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A study of process optimization using the combined submerged arc nanoparticle synthesis system for preparing TiO_2 nanoparticle suspension

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Abstract

Using ultrasonic-aided submerged arc nanoparticle synthesis system, which is an innovative nanoparticle preparation method, this paper employs some major parameters together with robust design to investigate the optimized parameters, such as peak current, pulse duration, open voltage and amplitude of ultrasonic vibration, for producing TiO_2 nanoparticle suspension by using the least number of experiments. The experimental results indicate that evenly distributed TiO_2 nanoparticles can be manufactured. The pH value of isoelectric point (IEP) of the produced particle suspension is pH 5. The suspension is dispersed when the potential value of the suspension is distant from the IEP, or it would be aggregated when the potential value is close to the IEP. The produced TiO_2 nanoparticle suspension would absorb UV when the wavelength is 300–380 nm.

Keywords: Oxide materials; Nanofabrications; Catalysis; Robustness design

1. Introduction

As environmental protection has become an important issue in recent years, to reduce environmental pollution, promote the quality of life and eliminate pollutants, materials that can function with natural resources, such as the photocatalyst materials (TiO_2, vulcanized cadmium, oxidized zinc, oxidized tungsten etc.) are being developed. Photocatalyst use solar light as the source of reactive energy. Among photocatalyst materials, TiO_2 is the most stable, inexpensive and durable consequently enabling its extensive use and study.

Electron–hole pairs recombination TiO_2 affects the photocatalytic ability of TiO_2. In order to prolong the survival period of electron–hole pairs and reduce the chances of recombination, photocatalytic deposition method is usually employed, allowing metallic particles (such as palladium, silver, rhodium, copper and nickel, etc.) to deposit on the surface of TiO_2. Since metal is a good electron catching agent, when TiO_2 is excitated by light to produce electron-hole pairs, its electrons would move towards the low-level conduction band before the combination of electron–hole pairs. Metallic ions can quickly transmit the electron to the adsorption molecules attaching on the surface. The hole firstly moves towards the high-level valence band, which then further moves towards the interface between TiO_2 and solution, and performs oxidization reaction with the solution. In other words, the electron–hole pairs are effectively separated before recombination, promoting the photocatalytic ability of TiO_2 [1–3].

Through the self-assembled equipment and the robustness design method, this work optimizes parameters of TiO_2 nanoparticle by using ultrasonic-aided submerged arc nanoparticle synthesis system. TEM and FE-SEM are employed to observe the morphology and particle size. X-ray diffractometer (XRD) and energy dispersive X-ray (EDX) are used to investigate elements of in the produced nanoparticles. Meanwhile, zetameter is used to analyze the produced nanoparticle suspension, and the isoelectric point of suspension is discovered from the surface potential under different pH values. Through UV–vis spectrophotometer, the absorbency of suspension can be tested.

2. Experimental

This paper uses ultrasonic-aided submerged arc nanoparticle synthesis system to produce TiO_2 nanoparticle suspension [4–6]. The main technique

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Table 1
The levels of the factor of the process parameter

Level	Factor				
	A (I)	B (V)	C ($t_{on/off}$) (μs)	D (V_{gap})	E ($V_{amplitude}$) (V)
1	1.5	90	2	1	10
2	3	210	6	4	40
3	4.5	215	100	7	70
4	6	220	1600	10	100

involved is use of bulk metal material as electrode and integration of the device with an ultrasonic vibrator. In the system, the high temperature of the submerged arc and the ultrasonic vibration produce nanoparticles. The experimental equipment include heating system, ultrasonic system, pressure balancing system and temperature control system. The heating device provides stable arc as the heat source required for producing nanoparticle. At the same time, some important parameters of the system, such as peak currents, open voltages, pulse duration, off time, gap voltage and time of discharge can be preset through this system. The ultrasonic system can preset different frequencies and amplitudes of vibration. With the aid of ultrasonic, the fluctuation of dielectric fluid can be increased, and the produced nanoparticles can be rapidly moved away from the arc zone. Meanwhile, the vaporized metal can be cooled down quickly, so as to suppress the growth of nanoparticles and acquire the ideal size. Pressure balancing system is applied inside the vacuum chamber, so as to maintain an appropriate vacuum pressure. Inside the vacuum chamber, deionized water is used as a dielectric fluid, and metallic rods are placed at the bottom of the vacuum chamber. A suitable gap is left between the rod and the heating system.

The bulk for producing nanoparticle is submerged in the dielectric fluid inside the vacuum chamber. Applied electrical energy then produces heating source for generating an adequate arc with a high temperature ranging from 6000 to 12,000 °C, the bulk material is melted and evaporated in the small area that causes the submerged arc. The submerged arc heats the dielectric fluid which is rapidly vaporized, and also makes its volume expanded and high pressure is created. The high pressure reaching 3.9–4.9 MPa [7] removes the evaporated material from the surface of metallic material rapidly. During this time, the vaporized metal in the cooling fluid inside the vacuum chamber goes through the processes of nucleus forming, growth and condensation. The produced nanoparticles are in the cooling fluid. Since the cooling system and ultrasonic system can control the temperature of dielectric fluid inside the vacuum chamber at a certain low temperature and the fluid is being fluctuated at high speed, the metal continues to be vaporized with the continuous creation of submerged arcs, and instant condensation in the dielectric fluid.

The heating system can stably create submerged arcs continuously, and pressure and temperature inside the vacuum chamber can be controlled under preset conditions.

By using ultrasonic-aided submerged arc nanoparticle synthesis system, this paper selects factor A as the current, factor B as the voltage, factor C as the pulse duration, factor D as the gap voltage, and factor E as the voltage of ultrasonic amplitude. Four levels are set for these five factors, as shown in Table 1. The degree of freedom is $5 \times (4-1) = 15$. Thus, the L16(4^5) orthogonal array, with degree of freedom greater than 15 and the least number of experiments is selected. The L16 orthogonal array can be put in five factors with maximum four levels for conducting analysis. Such disposition is also used to conduct analysis 16 times.

3. Results and discussion

S/N ratio (dB) is the only evaluation standard of robustness, implying that S/N ratio is the index of robustness. In Eq. (1), $\bar{y}$ is the mean of secondary particle size, m is the objective value, and s is the standard deviation. In Eq. (1), the objective value m is replaced by 0, inducing a S/N ratio as shown in Eq. (2), which is the smaller the better. When calculating the $\bar{y}$ and s of S/N ratio, this paper uses nm as the unit:

$$\text{S/N} = -10\ \log[(\bar{y}-m)^2 + s^2] \quad (1)$$

$$= -10\ \log(\bar{y}^2 + s^2) \quad (2)$$

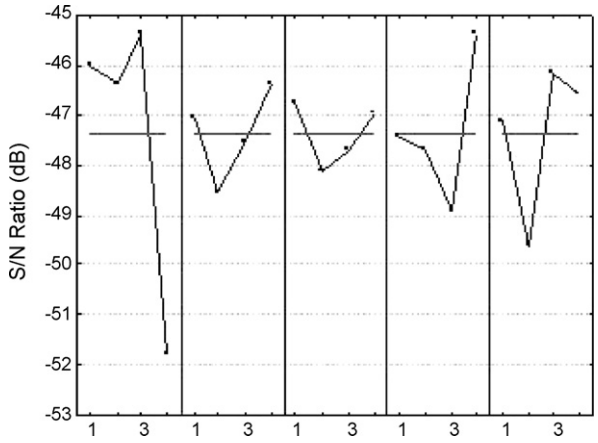

Fig. 1. S/N ratio response for various factors of Table 1 on particle size.

Since the peak value of the expected distribution of the particle size should be the smaller the better, the analysis of small-the-better characteristics is employed, and the ideal function of its quality characteristics is zero (suppose that the quality feature is a positive number). Therefore, the objective function is the smallest possible value. Having done the parameter experiments for 16 groups, each group has to undergo experiments five times. After the calculated means and standard deviations of all the data are recalculated by using Eq. (2), the S/N ratio of each group of parameters can be acquired. Then the extents of effects of various parameter factors on S/N ratio are analyzed, and shown in Table 2 and Fig. 1.

Focusing on the S/N ratio response for factors on particles size, an analysis of variance is made, and the extents of effects of various factors on S/N ratios is shown in Table 3. According to the data, in the ultrasonic process, factor A (processing current) and factor E (ultrasonic amplitude) have greater contribution values when taking the particle diameter of Fig. 1 as the objective. It is known from the chart of various factors' affect on S/N ratio that the S/N ratio parameter group of the factor parameters of A3–B4–C1–D4–E3 is the parameter group with the optimized particle size. These parameters include: the peak current 4.5 A, open voltage 220 V, pulse duration and off time both 2 μs, the gap voltage is the apparatus parameter 10, and the voltage of ultrasonic amplitude is 70 V. Based on these parameters, we can prove that the mean size of the secondary particles resulted from the experiment is 54.7 nm. Meanwhile, Fig. 2a and b uses TEM and FE-SEM to observe the size and appearance of the particle size. These two figures show that the particle shapes appear to be spherical, and the size distribution is narrow.

X-ray diffraction is used to investigate the lattice structure of nanoparticles. Before recovery of the powder, the produced nanoparticle suspension has to be dried. A vacuum funnel is used to sort out the particles of the suspension through a 100 nm filter paper for XRD, and place them in an oven for drying. Some dried powder is scraped from the filter paper for XRD. The

Table 2
S/N ratio response for various factors of Table 1 on particle size

Level	Factor				
	A	B	C	D	E
1	−46.0205	−47.0505	−46.7262	−47.4404	−47.14959965
2	−46.3536	−48.5287	−48.1084	−47.7251	−49.62374828
3	−45.375	−47.5547	−47.6965	−48.9468	−46.15345174
4	−51.7538	−46.369	−46.9718	−45.3905	−46.5760907
Effect	6.3788	2.1597	1.3822	3.5563	3.4703
Rank	1	4	5	2	3

Table 3
Analysis of the variance of the process parameter

	Sum of squares	Degree of freedom	Variance	F	Contribution (%)	Net sum of squares
A	104.2067	3	34.73555	21.27131	57.033	99.30772812
B	9.923033	3	3.307678	2.025551	2.885	5.024101711
C	4.898931	3	1.632977	1		
D	26.14256	3	8.714187	5.336381	12.200	21.24362966
E	28.95243	3	9.650811	5.909949	13.814	24.05350221
Error total (e)	174.1236	15	58.04121		100.000	174.1236159
	4.898931	3	1.632977		14.067	24.49465421

resulting pattern of the prepared TiO_2 nanoparticle is shown in Fig. 3. Nanoparticles produced by this process are constitued only TiO_2, with a majority of anatase phase and a minority of rutile phase.

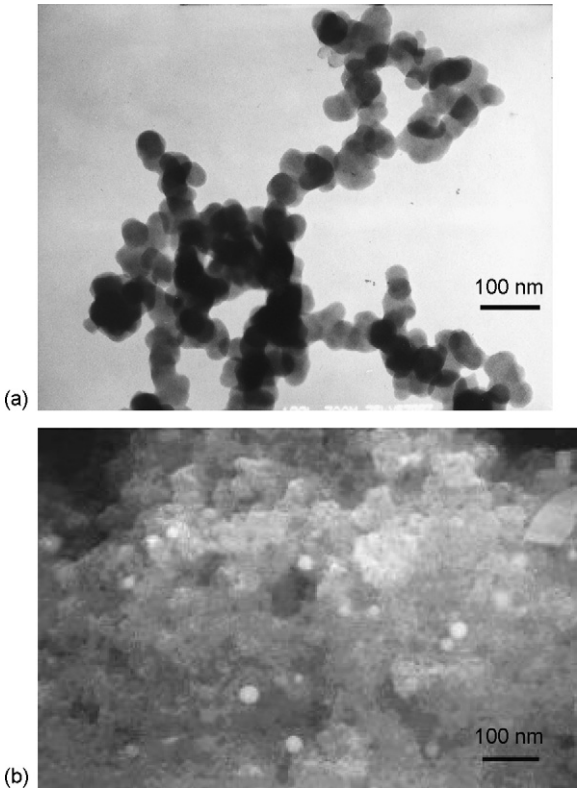

Fig. 2. (a) TEM image (bright field) and (b) FE-SEM backscattered image of powder obtained with optimized parameters using ultrasonic-aided submerged arc nanoparticle synthesis system.

When the charge density on the surface of particles is higher, the particles have higher zeta potential. The high charge density on the surface of particles brings about a greater electrostatic repulsion between particles. As a result, the suspension can be kept at a higher stability. Through the adjustment of the pH values, certain surface charge is created on the surface of particles, forming an electric double layers. The repulsion between the electric double layers offsets the attraction between particles. It is advantageous for the dispersion of particles [8,9].

Before measuring, hydrochloric acid and sodium hydroxide are respectively blended with deionized water to form a liquid of 10^{-1} M concentration, which is then blended with the produced TiO_2 suspension to form different pH values. As the pH value reaches 6.23, the particles begin to be aggregated; and near pH value 5.11, no suspension is found, and the particles are all

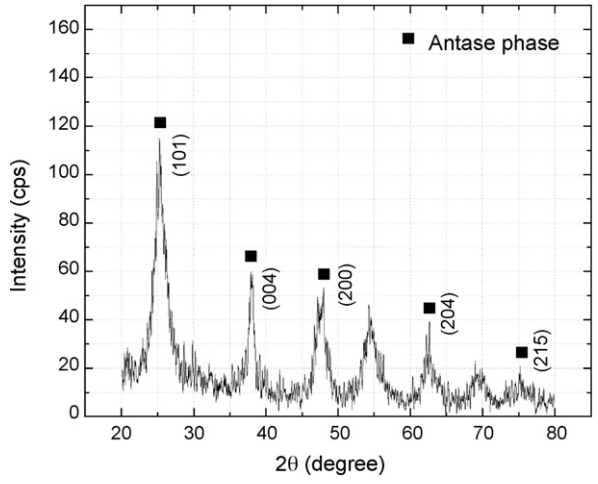

Fig. 3. XRD pattern of anatase TiO_2 nanoparticles prepared by the proposed system.

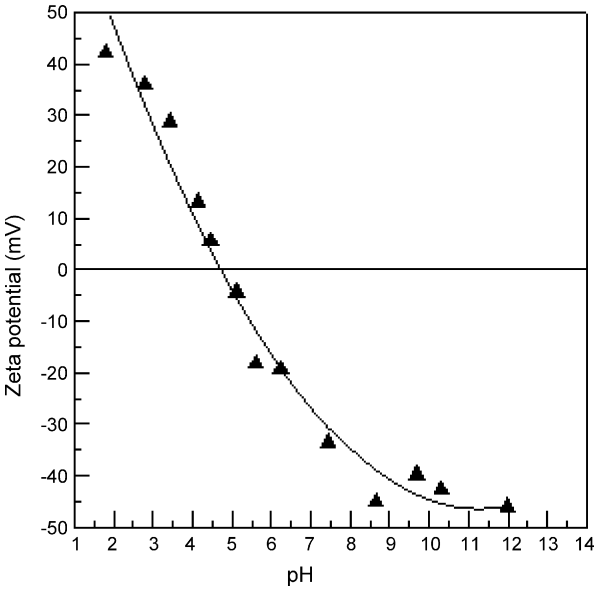

Fig. 4. Zeta potentials under various pH values.

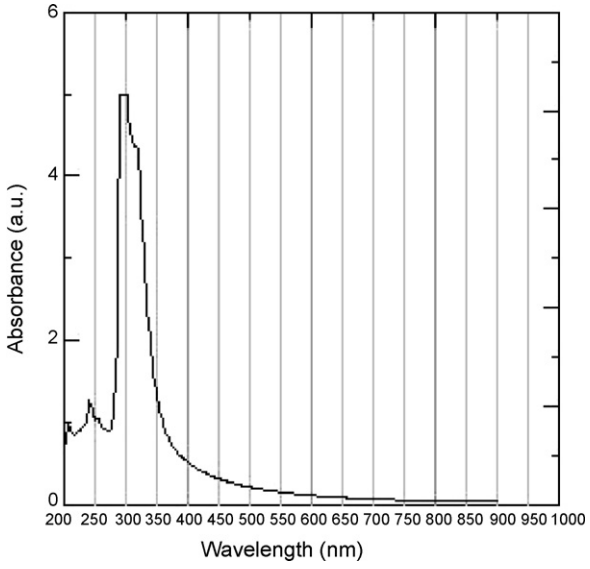

Fig. 5. UV–vis absorption spectrum of nanoparticle suspension.

aggregated and sunk. Having observed the above phenomena, a zeta potential analyzer is used to measure the zeta potentials of different fluids, as shown in Fig. 4. It is seen that for the pH value of the produced TiO_2 is about 5.0, the potential carried on the surface of particles is zero, which is known as isoelectric point (IEP). At pH value greater than 5.0, the surface of particles begins to carry negative electricity. At pH value less than 5.0, the surface of particle carries positive electricity. For surface potential is far from the IEP, the suspension is more stable.

Through the UV–vis absorption spectra of Fig. 5 clearly show absorbency of the TiO_2 suspension versus the wavelength. In other words, the UV energy with a wavelength of less than 400 nm would be absorbed by the TiO_2 particles in the suspension. During this time, the electrons can acquire sufficient energy for moving from valence band to conduction band. As the wavelength is set at 270 nm, the particles have no effects of absorbency.

4. Conclusions

This paper conducts analysis using the ultrasonic-aided submerged arc nanoparticle synthesis system together with robust experimental design method. As a result, the optimized production conditions are determined: the peak current is 4.5 A, the open voltage is 220 V, the on time/off time are both 2 μs, the gap voltage is the apparatus parameter 10, and the voltage of ultrasonic amplitude is 70 V. The TiO_2 nanoparticle suspension can be produced in a stable way. The produced TiO_2 suspension is for photocatalytic experiments. UV–vis absorption spectrum shows that at wavelength less than 400 nm, obvious absorption peak is created. As the wavelength is set at 270 nm, the particles have no effect of UV absorption.

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