water

MDPI

Supplementary Materials

Preparation of Cu-Ce@γ-Al_2O_3 and Study on Catalytic Ozone Oxidation for the Treatment of RO Concentrate Water

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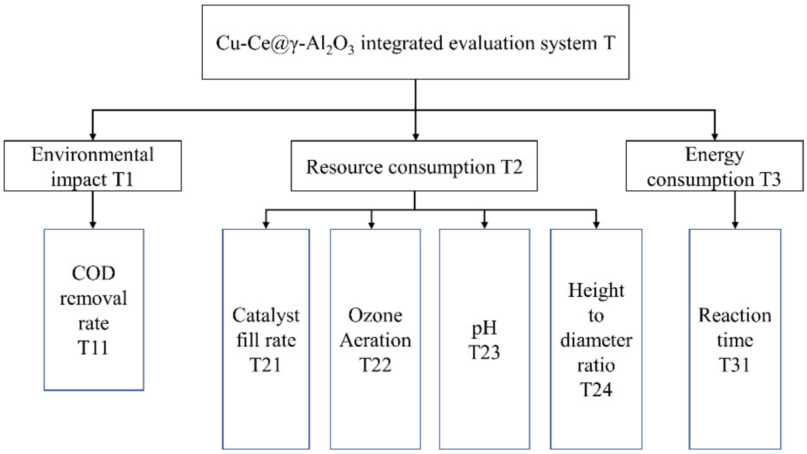


Figure S1. Comprehensive evaluation index system of Cu-Ce@γ-Al_2O_3 catalysts for catalytic oxidative degradation of RO concentrated water.

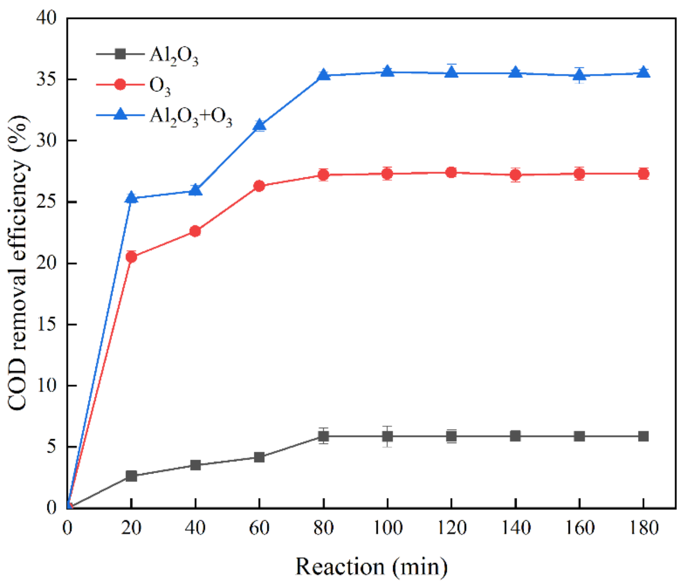


Figure S2. Effect of different reaction systems on COD removal efficiency.

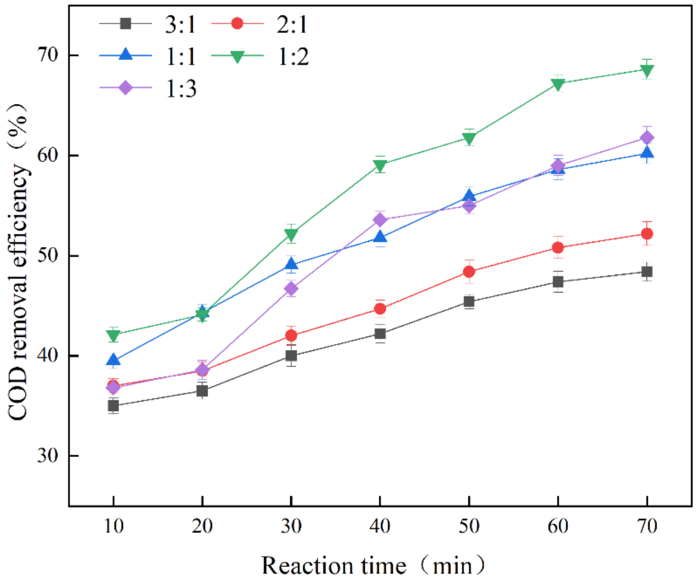


Figure S3. Effect of active component proportion of Ce:Cu on COD removal efficiency.

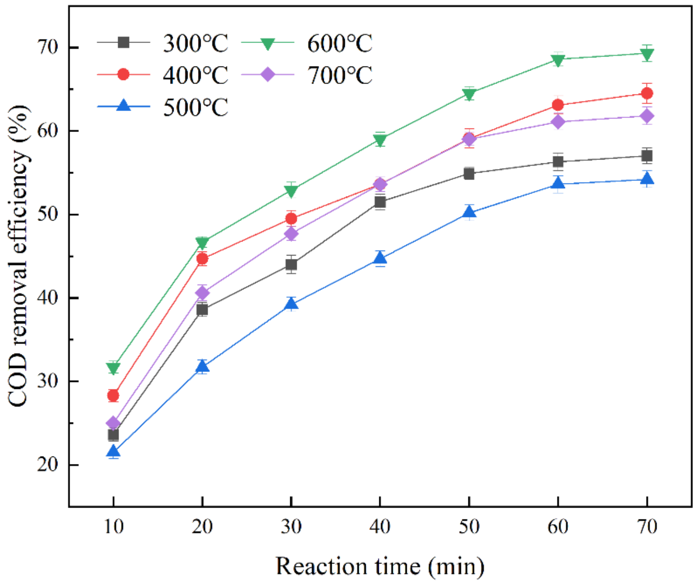


Figure S4. Effect of calcination temperature on COD removal efficiency.

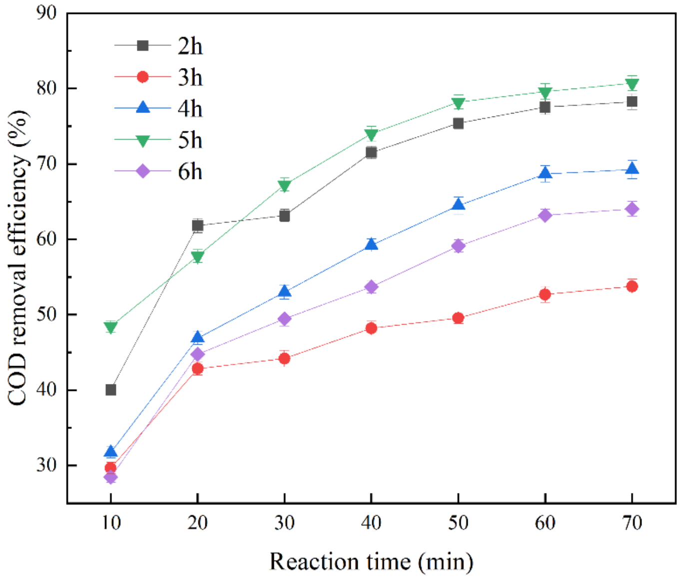
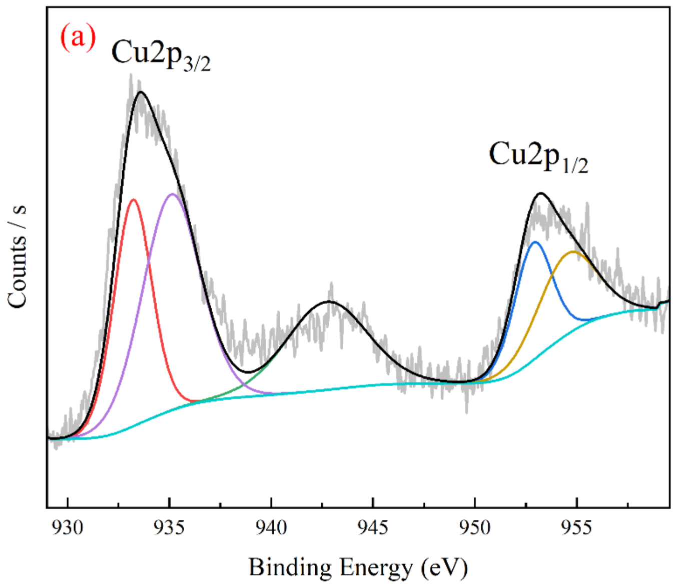


Figure S5. Effect of calcination time on COD removal efficiency.



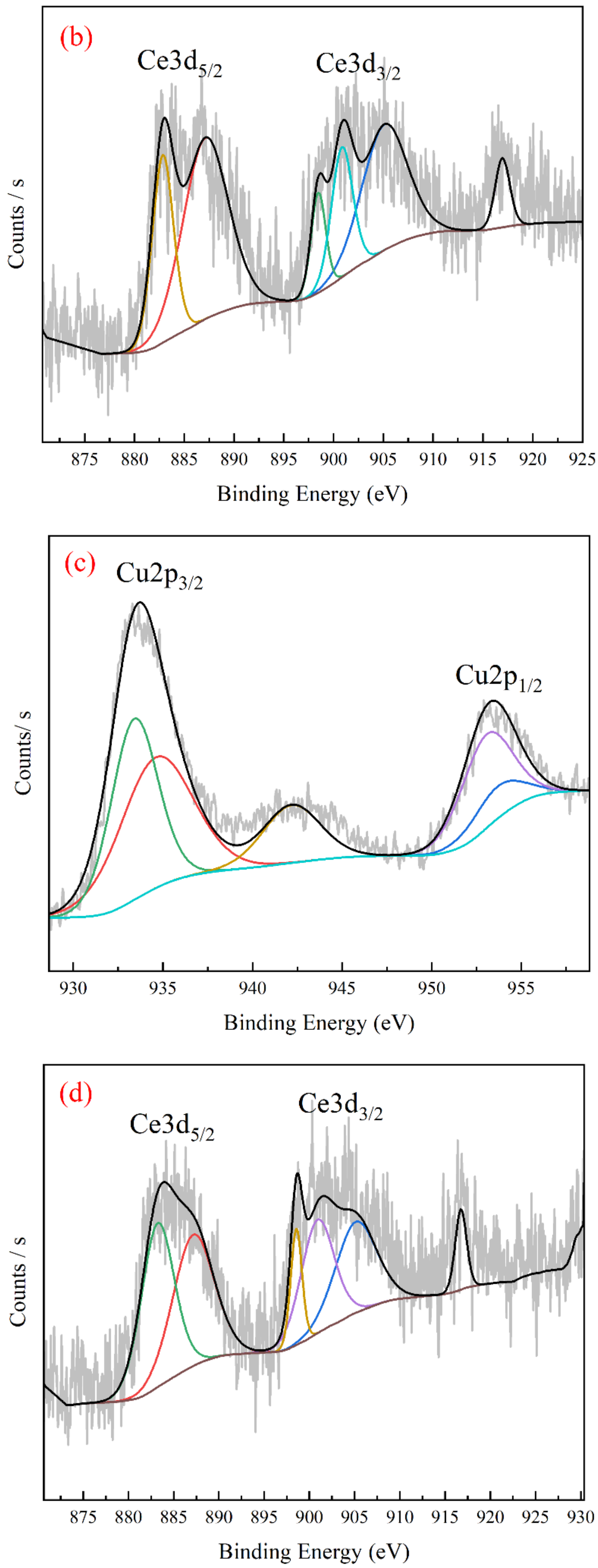

(b)
Ce3d5/2
Ce3d3/2
Counts / s
875 880 885 890 895 900 905 910 915 920 925
Binding Energy (eV)
(c)
Cu2p3/2
Cu2p1/2
Counts/ s
930 935 940 945 950 955
Binding Energy (eV)
(d)
Ce3d5/2
Ce3d3/2
Counts / s
875 880 885 890 895 900 905 910 915 920 925 930
Binding Energy (eV)

Figure S6. XPS characterization: (a) Cu2p spectrum, (b) Ce3d spectrum, (c) Cu2p spectrum after repeated use 30 times, (d) Ce3d spectrum after repeated use 30 times.

Table S1. 1–9 scaling method.

Intensity of Importance	Comparison between Ai and Aj
1	Equal importance
3	Moderate importance
5	Strong importance
7	Very strong importance
9	Extreme importance
2、4、6、8	Intermediate values

Table S2. The judgment matrix of criterion layer to target layer.

T	T1	T2	T3	Weight M_i
Environmental impact T1	1	2	3	0.5396
Resource consumption T2	1/2	1	2	0.2970
Energy consumption T3	1/3	1/2	1	0.1634

Table S3. Judgment matrix for environmental impact at the scheme layer.

Environmental impact T1	T11	Weight M_i
COD removal efficiency T11	1	1.0000

Table S4. Judgment matrix for resource consumption at the scheme layer.

T2	T21	T22	T23	T24	Weight M_i
Catalyst fill rate T21	1	2	3	4	0.4668
Ozone dosage T22	1/2	1	2	3	0.2776
Initial pH T23	1/3	1/2	1	2	0.1603
H/D T24	1/4	1/3	1/2	1	0.0953

Table S5. Judgment matrix for energy consumption at the scheme layer.

T3	T31	Weight M_i
Reaction time T31	1	1.0000

Table S6. The value standard of RI.

n	1	2	3	4	5	6	7	8	9
RI	0.00	0.00	0.58	0.90	1.12	1.24	1.32	1.41	1.45

Table S7. Consistency test.

Judgement matrix	The maximum eigenvalue corresponding to eigenvector	Maximum eigenvalue	CR	Consistency check
T	（0.5396，0.2970，0.1634）	3.0092	0.0079	Meet consistency

T1	（1）	1	0	Meet consistency
T2	（0.4668，0.2776，0.1603，0.0953）	4.0311	0.0115	Meet consistency
T3	（1）	1	0	Meet consistency

Table S8. The total ranking weight of each index layer.

Goal	Criteria	Sub-criteria	Single ranking weight	Total ranking weight
Cu-Ce@γ-Al_2O_3 Comprehensive Evaluation T	Environmental impact T1 (0.5396)	COD removal efficiency T11	1.0000	0.5396
	Resource consumption T2 (0.2970)	Catalyst fill rate T21	0.4668	0.1386
		Ozone dosage T22	0.2776	0.0824
		Initial pH T23	0.1603	0.0476
		H/D T24	0.0953	0.0284
	Energy consumption T3 (0.1634)	Reaction time T31	1	0.1634

Table S9. Qualitative index evaluation standard.

Qualitative index	Extremely reasonable	More reasonable	Medium	Less reasonable	Totally unreasonable
Initial pH T23	8–10	6–8	4–6	2–4	0–2

Table S10. Summary of experimental data.

NO	Environmental impact T1	Resource consumption T2				Energy consumption T3
	COD removal efficiency T11	Catalyst fill rate T21	Ozone dosage T22	Initial pH T23	H/D T24	Reaction time T31
	%	cm	g/L	/	/	min
1	45.5	8	0.2	7.49	6:1	20
2	66.5	8	0.2	7.49	6:1	40
3	78.2	8	0.2	7.49	6:1	60
4	78.8	8	0.2	7.49	6:1	80
5	51.5	8	0.2	3	6:1	60
6	53.8	8	0.2	5	6:1	60
7	68.2	8	0.2	7	6:1	60
8	79.8	8	0.2	9	6:1	60
9	80.3	8	0.2	11	6:1	60
10	64.8	8	0.1	9	6:1	60
11	81.5	8	0.3	9	6:1	60
12	82.2	8	0.4	9	6:1	60
13	83.3	8	0.5	9	6:1	60
14	65.2	4	0.2	9	6:1	60
15	82.2	12	0.2	9	6:1	60
16	82.4	16	0.2	9	6:1	60
17	82.6	20	0.2	9	6:1	60
18	63.2	12	0.2	9	3:1	60

19	85.2	12	0.2	9	5:1	60
20	77.3	12	0.2	9	7:1	60
21	63.3	12	0.2	9	9:1	60
22	61.2	12	0.2	9	11:1	60

Table S11. BET characterization analysis of Cu-Ce@γ-Al_2O_3 catalyst.

Sample	Specific surface area (m^2/g)	Average pore volume (cm^3/g)	Average pore size (nm)
γ-Al_2O_3	142.27	0.35	10.38
Cu-Ce@γ-Al_2O_3	181.93	0.44	9.73
Cu-Ce@γ-Al_2O_3 after utilization 30 times	146.84	0.37	9.61

Text S1： After weighing 25 g of catalyst prepared under optimal conditions into a conical flask, pure water was added until the catalyst was completely submerged, then the shaking speed of the shaker was set at 60, 90, 120, 150 and 180 rpm and the temperature was set at 25°C. The conical flask with the catalyst was then placed in a water bath shaker for 12 h. The catalyst was then removed and dried in an oven, weighed and the wear rate was calculated.

$$A = \frac{M_0 - M_1}{M_0} \times 100\% \quad \text{(S1)}$$

A： Catalyst wear rate；

M_0: Initial mass of catalyst；

M_1: Mass of catalyst after shaking.

Text S2： Ozone utilization

$$C_0 = \frac{C_T - C_W - C_R}{C_T} \times 100\% \quad \text{(S2)}$$

C_0 : Ozone utilization；

C_T : Total ozone dosing；

C_W : Residual ozone in water；

C_R : Ozone content in exhaust gas.

Text S3： The calculation of index weight and consistency check, the calculation of index membership, and the structure of factor evaluation set R.

1. Calculation of index weight and consistency test

(1) Calculation of weight vector

After establishing the hierarchical structure, by comparing the factors at the same level, the index weight is determined by AHP method. The indexes are compared by 1-9 scale method shown in Table S1. The specific comparison method is shown in Table S1。Calculation of index weight Wi′ is shown in functions 3 to 5:

$$A_i = \prod_{j=1}^{n} a_{ij}(i, j = 1,2,3 \cdots, n) \quad (S3)$$

$$W_i = (A_i)^{\frac{1}{n}} \quad (S4)$$

$$W_i' = \frac{W_i}{\sum_{j=1}^{n} W_j} \quad (S5)$$

A_i——Product of row elements in judgement matrix;

W_i'——Single level sorting weight corresponding to an indicator.

$W_e = \left[W_1^{'}, W_2^{'}, W_3^{'}, \ldots, W_n^{'}\right]^T$ is the desired weight vector。

(2) Consistency test

In order to ensure the credibility of the fuzzy analytic hierarchy process of Cu-Ce@γ-Al_2O_3 catalyst, the weights need consistency test, as shown in functions 6 to 8:

$$\lambda_{max} = \sum_{i=1}^{n} \frac{(AW_e)}{nW_i} = \frac{1}{n}\sum_{i=1}^{n} \frac{\sum_{j=1}^{n} b_{ij}W_j}{W_i^{'}} \quad (S6)$$

$$CI = \frac{\lambda_{max}-n}{n-1} \quad (S7)$$

$$CR = \frac{CI}{RI} \times 100\% \leq 0.1 \quad (S8)$$

RI is the mean consistency index, and its value is shown in Table S6. The consistency test is passed when CR$<$0.10. Use the method above to calculate the indicators selected in this article and rank them according to the importance of each indicator in this evaluation level relative to the indicators in the previous level. The index ranking results are shown in Table S2-S5. The consistency test result was shown in Table S7，Table S8 exhibited the total ranking weight of each indicator layer.

2. Calculation of degree of membership

According to the index system determined above, the set of evaluation factors are:

$T = \{\text{Environmental impact t1，Resource consumption t2，Energy consumption t3}\}$

$t_1 = \{\text{COD removal efficiency } t_{11}\}$

$t_2 = \left\{\text{Catalyst fill rate } t_{21}, \text{Ozone gas flow } t_{22}, \text{Initial pH } t_{23}, \frac{\text{H}}{\text{D}}\ t_{24}\right\}$

t_3 = {Reaction time t_{31}}

W = [0.5396, 0.1386, 0.0824, 0.0476, 0.0284, 0.1634]

For benefit index (the larger index value, the better evaluation) of quantitative indexes, use function 9 to determine the degree of membership:

$$\mu(a)=e^{-2.1(a_j^{\max}-a_{ij})/(a_j^{\max}-a_j^{\min})} \quad \text{(S9)}$$

Where, a_{ij} ——The j-th index of the i-th plan;

$a_j^{\max}$ ——The maximum value of the j-th index;

$a_j^{\min}$ ——The minimum value of the j-th index

For cost index (the smaller index value, the better evaluation) of quantitative indexes, use function 10 to determine the degree of membership:

$$\mu(a)=e^{-2.1(a_{ij}-a_j^{\min})/(a_j^{\max}-a_j^{\min})} \quad \text{(S10)}$$

Where, a_{ij} ——The j-th index of the i-th plan;

$a_j^{\max}$ ——The maximum value of the j-th index;

$a_j^{\min}$ ——The minimum value of the j-th index。

Since qualitative index cannot be directly numerically valued, the ten - point system is used to assign values to qualitative index. Table S9 shows specific assignment standards. The value obtained after the assignment is a benefit index. Therefore, function 9 is used to calculate the degree of membership. The experimental results of Cu-Ce@γ-Al_2O_3 catalytic ozonation degrading RO concentrated water are summarized in Table S10.

3. Factor evaluation set R

According to the comprehensive evaluation index weight of Cu-Ce@γ-Al_2O_3 catalyst determined by the AHP above, the weight set W is:

$$W = [0.5396,0.1386,0.0824,0.0476,0.0283,0.0134]$$

From the degree of membership value of the six indexes in the previous section, the single - factor evaluation set of Cu-Ce@γ-Al_2O_3 catalyst can be obtained:

$$R_1 = [0.1225,0.5916,0.5916,0.3980,0.4550,1.0000]$$

$$R_2 = [0.3719,0.5916,0.5916,0.3980,0.4550,0.4966]$$

$$R_3 = [0.6905,0.5916,0.5916,0.3980,0.4550,0.2466]$$

$$R_4 = [0.7128,0.5916,0.5916,0.3980,0.4550,0.1225]$$

$$R_5 = [0.1682,0.5916,0.5916,0.1225,0.4550,0.2466]$$

$$R_6 = [0.1900,0.5916,0.5916,0.2070,0.4550,0.2466]$$

$$R_7 = [0.4069,0.5916,0.5916,0.3499,0.4550,0.2466]$$

$$R_8 = [0.7515,0.5916,0.5916,0.5916,0.4550,0.2466]$$

$$R_9 = [0.7717,0.5916,0.5916,1.0000,0.4550,0.2466]$$

$$R_{10} = [0.3399,0.5916,1.0000,0.5916,0.4550,0.2466]$$

$$R_{11} = [0.8222,0.5916,0.3499,0.5916,0.4550,0.2466]$$

$$R_{12} = [0.8533,0.5916,0.2070,0.5916,0.4550,0.2466]$$

$$R_{13} = [0.9044,0.5916,0.1225,0.5916,0.4550,0.2466]$$

$$R_{14} = [0.3472,1.0000,0.5916,0.5916,0.4550,0.2466]$$

$$R_{15} = [0.8533,0.3499,0.5916,0.5916,0.4550,0.2466]$$

$$R_{16} = [0.8623,0.2070,0.5916,0.5916,0.4550,0.2466]$$

$$R_{17} = [0.8715,0.1225,0.5916,0.5916,0.4550,0.2466]$$

$$R_{18} = [0.3123,0.3499,0.5916,0.5916,1.0000,0.2466]$$

$$R_{19} = [1.0000,0.3499,0.5916,0.5916,0.5916,0.2466]$$

$$R_{20} = [0.6584,0.3499,0.5916,0.5916,0.3499,0.2466]$$

$$R_{21} = [0.3140,0.3499,0.5916,0.5916,0.2070,0.2466]$$

$$R_{22} = [0.2810,0.3499,0.5916,0.5916,0.1225,0.2466]$$

Then the multi-factor judgment set R of the comprehensive evaluation of Cu-Ce@γ-Al_2O_3 catalyst is:

$$R = [R_1, R_2, W_3, \dots, W_{22}]^T$$

The fuzzy decision vector A was obtained as function 11：

$$A=W\times R \qquad (S11)$$

Combine the weight vector W obtained above with the multi‐factor judgment set R to obtain the fuzzy decision vector A:

$$A=\begin{bmatrix} 0.3921,0.4444,0.5755,0.5672,0.2805,0.2963,0.4202,0.6176 \\ 0.6479,0.4292,0.6359,0.6408,0.6615,0.4561,0.6390,0.6241 \\ 0.6173,0.3626,0.7221,0.5309,0.3410,0.3208 \end{bmatrix}$$