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# Formation of nanoparticles in water-in-oil microemulsions controlled by the yield of hydrated electron: The controlled reduction of Cu<sup>2+</sup>

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#### Abstract

In the water-in-oil (W/O) microemulsions based on nonionic surfactants, i.e., Brij 30, Brij 56, or Triton X-100, the  $\omega$  value (molar ratio of water to surfactant), anion, and surfactant could remarkably affect the radiolytic reduction of Cu

cles with great freedom and will be helpful for the synthesis of other nanoparticles in microemulsion.

According to the results of pulse radiolytic investigation of the microemulsion system, when a microemulsion is irradiated, hydrated electrons ( $e_{aq}^-$ ) can be generated mainly from the scavenging of excess electrons, which are produced originally through the radiolysis of oil, by the water pool [25–28]. In addition, the radiolysis of water in the water pool can also generate  $e_{aq}^-$  directly, but it is less important [25–28]. As the  $\omega$ value increases, the yield of  $e_{aq}^-$  usually increases, except in the cationic-surfactant-based microemulsions [25–30]. In the SDS-based microemulsion, Kapoor et al. [16,19] have used this regularity to explain the radiolytic synthesis of Ag, Cd, Pd, and Cu nanoparticles. In the same microemulsion, they also studied the reduction of Tl<sup>+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> by pulse radiolysis and found that the rate constants for the reduction of these cations by  $e_{aq}^-$  were much lower than those in aqueous solution [17].

In this paper, a more systematic work will be reported, in which we explore how the  $\omega$  value, the anion (the counterion of Cu<sup>2+</sup>), and the structure of the surfactant affect the radiolytic reduction of Cu<sup>2+</sup> in nonionic-surfactant-based microemulsions. Our results demonstrate that their effects on the yield of  $e_{aq}^-$  play a key role. It is also suggested that the morphology of nanoparticles may be controlled by the yield of  $e_{aq}^-$ . Here, it should be pointed out that the above results are remarkably different from the mechanism of  $\omega$  value, anion, and surfactant only affecting the morphology of nanoparticles synthesized by routine chemical methods, as mentioned above. It should also be noted that the present work further confirms the validation of the mechanism for the producing of hydrated electrons in W/O microemulsions, which is quite important in radiation chemistry.

#### 2. Materials and methods

# 2.1. Chemicals

Brij 30 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>OH, Acros), Brij 56 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>10</sub>OH, Aldrich), Triton X-100 ((CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>10</sub>OH, CP, Beijing Chemical Reagents Inc.), cyclohexane (AR, Beijing Chemical Reagents Inc.), copper sulfate, copper chloride, toluene, naphthalene, nitric acid (AR, Beijing Chemical Plant), *n*-hexanol, copper nitrate (AR, Beijing Yili Fine Chemical Products Inc.), copper bromide (AR, Shanghai Zhenxin Reagent Plant), and dodecyl mercaptan (CP, Nankai Fine Chemical Plant) were used as received. Deionized and tridistilled water was used in the experiments.

#### 2.2. Synthesis of nanoparticles

A certain amount of copper salt was dissolved in water to obtain a 0.02 mol/L stock solution. To prepare microemulsions, surfactant (Triton X-100 or Brij 56), *n*-hexanol, and cyclohexane with the molar ratio 1.0:1.6:57.6 were first mixed and then a certain volume of the above stock solution was added, with the  $\omega$  value fixed at 9.0. The mixtures were stirred at room temperature until they became transparent. In the Brij 30-based microemulsions, the cosurfactant was not used and the  $\omega$  value was fixed at 7.0 except as stated otherwise. After being bubbled with high-purity N<sub>2</sub> under anaerobic conditions, the microemulsions were irradiated in a field of a  $^{60}$ Co  $\gamma$ -ray source for 16 h and 40 min with an absorbed dosage of 40 kGy.

# 2.3. Characterization

After irradiation, the absorption spectra were recorded immediately on a U-3010 spectrometer with the identical systems without being irradiated as standard. If the absorption spectra did not change with time, the corresponding samples were deemulsified, washed by ethanol, and then dispersed in ethanol by ultrasonication. In the case of the absorption spectra changing with time, plenty of dodecyl mercaptan was added into the microemulsions. After 48 h, the precipitate was collected by centrifugation, rinsed with ethanol, and dispersed in chloroform by ultrasonication. The obtained dispersion was dropped onto a carbon-coated copper grid. After the solvent was evaporated at room temperature, the transmission electron microscopy (TEM) and the selected area electron diffraction (SAED) images were conducted on a JEOL JEM-200CX microscope operated at 160 kV. The range of the nanoparticles' size was determined after measuring the dimensions of more than 500 nanoparticles in sight of the obtained micrograph. After the dispersed sample was deposited on a piece of glass, powder X-ray diffraction (XRD) pattern was recorded on a Rigaku Dmax-2000 diffractometer with  $CuK\alpha$  radiation  $(\lambda = 0.15418 \text{ nm})$  and X-ray photoelectron spectrum (XPS) was collected on a Kratos Axis Ultra spectrometer with monochromatized AlK $\alpha$  radiation.

# 3. Results

In the experiments, we found that the  $\omega$  value, surfactant, and anion in W/O microemulsions could remarkably affect the radiolytic reduction of Cu<sup>2+</sup> and that the morphologies of the reduction products could also be changed simultaneously. Moreover, the effects of aromatic ring, pH value, and cosurfactant were also investigated.

# 3.1. Effect of the $\omega$ value

In the Brij 30-based microemulsion with Cu(NO<sub>3</sub>)<sub>2</sub> as precursor, the absorption spectra of the reduction products are clearly different when the  $\omega$  value increases (Fig. 1A). With an  $\omega$  value of 4.5, the absorption spectrum of the reduction product exhibits characteristic excitonic structures of semiconductor at ca. 450 nm, suggesting the generation of Cu<sub>2</sub>O [31]. With a higher  $\omega$  value of 7.0, an absorption peak at ca. 570 nm, corresponding to the surface plasma (SP) absorption of Cu nanoparticles [8,32], was observed, which indicates the formation of Cu nanoparticles. Adjusting the  $\omega$  value to 5.4 between the above two values, a peak at ca. 570 nm and a shoulder peak at ca. 450 nm were observed, implying the generation of Cu and Cu<sub>2</sub>O simultaneously.





Fig. 1. Absorption spectra (A) and XRD patterns (B) of the reduction products of Cu(NO<sub>3</sub>)<sub>2</sub> in the Brij 30-based microemulsions by  $\gamma$ -irradiation at different  $\omega$  values (from 1 to 3,  $\omega = 4.5, 5.4, 7.0$ ). \* represents Cu<sub>2</sub>O; # represents Cu. Before irradiation, the compositions of the microemulsion are  $n_{\text{Brij30}} = 2.47$  mmol,  $n_{\text{cvclohexane}} = 0.142$  mol. In the water pool, [Cu<sup>2+</sup>] = 0.02 mol/L.

Fig. 1B shows the XRD patterns of the reduction products. With an  $\omega$  value of 4.5, the interplanar distances calculated for (111), (200), and (220) from the XRD pattern match well with the standard data of cubic phase Cu<sub>2</sub>O (JCPDS file No. 05-0667), confirming the formation of cubic phase Cu<sub>2</sub>O. This has been further confirmed from the corresponding SAED analysis (inset, Fig. 2A), in which the observed six fringe patterns with plane distances of 0.301, 0.246, 0.213, 0.174, 0.151, and 0.128 nm are consistent with the cubic phase  $Cu_2O$  (110), (111), (200), (211), (220), and (311) plane distances of 0.3020, 0.2465, 0.2135, 0.1743, 0.1510, and 0.1287 nm. At a higher  $\omega$ value of 7.0, the interplanar distances calculated for (111) and (200) from the XRD pattern (Fig. 1B) match well with the standard data of fcc metal Cu (JCPDS file No. 04-0836), demonstrating the formation of Cu particles. The corresponding SAED image (inset, Fig. 2C) reveals that the observed four fringe patterns with plane distances of 0.209, 0.180, 0.127, and 0.109 nm are consistent with the fcc metal Cu (111), (200), (220), and (311) with the corresponding plane distances of 0.2088, 0.1808, 0.1273, and 0.1090 nm, respectively, which further confirms the generation of Cu particles. When the  $\omega$  value is 5.4, four apparent diffraction peaks appear in its XRD spectrum (Fig. 1B), which correspond to the (111), (200) diffraction peaks of cubic phase Cu<sub>2</sub>O and fcc metal Cu, respectively, displaying the generation of both Cu and Cu<sub>2</sub>O. This is further confirmed by the corresponding SAED analysis (inset, Fig. 2B), which shows the (111), (200), (220), (311) diffraction rings of the fcc metal Cu and the (110), (111), (220) diffraction rings of the cubic phase Cu<sub>2</sub>O.

At the  $\omega$  value of 4.5, the reduction product is composed of aggregated quasi-spherical nanoparticles, whose diameter is about 10 nm (Fig. 2A). At the  $\omega$  value of 5.4, the reduction products are composed of rodlike, square-shaped, triangular, and quasi-spherical nanoparticles (Fig. 2B). Contrasting Fig. 2C and the supporting information (SI-1), it can be found that the aspect ratio of the rodlike nanoparticles increases with increasing  $\omega$  value from 6.0 to 7.0, while the reduction products are still Cu nanoparticles. Thus, it can be concluded that the reduction product of Cu(NO<sub>3</sub>)<sub>2</sub> can be transformed from Cu<sub>2</sub>O to Cu when the  $\omega$  value increases.

# 3.2. Effect of anion

In the Triton X-100-based microemulsions, where the  $\omega$ value is fixed at 9.0, the absorption spectra of the reduction products of different precursors by  $\gamma$ -irradiation are shown in Fig. 3A. When  $Cu(NO_3)_2$  is used as precursor, a shoulder peak with characteristic semiconductor excitonic structures appears around 450 nm in the absorption spectrum, indicating the generation of Cu<sub>2</sub>O according to the discussion above. This is confirmed by the corresponding SAED (inset, Fig. 4A<sub>1</sub>) and XRD (curve a in Fig. 5) measurements. As illustrated by the TEM picture in Fig. 4A<sub>1</sub>, the projective images of these nanoparticles are almost quadrilateral, with smooth edges of  $65 \pm 5$  nm length, and the equatorial part is darker than the polar part. According to our previous results [23], these nanoparticles are octahedral. When CuSO<sub>4</sub> is used as precursor, a broad absorption peak at ca. 470 nm suggests the formation of Cu<sub>2</sub>O according to its characteristic absorption [23,33]. This is further verified by the corresponding SAED (inset, Fig. 4A<sub>2</sub>) analysis. From the corresponding TEM picture shown in Fig. 4A<sub>2</sub>, it can be clearly seen that the projective images of these nanoparticles are almost square, with coarse edges of  $160 \pm 20$  nm length. The occurrence of coarse surface of these nanoparticles may be attributed to the effect of anion on the shape of nanoparticles [34]. When CuCl<sub>2</sub> and CuBr<sub>2</sub> are used as precursors, the peak at ca. 570 nm appears in their absorption spectra (curves c and d in Fig. 3A) corresponding to the SP absorption of Cu nanoparticles. This is verified by the XRD patterns of the reduction product of CuCl<sub>2</sub> (curve b in Fig. 5). The corresponding TEM images (Figs.  $4A_3$  and  $4A_4$ ) show that these reduction products are almost composed of monodispersed spherical nanoparticles, with diameter of about 5 and 5-10 nm, respectively. Especially, the Cu nanoparticles obtained from CuCl2 tend to form a superlattice structure.

In the Brij 56-based microemulsions with the  $\omega$  value fixed at 9.0, the absorption spectra of the reduction products of different precursors by  $\gamma$ -irradiation are shown in Fig. 3B. When CuSO<sub>4</sub>, CuCl<sub>2</sub>, and CuBr<sub>2</sub> are used as precursors, respectively, it can be seen that there appears SP absorption of Cu nanoparticles at ca. 570 nm, indicating that Cu nanoparticles are formed.



Fig. 2. Morphologies of the reduction products of  $Cu^{2+}$  in the Brij 30-based microemulsions by  $\gamma$ -irradiation at different  $\omega$  values (from A to F,  $\omega = 4.5$ , 5.4, 7.0, 7.0, 7.0, 7.0, and in the presence of different precursors: (A–C) Cu(NO<sub>3</sub>)<sub>2</sub>, (D) CuSO<sub>4</sub>, (E) CuCl<sub>2</sub>, (F) CuBr<sub>2</sub>. The insets show the SAED patterns of the corresponding products.



Fig. 3. Absorption spectra of the reduction products of  $Cu^{2+}$  in the Triton X-100-based (A) and Brij 56-based (B) microemulsions ( $\omega = 9.0$ ) by  $\gamma$ -irradiation in the presence of different precursors: (a)  $Cu(NO_3)_2$ , (b)  $CuSO_4$ , (c)  $CuCl_2$ , (d)  $CuBr_2$ . The inset shows the enlargement of curve a in part B. Before irradiation, the compositions of the microemulsion are  $n_{Triton X-100}$  (or  $n_{Brij56}$ ) = 2.47 mmol,  $n_{n-hexanol} = 3.95$  mmol,  $n_{cyclohexane} = 0.142$  mol. In the water pool,  $[Cu^{2+}] = 0.02 \text{ mol/L}$ .



Fig. 4. Morphologies of the reduction products of  $Cu^{2+}$  in the Triton X-100-based (A) and Brij 56-based (B) microemulsions ( $\omega = 9.0$ ) by  $\gamma$ -irradiation in the presence of different precursors:  $Cu(NO_3)_2$  (A<sub>1</sub>, B<sub>1</sub>),  $CuSO_4$  (A<sub>2</sub>, B<sub>2</sub>),  $CuCl_2$  (A<sub>3</sub>, B<sub>3</sub>),  $CuBr_2$  (A<sub>4</sub>, B<sub>4</sub>). The insets show the SAED patterns of the corresponding products.

In the case of CuSO<sub>4</sub> as precursor, the formation of Cu nanoparticles is substantiated by the SAED analysis (inset, Fig. 4B<sub>2</sub>). The corresponding TEM images for three cases (Figs. 4B<sub>2</sub>– 4B<sub>4</sub>) show that these reduction products are all composed of monodispersed spherical nanoparticles, with the diameters of 4–10, 4–6, and 3–6 nm, respectively. When Cu(NO<sub>3</sub>)<sub>2</sub> is used as precursor, there exist a shoulder peak at ca. 450 nm and a broad absorption peak at ca. 700 nm in the absorption spectrum (curve a in Fig. 3B), implying the generation of Cu<sub>2</sub>O according to the results in the literature [35]. This is approved by the corresponding SAED analysis (inset, Fig. 4B<sub>1</sub>), which indicates a highly preferred (001) orientation texture structure. The further evidence comes from the XPS analysis, which presents a binding energy of 932.32 eV for Cu  $2p_{3/2}$ , close to the value in the literature [36,37]. The broad absorption peak at ca. 700 nm (curve a in Fig. 3B) may be ascribed to the presence of some surface states of Cu<sub>2</sub>O nanoparticles within the band gap [35]. The corresponding TEM images (Fig. 4B<sub>1</sub>) show that the reduc-



Fig. 5. XRD patterns of the reduction products of  $Cu^{2+}$  in the Triton X-100-based (a and b) and Brij 56-based (c, [toluene] = 1.86 mol/L) microemulsions ( $\omega = 9.0$ ) by  $\gamma$ -irradiation in the presence of different precursors: (a) Cu(NO<sub>3</sub>)<sub>2</sub>, (b) CuCl<sub>2</sub>, (c) CuSO<sub>4</sub>.

Table 1 Summary of the reduction products of  $Cu^{2+}$  under different conditions

Surfactant	ω	$Cu(NO_3)_2$	CuSO <sub>4</sub>	CuCl <sub>2</sub>	CuBr <sub>2</sub>
Triton X-100	9.0	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu	Cu
	12.0	Cu <sub>2</sub> O	_	_	_
Brij 56	9.0	$Cu_2O$	Cu	Cu	Cu
Brij 30	4.5	Cu <sub>2</sub> O	_	-	_
-	5.4	Cu <sub>2</sub> O & Cu	_	_	-
	6.0	Cu	_	-	_
	7.0	Cu	Cu	Cu	Cu

tion products are mostly composed of square-shaped nanoparticles with edge length ranging from 300 to 550 nm.

In the Brij 30-based microemulsions, where the  $\omega$  value is fixed at 7.0, the absorption spectra (Fig. 1A and SI-2 in supporting information) and SAED analysis (insets, Figs. 2C–2E) show that the reduction products of Cu(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub>, CuCl<sub>2</sub>, and CuBr<sub>2</sub> are all Cu. The corresponding TEM images indicate that the reduction products of CuSO<sub>4</sub>, CuCl<sub>2</sub>, and CuBr<sub>2</sub> are all composed of quasi-spherical nanoparticles besides a few rodlike nanoparticles (Figs. 2D–2F), while that of Cu(NO<sub>3</sub>)<sub>2</sub> is composed of rodlike, square-shaped, triangular, and quasispherical nanoparticles (Fig. 2C).

According to the above results, it can be seen that the  $\omega$  value, surfactant, and anion could remarkably affect the radiolytic reduction of Cu<sup>2+</sup>. All these results are summarized in Table 1. Moreover, it can be found that the morphology of the reduction products could also be changed simultaneously.

#### 3.3. Effect of aromatic ring

In the Triton X-100 and Brij 56 systems, it is strange that the reduction products of  $CuSO_4$  are markedly different (Table 1) although the structures of the two nonionic surfactants' hydrophilic chains are similar. Based on the molecular structures, it can be inferred that the phenyl ring in the hydrophobic chain of Triton X-100 may scavenge excess electrons in the oil



Fig. 6. Absorption spectra of the reduction products of CuSO<sub>4</sub> in the Brij-56 based microemulsions ( $\omega = 9.0$ ) by  $\gamma$ -irradiation in the presence of toluene (from a to c, [toluene] = 0.56, 1.13, 1.86 mol/L,  $n_{cyclohexane} = 0.134, 0.128, 0.107$  mol) and naphthalene (from d to e, [naphthalene] = 0.16, 0.28 mol/L,  $n_{cyclohexane} = 0.142$  mol). Before irradiation, the compositions of the microemulsion are  $n_{Brij}$  56 = 2.47 mmol,  $n_{n-hexanol} = 3.95$  mmol. In the water pool, [Cu<sup>2+</sup>] = 0.02 mol/L.

phase  $(e_{oil})$  and H as shown in the following reactions [38–40]:

$$CH_{3}C_{6}H_{5} + e_{oil}^{-} \xrightarrow{\text{solvent: cyclohexane}} CH_{3}C_{6}H_{5}^{-},$$

$$k = 4.0 \times 10^{9} \text{ L/(mol s)},$$
(1)

$$CH_3C_6H_5 + H \to CH_3C_6H_6^{-}, \quad k = 2.6 \times 10^9 \text{ L/(mol s)}.$$
 (2)

In the present work, in order to verify the above speculation, toluene was added to the Brij 56-based microemulsion, while the total volume was not changed. Fig. 6 (curves a– c) shows the absorption spectra of the reduction products of  $CuSO_4$  thalene. In other words, the efficiency of naphthalene is obviously higher than that of toluene.

# 3.4. Effect of pH value

Nanometer-sized Cu<sub>2</sub>O could be obtained in aqueous systems containing SDS by the  $\gamma$ -irradiation method, when the pH value was carefully controlled in the range 4.0–5.0 [41]. If the pH value was in the range 3.0-3.5, Cu would appear and mix with Cu<sub>2</sub>O [41]. However, in our previous work, Cu<sub>2</sub>O octahedral nanocrystals were obtained without any pH adjustment of the salt solution in the Triton X-100-based W/O microemulsion by  $\gamma$ -irradiation [23]. We suggested that the formation mechanism of the Cu<sub>2</sub>O nanoparticles in the microemulsion was different from that in the aqueous systems [23]. Nevertheless, no experiments have been designed to verify this speculation as yet. Here, in order to further explore the effect of pH value on the radiolytic reduction of Cu<sup>2+</sup>, a control experiment was performed, in which Cu(NO<sub>3</sub>)<sub>2</sub> was used as precursor and 0.01 mol/L HNO3 was added to the three kinds of microemulsions. As illustrated by absorption spectra and SAED analysis of these reduction products in SI-3 (supporting information), the transformation from Cu<sub>2</sub>O to Cu or from Cu to Cu<sub>2</sub>O does not appear. In other words, the pH value cannot affect the radiolytic reduction of Cu<sup>2+</sup> in these microemulsions. However, the morphologies of these nanoparticles are altered, which can be clearly seen in SI-3 (supporting information).

# 3.5. Effect of cosurfactant

The radiolytic reduction of  $Cu(NO_3)_2$  in the Brij 30 system is different from those in the Triton X-100 and Brij 56 systems. Because Brij 30 can form W/O microemulsion free away from cosurfactant, *n*-hexanol, which was used as cosurfactant in the other two systems, is naturally questioned to affect the reduction of  $Cu(NO_3)_2$ . When *n*-hexanol was added to the Brij 30 system, the absorption spectrum and SAED analysis (SI-4, supporting information) showed that the reduction product is still Cu. Nevertheless, the aspect ratio of the rodlike Cu nanoparticles decreases (SI-4, supporting information). Thus, the above suspicion can also be excluded.

# 4. Discussion

The following equations [39] show the reducing reactions of  $Cu^{2+}$  by the reducing species, which are generated in the radiolysis of microemulsion, and the corresponding rate constants:

$$Cu^{2+} + e_{aq}^{-} \to Cu^{+}, \quad k = 3.3 \times 10^{10} \text{ L/(mol s)},$$
 (3)

$$Cu^{2+} + H \rightarrow Cu^{+} + H^{+}, \quad k = 9.1 \times 10^{7} L/(mol s),$$
 (4)

$$Cu^+ + e^-_{aq} \to Cu, \quad k = 2.7 \times 10^{10} \text{ L/(mol s)},$$
 (5)

$$Cu^+ + H \to CuH^+, \quad k = 5.0 \times 10^9 \text{ L/(mol s)}.$$
 (6)

It can be seen that  $e_{aq}^-$  plays an important role in the radiolytic reduction of Cu<sup>2+</sup>. Moreover, the disproportionation of Cu<sup>+</sup> can also produce Cu atoms:

$$2\mathrm{Cu}^+ \to \mathrm{Cu} + \mathrm{Cu}^{2+}.\tag{7}$$



Fig. 7. Morphology of the reduction product of CuSO<sub>4</sub> in the Brij 56-based microemulsion ( $\omega = 9.0$ ) by  $\gamma$ -irradiation in the presence of toluene (1.86 mol/L). The inset shows the SAED pattern.

However, a nonnegligible fact is that  $Cu_2O$  can be generated through the hydrolysis of  $Cu^+$ , which is the only source of  $Cu_2O$ :

$$Cu^+ + H_2O \rightarrow CuOH + H^+$$
,  $2CuOH \rightarrow Cu_2O + H_2O$ . (8)

Moreover, the addition of toluene or naphthalene can transform the reduction products from Cu to Cu<sub>2</sub>O in the Brij 56based microemulsion, and the efficiency of naphthalene is obviously higher than that of toluene. This indicates that electrons play a key role in the radiolytic reduction of CuSO<sub>4</sub> because the ability of naphthalene to scavenge  $e_{oil}^-$  is much stronger than that of toluene [38], while in regards of the ability to scavenge H, both of them are almost equal [39]. This is shown in Eqs. (1), (2) and the following equations:

$$C_{10}H_8 + e_{oil}^{-} \xrightarrow{\text{solvent: cyclohexane}} C_{10}H_8^{-},$$

$$k = 2.0 \times 10^{12} \text{ L/(mol s)},$$

$$C_{10}H_8 + \text{H} \rightarrow C_{10}\text{H}_9, \quad k = 3.4 \times 10^9 \text{ L/(mol s)}.$$
(10)

Although toluene and naphthalene are difficult to dissolve in water and Triton X-100 is mainly distributed at the interface, they can evidently affect the radiolytic reduction of CuSO<sub>4</sub>, implying that oil phase is the main source of  $e_{aq}^-$ . Therefore, the mechanism of radiolytic reduction of Cu<sup>2+</sup> in microemulsion should be clarified as follows.

#### 4.1. Effect of the $\omega$ value

As mentioned in the introduction, the yield of  $e_{aq}^-$  usually increases when the  $\omega$  value increases. Thus, it is not difficult to understand that the reduction product of Cu(NO<sub>3</sub>)<sub>2</sub> can be transformed from Cu<sub>2</sub>O to Cu when the  $\omega$  value is increased in the Brij 30 system (Table 1).

#### 4.2. Effect of anion

Table 2 shows the reactions between  $e_{aq}^-$  and different anions used in this work and the corresponding rate constants. It can be found that the rate constant of the reaction between  $e_{aq}^$ and NO<sub>3</sub><sup>-</sup> is much higher than those of other reactions. In other

Table 2 Rate constants for the reactions between  $e_{aq}^-$  and different anions [39]

Anion	Reaction	Rate constant (L/(mol s))
$NO_3^-$	$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}$	$9.7 \times 10^{9}$
$SO_4^{2-}$	$SO_4^{2-} + e_{aq}^{-} \rightarrow \text{products}$	$< 1.0 \times 10^{6}$
Cl-	$Cl^{-} + e_{aq}^{-} \rightarrow products$	$< 1.0 \times 10^{6}$

words, NO<sub>3</sub><sup>-</sup> can scavenge  $e_{aq}^-$  and decrease its yield effectively, while the ability of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> is much weaker. Although the rate constant of the reaction between  $e_{aq}^-$  and Br<sup>-</sup> is short, it can be supposed that the ability of Br<sup>-</sup> and Cl<sup>-</sup> to scavenge  $e_{aq}^-$  is similar because of their similar nature. Thus, in the Brij 56 system, it is easy to understand that the reduction product of Cu(NO<sub>3</sub>)<sub>2</sub> is Cu<sub>2</sub>O, while the reduction products of CuSO<sub>4</sub>, CuCl<sub>2</sub>, and CuBr<sub>2</sub> are Cu.

In the Triton X-100 system, the reduction products of CuCl<sub>2</sub> and CuBr<sub>2</sub> are different from that of CuSO<sub>4</sub>, which is not similar to the phenomenon in the Brij 56 system (Table 1). There may be a different mechanism of reduction. Kapoor et al. [42] have studied the influence of I<sup>-</sup> on the formation and stabilization of Cu nanoparticles and considered that I<sup>-</sup> can stabilize the Cu<sup>+</sup> intermediate and the final Cu nanoparticles. They also found that Cl<sup>-</sup> and Br<sup>-</sup> have similar behavior [42]. Here, it may be the X<sup>-</sup> (X = Cl, Br) that prevents the hydrolysis of Cu<sup>+</sup> and the generation of Cu<sub>2</sub>O. Thus, although the rate constant of the reaction of  $e_{aq}^-$  with SO<sub>4</sub><sup>2-</sup> is close to those of  $e_{aq}^$ with Cl<sup>-</sup> and Br<sup>-</sup>, the reduction product of CuSO<sub>4</sub> is Cu<sub>2</sub>O, while those of CuCl<sub>2</sub> and CuBr<sub>2</sub> are Cu in the Triton X-100 system (Table 1).

Besides the effect on the chemical composition, the anion can also affect the morphology of the reduction product of Cu<sup>2+</sup>. In the Brij 30 system, the morphologies of the radiolytic reduction products of Cu<sup>2+</sup> are different (Figs. 2C-2F). The aspect ratio of rodlike Cu nanoparticles obtained from Cu(NO<sub>3</sub>)<sub>2</sub> is obviously higher than those obtained from  $CuSO_4$  and  $CuCl_2$ . and rodlike Cu nanoparticles seldom appear when CuBr<sub>2</sub> is used as precursor. This does not accord with the Hofmeister series of anions,  $SO_4^{2-} > Cl^- > Br^- > NO_3^-$  [34], which was suggested to occur in the effect of anions on the morphology of Mg(OH)<sub>2</sub> nanoparticles [43]. Moreover, our result does not agree with the result of Pileni and co-workers [34], either. It was found that Cl<sup>-</sup> favored the generation of Cu nanorods with higher aspect ratio in the Cu(AOT)<sub>2</sub>-isooctane-water system, where hydrazine was used as a reducing agent [34]. This phenomenon was ascribed to the preferential adsorption of Cl<sup>-</sup> on the (001) faces and the faster growth on the (111) faces of Cu nanocrystals [34]. However, NO<sub>3</sub><sup>-</sup> did not exhibit a similar action [34]. Considering the different situation from that in the literature, we suggest here that the unique phenomenon of  $NO_3^-$  in this study can be attributed to its strong effect on the yield of  $e_{aq}^-$ . In detail, NO<sub>3</sub><sup>-</sup> can greatly decrease the yield of  $e_{aq}^$ and thus the rate of reduction to such an extent that the differbeen used to control the synthesis of nanoparticles, which is impossible in routine chemical methods. Moreover, anions, especially NO<sub>3</sub><sup>-</sup>, may affect the composition and morphology of nanoparticles via their effect on the yield of  $e_{aq}^-$ , which is remarkably different from the mechanism in routine chemical method. It is believed that the results reported herein will make the synthesis of nanoparticles in microemulsion more abundant. At the same time, our results further confirm the validation of the mechanism concerning the producing of  $e_{aq}^-$  in microemulsion and indicate its wide application in the controlled synthesis of nanoparticles. The generation, migration, and quenching of electrons can also afford us some structural information on microemulsions.

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# **Supporting information**

The online version of this article contains additional supporting information.

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