzu LC-5A, ZORBAX ODS column), while gaseous products with a gas chromatography (Ohkura 1-802, MS-5A column). The

absorption spectra of the products were also compared with those of standard reagents by Shimadzu SPD-M1A.

The irradiation of the reactants in the presence of the photocatalyst powder leads to the production of peptides in the aqueous glycine solution as shown in Table 1 which lists up the yield of diglycine and triglycine for all the photocatalysts, with and without Pt deposition. The platinization has a remarkable effect for every photocatalyst, particularly for TiO_2 and CdS. The platinization increased the activity by 40 to 80 times for CdSe, MoS_2, In_2O_3, and GaP, and 200 to 400 times for TiO_2 and CdS. The effect of platinization may be due to the efficient separation of photogenerated electrons and holes[4] or due to the catalytic effect of platinum in this reaction. The concentration of glycine, the pH of the solution, and the irradiation time have also large effects as shown in Table 2 for TiO_2 and CdS. The yield of peptide from glycine decreases in the order of pH of 7, 14, and 2 in the TiO_2/Pt system (runs 3, 4, 5). Under the acidic and basic conditions, the yield of peptide decreases presumably because the formed peptide bonding is hydrolyzed. The yield and the degree of polymerization increases with the irradiation time (runs 1 and 2, 7 and 8, 11 and 12). The best condition for the production of peptides both in amount and in the degree of polymerization is, therefore, the neutral condition with the platinized photocatalyst (run 3). Quantum yield at λ =380 nm is 0.6—1.1% for diglycine formation with TiO_2/Pt system. Under this condition, even tetraglycine is formed after 10 days irradiation (run 8). Though diketopiperazine can be formed by thermal condensation of glycine,[5] it was not detected in the present system.

Besides the peptide synthesis in aqueous solution, there have been considerable amounts of reports of peptide formation from amino acid by thermal condensation in the solid phase at high temperature.[6] We also examined peptide formation from glycine in the solid phase using TiO_2 and CdS, with and without Pt deposition. As shown in Table 2, there is also a remarkable effect of platinization for TiO_2 and CdS (runs 9 and 10, 16 and 17). The TiO_2/Pt system produces diglycine more than twice as much as the CdS/Pt system. The CdS/Pt system produces only a trace of tetraglycine, whereas it produces pentaglycine more than four times as much as the TiO_2/Pt system. Although the difference of activity of each photocatalyst is not clearly understood at this stage, this may

Table 1. Amount of peptides produced from glycine for various semiconductor photocatalysts. (μmol) An aqueous solution (30 ml) of 10 mmol of glycine with 300 mg of a photocatalyst powder was irradiated with a 500 W Xe lamp. (Pt: 10 wt%)

Photocatal.	Pt	Duration/day	$(Gly)_2$	$(Gly)_3$
TiO_2	-	5	0.03	--
CdS	-	5	0.04	--
CdSe	-	5	0.02	--
MoS_2	-	5	0.02	--
In_2O_3	-	5	0.02	--
GaP	-	5	0.03	--
TiO_2	+	1	2.59	0.52
CdS	+	1	1.73	0.42
CdSe	+	1	0.29	0.27
MoS_2	+	1	0.29	--
In_2O_3	+	1	0.58	--
GaP	+	1	0.58	--

Table 2. Amount of peptides in μmol from glycine under various conditions

	Run number	a) mol dm^{-3}	pH	Pt	Duration/day	$(Gly)_2$	$(Gly)_3$	$(Gly)_4$	$(Gly)_5$
TiO_2	1	0.33	7	-	1	--	--	--	--
	2	0.33	7	-	5	0.03	--	--	--
	3	0.33	7	+	1	2.59	0.52	--	--
	4	0.33	2	+	1	trace	--	--	--
	5	0.33	14	+	1	0.86	0.58	--	--
	6	3.33	7	-	1	--	--	--	--
	7	3.33	7	+	1	1.73	0.52	--	--
	8	3.33	7	+	10	2.88	1.04	0.55	--
	9	solid b)		-	1	trace	--	--	--
	10	solid b)		+	1	10.06	0.21	0.18	0.10
CdS	11	0.33	7	-	1	--	--	--	--
	12	0.33	7	-	5	0.04	--	--	--
	13	0.33	7	+	1	1.73	0.42	--	--
	14	3.33	7	-	1	--	--	--	--
	15	3.33	7	+	1	1.15	1.46	--	--
	16	solid b)		-	1	0.86	0.16	--	--
	17	solid b)		+	1	4.31	0.31	trace	0.42
Pt alone	18		7		1	--	--	--	--
SiO_2	19	3.33	7	+	1	--	--	--	--
Light only	20	3.33	7	-	1	--	--	--	--

a) The concentration of glycine.

b) The mixture of 10 mmol of glycine with 300 mg of photocatalyst powder in the absence of water.

be due to the differences of the surface structure and of the conduction band and valence band positions of the photocatalyst.

Since Pt black alone or platinized SiO_2 as a photo-inactive catalyst exibit no activity for the peptide formation (runs 18, 19, 20), this reaction is not due to the thermal effect of irradiation, but due to the photocatalysis. In this reaction, photogenerated holes are used not only for the formation of peptide, but also for the decorboxylation of carboxylic acids.[7] Actually, the photocatalytic CO_2 formation due to the decarboxylation of glycine occurs. The yield of peptide against the decarboxylation of glycine was 3% for the TiO_2/Pt system, while 2% for the CdS/Pt system.

In conclusion, (1) peptides of diglycine to pentaglycine are formed from glycine under irradiation in the presence of particulate semiconductor photocatalysts, such as TiO_2 and CdS. (2) There is a remarkable effect of platinization for all the photocatalysts. (3) The yield of peptides is highest at pH=7 among several pH conditions. (4) The longer irradiation time leads to the higher yield and the higher degree of polymerization.

The photocatalytic peptide formation from amino acid is interesting not only as a new method of peptide synthesis, but also from the view point of the origins of life which might occur under solar irradiation.

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