Phase Transfer of AMIET-functionalized Gold Nanoparticles from Aqueous to Organic Solvents

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Abstract: This paper presents a feasible and reliable phase transfer protocol for polyoxyethylene alkyl amine surfactant (AMIET)-coated gold nanoparticles (AuNPs) in aqueous media to chloroform using a pH-triggered method, through the liquid-liquid interface. In the initial stage, the colloidal aqueous dispersion is destabilized by pH adjustment towards the isoelectric pH of the nanoparticle, which promotes the separation of the particles from water. We further explored a mechanistic view of this phase transfer phenomenon, considering the orientation of hydrophilic and hydrophobic moieties depending on the nature of the surrounding solvent. It was proposed that the AMIET molecules bound to the AuNPs undergo conformational changes through phase transfer. Ultraviolet visible absorption spectra before and after the phase transfer reveal that the original morphology and dispersion states of the particles were preserved.

Key words: gold nanoparticles, polyoxyethylene alkyl amine, phase transfer

1 Introduction

Metallic nanoparticles differ markedly from their bulk counterparts because of their unique size and shape-dependent optical, electrical, and thermal properties. This difference can be attributed to their large surface area, large surface energies, plasmonic excitation, quantum confinement, and the presence of a large number of coordination sites. These unique properties could significantly impact their application in electronics, textile, catalysis, biomedicine, fuel cells, and so on. Among metal nanoparticles, gold nanoparticles (AuNPs) have attracted remarkable interest owing to their capability for strong absorption of electromagnetic waves in the visible region due to surface plasmon resonance, chemical inertness, and highly stable dispersion. The optoelectronic properties of AuNPs make them versatile materials for a broad range of applications such as sensory probes, electronic conductors, therapeutic agents, organic photovoltaics, drug delivery, and catalysis. Moreover, the optical and electronic properties of AuNPs can be tuned by changing their size, shape, and surface chemistry, which in turn broadens the scope of their application. However, while the nanoparticles (NPs) can be synthesized in both hydrophilic and hydrophobic media, the preparation of the desired particles in organic solvents requires more complicated and meticulous steps because of the low solubility of gold salts in the organic phase, and the complexity in controlling the size and shape of AuNPs.

In contrast, the synthesis of AuNPs in the aqueous phase is more prevalent because it is simple, rapid, and environmentally friendly. Moreover, the synthesis in aqueous media has many well-defined preparation procedures. Therefore, the synthesis of AuNPs in water is the most convenient and economical method, considering its applications. However, it is noteworthy to mention that the use of NPs in electrical elements requires the incorporation of metallic NPs that are free from contact with water, and are dispersed in an organic matrix as well. The organic dispersion is also mandatory for the formation of a thin film monolayer of AuNP to weaken the interfacial energy between metal NPs.

Furthermore, in organic catalysis, solution-processable optoelectronic applications, and composite materials, the nanoparticles are needed to be dispersed and stabilized in a nonaqueous liquid phase. Therefore, the transfer of AuNPs, especially from aqueous to water-immiscible organic solvents, is often required to increase their range of application and also to take advantage of the preparation...
process in water. However, the colloidal stability of NPs remains the critical issue with their phase transfer\(^{19}\). It is often challenging to transfer NPs from a stable colloidal system to another phase. Although numerous promising approaches have been carried out for the successful phase transfer of NPs from the aqueous to the organic phase, one of the major drawbacks of these techniques is either exploiting post-synthesis ligand exchange\(^{20}\), adding of cosolvents\(^{21}\), or employing ionic-liquids\(^{21, 22}\), which may disrupt the integrity of NPs in the second solvent. Several studies have been conducted using various methods for phase transfer. For instance, the centrifugation method was extensively studied by Lee et al.\(^{23}\), which is useful for organic solvents that are denser than water, and pH-sensitive zwitterionic amphiphiles were used for the recovery and redispersion of AuNPs\(^{24, 25}\). Imura et al. showed reversible phase transfer by changing the pH of the colloid\(^{26}\). Chakraborty and Christopher have also investigated the reusability of pH-responsive gold AuNP catalysts\(^{27}\). Despite their success, several critical issues exist, including incomplete transfer with few residual particles remaining in the aqueous phase and the instability of transferred NPs in non-aqueous solvents during storage. Additionally, most ligand exchange processes are applicable to very limited types of NPs\(^{18, 28}\). Therefore, it is necessary to develop a more general and robust phase transfer strategy for the dispersion of the synthesized AuNPs in the organic phase.

In this study, AuNPs were produced via a single-step synthesis with the reduction of tetra chloroauric (III) acid by AMIET, a polyoxyethylene alkyl amine surfactant with a weak cationic character. In the industry, AMIET has been used for various applications as an antistatic agent, emulsifier, dispersant, detergent for textiles, and so on, but in this work, it acts as a reducing and capping agent for AuNP synthesis. Furthermore, we present an effective, straightforward phase transfer method for laboratory-synthesized AMIET-AuNPs without the addition of any specific chemical. The phase transfer of AuNPs was investigated by applying three strategies to establish a robust and repeatable phase transfer methodology for AMIET-AuNPs: simple vigorous shaking 3-4 times daily, centrifugation method, and pH-triggered phase transfer method. It was observed that the phase transfer of AMIET functionalized AuNPs depends on the particle’s surface charge and its dispersion pH. Hence, this study attempted to destabilize the aqueous colloidal system by changing its pH to obtain nearly zero surface-charged particles\(^{29}\). Consequently, efficient phase transfer was promptly achieved at a state known as isoelectric pH. It has been suggested that the surface-bound ligand shell can undergo conformational changes depending on the surrounding solvents that favor the particles for phase transfer\(^{29, 30}\). Ultraviolet-visible (UV-vis) spectroscopy and scanning transmission electron micrographs confirmed that the particles preserve their size and morphology while transferring to chloroform. Furthermore, the ligand arrangement in both phases or the orientational changes of surface-bound AMIET have been explained and well supported by their nuclear magnetic resonance (NMR) spectra.

2 Experimental Section

2.1 Chemicals & apparatus

Hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl\(_4\cdot 4\text{H}_2\text{O}>99.0\%\)) was sourced from Fujifilm Wako Pure Chemicals and used as received. Polyoxyethylene alkyl amines (AMIET320 (HLB = 15.4), AMIET302 (5.1), AMIET105A (10.8), AMIET105 (9.8), and AMIET102 (6.3) (Fig. 1) were obtained from Kao Corporation and used for the synthesis of AuNPs. Because AMIETs have been produced from natural sources for industrial purposes, each AMIET is essentially a mixture of polyoxyethylene alkyl amines with a certain number of x + y in polyoxyethylene parts and distributed alkyl chain lengths. The safety data sheets indicate that AMIETs whose names began with 3 and 1 are polyoxyethylene hydrogenated tallow amines and polyoxyethylene cocoamines, respectively, and the last two digits express the total number of oxyethylene units (i.e., for AMIET320, x + y = 20). Sodium hydroxide (Kanto Chemical Co. Inc.), 37% hydrochloric acid (Kanto Chemical Co. Inc.), and chloroform (FUJIFILM Wako Pure Chemical Corporation) were used as received. Ultrapure water obtained by Merck Direct-Q UV was used both as a solvent and for cleaning the glass wares throughout the experiments. Prior to use, the glass wares were immersed overnight in a 5% Cica Clean (Kanto Chemicals) solution and sonicated with ultrapure water twice for 15 min, followed by drying for 3 h at 100°C in an electric oven.

2.2 Preparation of AuNPs

The AuNPs were prepared using a chemical reduction method. Initially, a fixed amount of AMIET and ultrapure water was heated in a three-necked round bottom flask (Table 1). When the temperature reached 80°C, a desired amount of 48.6 mM hydrogen tetrachloroaurate (III) tetrahydrate aqueous solution (yellow color) was added to the flask. After a few minutes, the entire solution became wine red, indicating the reduction of gold chloride with the surfactant and the formation of AuNPs. At this stage, the mixture was allowed to reflux for 1 h to ensure the completion of the reaction while maintaining a temperature of 100°C.
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J. Oleo Sci. 71, (5) 685-692 (2022)

The factors affecting the zeta potential include pH, ionic

80°C and a stirring rate of 100 rpm. Then heating was
turned off and the mixture was allowed to cool to room
temperature with continuous stirring. Finally, the synthe-
sized AuNPs were stored in a clean glass container with a
screw cap at room temperature.

2.3 Characterization

The UV-vis absorption spectra of the AuNPs were mea-
sured using a JASCO V-600 spectrometer with a 1 cm path
length quartz cuvette within the range of 300 nm – 700 nm,
and baseline correction was performed with ultrapure
water as reference. Zeta potential measurements were
carried out by laser Doppler electrophoresis using a Zeta-
sizer Nano ZS (Malvern) with a DTS1061-disposable
cuvette. The pH of the AMIET-AuNP dispersion was ad-
justed using 0.01 M HCl or 0.01 M NaOH and measured
using a pH meter (Mettler Toledo). Transmission electron
microscopy (TEM) observations were performed using a
JEOL JEM 2010 at an accelerating voltage of 200 kV with a
copper grid coated with an elastic carbon film (ELS-C10
STEM Cu100P, OKENSHOJI). To prepare size distribution
histograms, 100 particles were selected randomly from
TEM images to estimate their diameter using ImageJ soft-
ware. Proton nuclear magnetic resonance (NMR) spectra
were recorded using an Agilent-NMR-vnmr 500 spectrom-
eter to understand the ligand arrangement on the particle
surface upon phase transfer. In the preparation of NMR
samples.

3 Results and Discussion

3.1 Formation of AMIET-coated AuNPs

Research has been carried out previously on the strong
ability of tertiary amines to form AuNPs. Similar to this
research, AMIET as a tertiary amine contributed to the for-
mation of AMIET-coated AuNPs in the present work, as
confirmed by the appearance of a red color and surface
plasmon resonance absorption in the UV-vis absorption
spectra of the reaction solutions, as well as TEM obser-
vation of the formed particles. A photograph of the AMIET320-
AuNP aqueous dispersion is shown in Fig. 2(a), as an
example. All the reaction solutions showed a typical red
color, as shown in the photograph after the formation of
AuNPs. The typical wavelength of the absorption peak due
to surface plasmon resonance for spherical gold nanoparti-
cles varies from 520 to 530 nm. Therefore, the peaks ob-
served in the UV-vis spectra of the as-prepared AMIET-
AuNPs (Fig. 2(a) and Table 2) were assigned to the
characteristic surface plasmon resonance absorption of
spherical AuNPs. The complete conversion of Au⁺ to Au⁰
was confirmed by the absence of a peak near 300 nm, on
which is the characteristic peak of Au⁺⁺ due to ligand metal
charge transfer, although the corresponding wavelength
region of the spectra is not shown in Fig. 2(a). A TEM
image of the as-prepared AMIET320-AuNPs is shown in
Fig. 4. TEM observation also confirmed the formation of
spherical AuNPs of a few to 20 nm diameter for all AMIET-
AuNPs. Figure 5 shows the size distribution histograms
obtained through TEM image analysis of AMIET-AuNPs dried
from aqueous dispersions. Although all AMIET-AuNPs
were polydisperse and AMIET302-AuNPs were smaller
than those of the other AMIET-AuNPs, no difference was
observed in the phase transfer using the pH-triggered
method.

3.2 Determination of isoelectric point of AMIET-AuNPs

The factors affecting the zeta potential include pH, ionic

Table 1 Amounts of reactants in the synthesis of AMIET-coated
AuNPs.

| Surfactant     | AMIET | ultrapure water | 48.6 mM HAuCl₄ aq |
|---------------|-------|-----------------|-------------------|
| AMIET320      | 0.8 mL| 300 mL          | 2.5 mL            |
| AMIET302*     | 0.4 g | 200 mL          | 1.5 mL            |
| AMIET105A     | 1.0 mL| 300 mL          | 2.5 mL            |
| AMIET105      | 1.0 mL| 300 mL          | 2.5 mL            |
| AMIET102      | 0.3 mL| 300 mL          | 2.5 mL            |

* Solid at room temperature
strength, and concentration of the nanocolloid. However, pH is the most leading parameter in zeta potential measurements of NPs in an aqueous medium. The plots of zeta potentials as a function of pH are shown in Fig. 6 for different AMIET-AuNPs. The derived isoelectric points from the plots are 5.4 for AMIET320-AuNP, 7.9 for AMIET302-AuNP, 105A-AuNP, and 105-AuNP, and 9.0 for AMIET102-AuNP. Because AMIETs are mixtures of polyoxyethylene alkyl amines as mentioned above, the isoelectric point would be determined as averaged or apparent one due to the complicated effects of the ingredients; thus, it is not easy to fully understand the difference in isoelectric point on the basis of molecular structure. However, the number of ethyleneoxy (EO) units seems to have an effect on the isoelectric point because AuNPs prepared using AMIET320 with 20 EO units showed a much lower isoelectric point.

**Table 2** Wavelengths of surface plasmon peaks for AMIET-AuNPs as-prepared in water and after phase transfer in chloroform.

| AuNPs          | Wavelength / nm in water | Wavelength / nm in CHCl$_3$ |
|----------------|--------------------------|-----------------------------|
| AMIET320-AuNP  | 528                      | 529                         |
| AMIET302-AuNP  | 520                      | 533                         |
| AMIET105A-AuNP | 530                      | 524                         |
| AMIET105-AuNP  | 525                      | 527                         |
| AMIET102-AuNP  | 526                      | 525                         |

**Fig. 2** UV-vis spectra of AMIET-AuNP dispersions: (a) as-prepared AMIET-AuNPs in water and (b) after phase transfer to chloroform at isoelectric pH.

**Fig. 3** Photographs of AMIET320-AuNP dispersions: (a) as-prepared AMIET-AuNPs in water, (b) at isoelectric pH, followed by phase transfer to (c) chloroform.

**Fig. 4** A TEM image of as-prepared AMIET320-AuNPs.
compared to the other AuNPs coated by AMIETs with two or five EO units.

3.3 Phase transfer to organic solvent

Initially, the phase transfer experiments were performed by a simple addition method in which 5 mL of chloroform was added to 5 mL of AuNP dispersion, shaken vigorously, and then left for a few days (with shaking 3-4 times daily), in order to observe the phase transfer process. The phase transfer occurred by this method, but it was also observed that the holding periods for phase transfer were not identical. In addition, more than 90% of the particles moved towards the chloroform phase after 7 days, according to the decrease in intensity of the plasmon peak in the UV-vis spectra, but achieving complete transfer was expected to take a long time. The second attempt was made by the centrifugation method, where 5 mL of chloroform was added to 5 mL of AuNP dispersion and the mixture was centrifuged twice for 80 min using 10,000 rpm rotation. This method efficiently reduced the time for the phase transfer as compared to the simple addition and shaking method, but not all the cases recorded a complete transfer. An alternative approach is the pH-triggered method, in which the pH of the AuNP dispersion is adjusted to the isoelectric point. Using this method, it was confirmed that the AMIET rapidly functionalized AuNPs and efficiently transferred to the organic phase. The UV-vis spectra of AMIET-AuNPs in chloroform after phase transfer at the isoelectric points are shown in Fig. 2 (b). At the isoelectric point, the AuNPs may be in an unstable state, depending on the nature of the colloids (Fig. 3 (b)), but the phase transfer easily occurred immediately after the addition of the organic solvent (Fig. 3 (c)). The complete transfer of AuNPs was confirmed by UV-vis analysis of the aqueous phase after the transfer process, where no plasmonic absorption was observed (data not shown). In chloroform, as the refractive index of the solvents increases ($n_{\text{water}} = 1.33$, $n_{\text{chloroform}} = 1.45$), a small red shift of ~3 nm is typically observed$^{35}$. However, not all the peak positions of the spectra in Fig. 2 (b), which are summarized in Table 2, follow the expected change due to solvent exchange, suggesting that the dispersion state of AMIET-AuNPs would change de-

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Fig. 5 Size distribution histograms measured for AMIET-AuNPs dried from aqueous dispersions through TEM image analysis: (a) AMIET320, (b) AMIET302, (c) AMIET105A, (d) AMIET105, and (e) AMIET102-AuNPs.

Fig. 6 Plots of zeta potential vs pH of AMIET-AuNP dispersions.
pending on the solvent. Nevertheless, except for AMIET302-AuNPs, no significant change in the plasmon peak position was observed, which indicates that the dispersion state of AuNPs did not change significantly between water and chloroform. Even for AMIET302-AuNPs, although the peak position was shifted to a relatively large extent, the particles were stably dispersed in chloroform for a long time.

3.4 Interpretation of 1H-NMR results

The orientation of the hydrophobic and hydrophilic moieties of AMIET on AuNPs in both phases was evaluated by 1H-NMR spectra, based on the relative signal intensity depending on molecular mobility30, 36. Figure 7 presents the 1H-NMR spectra of AMIET and AMIET-AuNPs in CDCl3 and D2O. The signals of the terminal methyl head (peaks α) and methylene group (peaks β) of long alkyl chains were observed with high intensity whether AMIET molecules were free or bound to AuNPs in CDCl3, suggesting that the chains were exposed in the solvent. The signals of EO chains (peaks γ) also appeared in AMIET dissolved in CDCl3, which is due to the fact that the EO unit is not extremely hydrophilic because it contains two methylene units37 and thus soluble in organic solvents. However, the signals γ were weakened for the AMIET320-AuNP dispersion in CDCl3 and almost disappeared for the other AMIET-AuNPs in CDCl3, implying tight packing of the EO parts on the AuNPs. The weak appearance of the signal γ in the spectrum for the AMIET320-AuNP dispersion in CDCl3 arises from some parts of the longer EO chains (i.e., x + y = 20) which are not tightly fixed on the surface of the AuNPs. These observations indicate that the alkyl moiety is oriented toward CDCl3, whereas the EO chains are oriented away from CDCl3 (Fig. 8(a)), which makes the dispersion feasible and ensures nanoparticle stability in chloroform. In contrast, for AMIET molecules in D2O, the signals α and β were much weaker, and the signals γ appeared relatively strong. This tendency was enhanced for AMIET-AuNPs in D2O, except in the case of AMIET102-AuNP. The exception might be due to the fewer number of EO groups along with their close attachment to the AuNP surface. According to the observed changes in the relative intensity, the most

**Fig. 7** 1H-NMR spectra of AMIETs and AMIET-AuNPs in CDCl3 and D2O: (a) AMIET320, (b) AMIET302, (c) AMIET105A, (d) AMIET105, (e) AMIET102, and (f) assignments of NMR peaks (α to γ) with the molecular structure.

**Fig. 8** Schematic illustration of proposed surface ligand orientation in (a) chloroform and (b) water.
plausible orientation of AMIET molecules in D₂O would be the reversed one from the case in CDCl₃ (Fig. 8 (b)).

4 Conclusion
In this work, the preparation of AuNPs using AMIET via a simple heating method in an aqueous phase, and the phase transfer of the synthesized AuNPs to a chloroform phase without the addition of a surface modifier, were demonstrated. It was found that the phase transfer efficiently progressed while preserving the shape and size of AuNPs by the pH-triggered method, where the pH of the aqueous phase was adjusted to an isoelectric one. The changes in 1H-NMR spectra imply that the phase transfer would accompany the orientational switching of hydrophobic and hydrophilic groups of AMIET molecules depending on the environmental solvent. The present work not only confirms the emerging role of AMIET ligands but also predicts the very promising direction of using AMIET in direct synthesis as well as the phase transfer of AuNPs. Moreover, the pH-triggered phase transfer method would be advantageous for other combinations of aqueous/organic solvents other than water/chloroform, regardless of the density of the organic solvent. Experiments are underway on the phase transfer of AuNPs to nonaqueous solvents other than chloroform.

Acknowledgements
This work was supported by JSPS KAKENHI Grant Number JP18K05056. Md. Abdullah Al Nahid is very grateful to the MEXT of Japanese Government for the fruitful scholarship.

References
1) Khan, I.; Saeed, K.; Khan, I. Properties, applications and toxicities. Arab. J. Chem. 12, 908-931 (2019).
2) Sousa, L.M.; Vilarinho, L.M.; Ribeiro, G.H.; Bogado A.L.; Dinelli, L.R. An electronic device based on gold nanoparticles and tetraurathenated porphyrin as an electrochemical sensor for catechol. Royal Soc. Open Sci. 4, 170675 (2017).
3) Giannossa, L.C.; Longano, D.; Ditaranto, N.; Nitti, M.A.; Paladini, F. et al. Metal nanoantimicrobials for textile applications. Nanotechnol. Rev. 2, 307-331 (2013).
4) Liu, L.; Coroma, A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. Chem. Rev. 118, 4981-5079 (2018).
5) Chen, G.; Roy, I.; Yang, C.; Prasad, P.N. Nanochemistry and nanomedicine for nanoparticle-based diagnostics and therapy. Chem. Rev. 116, 2826-2885 (2016).
6) Stephen, A.J.; Rees, N.V.; Mikheenko, I.; Macaskie, L.E. Platinum and palladium bio-synthesized nanoparticles as sustainable fuel cell catalysts. Front. Energy Res. 7, 1-13 (2019).
7) Li, N.; Zhao, P.; Astruc, D. Anisotropic gold nanoparticles: Synthesis, properties, applications, and toxicity. Angew. Chem. Int. Ed. 53, 1756-1789 (2014).
8) Zhang, J.; Mou, L.; Jiang, X. Surface chemistry of gold nanoparticles for health-related applications. Chem. Sci. 11, 923-936 (2020).
9) Sapoletova, N.A.; Kushnir, S.E.; Kushnir, A.E.; Korcherginskaya, P.B.; Kazin, P.E.; Napol'skii, K.S. Simple phase transfer of nanoparticles from aqueous to organic media using polymer colloids as carriers. RSC Adv. 6, 112409-112412 (2016).
10) Terekhin, V.V.; Senchikhin, I.N.; Dement’eva, O.V.; Rudy, V.M. Conjugs of gold nanoparticles and poly(ethylene glycol): Formation in hydrosol, direct transfer to organic medium, and stability of organosols. Colloid Journal 77, 511-519 (2015).
11) Sachin, T.; Trupti, C.N.; Shaebrao, M.; Jalindar, D.A.; Bharat, B.K.; Nageshwar, D.K.: Ionic liquid-responsive phase transfer of gold nanoparticles: Anionic metathesis. Langmuir 35, 9213-9218 (2019).
12) Wang, X.; Xu, S.; Zhou J.; Xu, W. A rapid phase transfer method for nanoparticles using alkylamine stabilizers. J. Colloid Interface Sci. 348, 24-28 (2010).
13) López-Millán, A.; Zavala-Rivera, P.; Esquivel, R.; Carrillo, R.; Alvarez-Ramos, E. et al. Aqueous-organic phase transfer of gold and silver nanoparticles using thiol-modified oleic acid. Appl. Sci. 7, 273 (2017).
14) Soliwoda, K.; Tomaszewska, E.; Tkacz-Szczesna, B.; Rosowski, M.; Celichowski, G.; Grobelny, J. The influence of the chain length and the functional group steric accessibility of thiols on the phase transfer efficiency of gold nanoparticles from water to toluene. Pol. J. Chem. Technol. 16, 86-91 (2014).
15) Radoszewski-Soliwoda, K.; Girleanu, M.; Tkacz-Szczesna, B.; Rosowski, M.; Celichowski, G. et al. Efficient surface functionalization of gold nanoparticles: Towards controlled nanoparticle dispersion in a polymer matrix. J. Nanomater. 2016, 9058323 (2016).
16) Serrano-Montes, A.B.; De Aberasturi, D.J.; Langer, J.; Giner-Casares, J.J.; Scarabelli, L. et al. A general method for solvent exchange of plasmonic nanoparticles and self-assembly into SERS-active monolayers. Langmuir 31, 9206-9213 (2015).
17) Zhou, J.; Cao, X.; Li, L.; Cui, X.; Fu, Y. A novel strategy for fabricating a strong nanoparticle monolayer and its enhanced mechanism. Nanomaterials 9, (2019).
18) Cao, M.; Liu, Q.; Chen, M.; Yang, P.; Xu, Y. et al. Dispersing hydrophilic nanoparticles in nonaqueous solvents with superior long-term stability. RSC Adv. 7,
25535-25541 (2017).

19) Yu, W.; Xie, H. A review on nanofluids: Preparation, stability mechanisms, and applications. Journal of Nanomaterials J. Nanomater. 2012, 435873 (2012).

20) Honold, T.; Skybeck, D.; Wagner, K.G.; Karg, M. Fully reversible quantitative phase transfer of gold nanoparticles using bifunctional PNIPAM ligands. Langmuir 33, 253-261 (2017).

21) Kittler, S.; Hickey, S.G.; Wolff, T.; Eychmüller, A. Easy and fast phase transfer of CTAB stabilised gold nanoparticles from water to organic phase. Z. Phys. Chem. 229, 235-245 (2015).

22) Qu, M.; Chen, S.; Ma, W.; Chen, J.; Kong, K. et al. Phase Transfer of nanoparticles using an amphiphilic ionic liquid. Langmuir 32, 13746-13751 (2016).

23) Park, J.O.; Cho, S.H.; Lee, J.S.; Lee, W.; Lee, S.Y. A foolproof method for phase transfer of metal nanoparticles via centrifugation. Chem. Commun. 52, 1625-1628 (2016).

24) Morita-Imura, C.; Zama, K.; Imura, Y.; Kawai, T.; Shindo, H. Stimuli-responsive extraction and ambidextrous redispersion of zwitterionic amphiphile-capped silver nanoparticles. Langmuir 32, 6948-6955 (2016).

25) Popowich, A.; Zhang, Q.; Le, X.C. Removal of nanoparticles by coagulation. J. Environ. Sci. (China) 38, 168-171 (2015).

26) Imura, Y.; Morita, C.; Endo, H.; Kondo, T.; Kawai, T. Reversible phase transfer and fractionation of Au nanoparticles by pH change. Chem. Commun. 46, 9206-9208 (2010).

27) Chakraborty, S.; Kitchens, C.L. Modifying ligand chemistry to enhance reusability of pH-responsive colloidal gold nanoparticle catalyst. J. Phys. Chem. C 123, 26450-26459 (2019).

28) Van Der Vegt, N.F.; Nayar, D. The hydrophobic effect and the role of cosolvents J. Phys. Chem. B 121, 9986-9998 (2017).

29) Surawanvijit, S.; Kim M.; Cohen, Y. Analysis of membrane filtration efficiency for the removal of metal oxide nanoparticles from aqueous nanoparticle suspension with feed coagulation pretreatment. NSTI-

30) Sekiguchi, S.; Niikura, K.; Matsuo, Y.; Ijiro, K. Hydrophilic gold nanoparticles adaptable for hydrophobic solvents. Langmuir 28, 5503-5507 (2012).

31) Rossi, L.M.; Fiorio, J.L.; Garcia, M.A.; Ferraz, C.P. The role and fate of capping ligands in colloidally prepared metal nanoparticle catalysts. Dalton Trans. 47, 5889-5915 (2018).

32) Kamo, H.; Ishibashi, H.; Kobayashi, T. Preparation of concentrated gold nanoparticle paste and its application to paint colorant. J. Jpn. Soc. Colour Mater. 76, 469-475 (2003).

33) Murawska, M.; Skrzypczak, A.; Kozak, M. Structure and morphology of gold nanoparticles in solution studied by TEM, SANS and UV-Vis. Acta Physica Polonica A 121, 888-892 (2012).

34) King, S.R.; Massicot, J.; McDonagh, A.M. A straightforward route to tetrachloroauric acid from gold metal and molecular chlorine for nanoparticle synthesis. Metals 5, 1454-1461 (2015).

35) Wielgus, M.; Gordel, M.; Samoć M.; Bartkowiak, W. Solvent effects on the optical properties of PEG-SH and CTAB capped gold nanorods. Acta Physica Polonica A 130, 1380-1384 (2016).

36) Tsekov, R.; Georgiev, P.; Simeonova S.; Balashev, K. NMR techniques for noble metal nanoparticles. Comptes Rendus de l’Academie Bulg. des Sci. 70, 1237-1246 (2017).

37) Salager, J.L. Surfactants: types and uses. Teaching aid in surfactant science and engineering, Laboratory of Formulation, Interfaces, Rheology, and Processes, Firp Booklet # E300-A. 2 (2002).

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