Recent progress in the synthesis
of luminescent copper clusters

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Abstract. Luminescent metallic clusters have attracted great interest due to their unique optical, electronic and chemical features. Comparing with intensively studied Au and Ag Clusters, Cu clusters are superior in the aspects of cost and wide industrial demanding. However, tiny copper clusters are extremely prone to aggregate and undergo susceptibility of oxidation, thereby the synthesis of fluorescent zero valent copper clusters is rather challenging. In this review, synthetic strategies towards luminescent copper clusters, including macromolecule-protection and micro molecule-capping, have been systematically surveyed. Both "bottom-up" and "top-down" synthetic routes are found to be effective in fabricating luminescent copper clusters, some of which are quite stable and possess decent luminescence quantum yields. In general, the synthesis of fluorescent copper clusters remains at its infant stage. A great deal of effort on developing novel and economic synthetic routes to produce bright and stable copper clusters is highly expected in future.

Keywords: photoluminescence; copper clusters; synthesis; metal nanoclusters; chemical synthesis

1. Introduction

Metallic clusters (MCLs), composed of several to hundreds of atoms, have attracted tremendous attention during the last decades because of their unique physical and chemical properties (Chakraborty 1998, Aiken and Finke (1999), Widegren and Finke 2003, Wilcoxon and Abrams 2006, Shang *et al.* 2011). Photoluminescence is one intriguing feature that emerges as the size of MCLs becomes comparable to electrons' Fermi wavelength (Zhang and Wang 2014). The strong quantum confinement effect, which arises from such ultra small dimension, changes continuous density of states into discrete energy levels (Zheng *et al.* 2004). Therefore, luminescent MCLs are significantly different from either nanoparticles or atomic metals (Jin *et al.* 2011), and have valuable applications in biology, environment and energy fields (Mathew and Pradeep 2014). Due to relative high quantum yield and stability, fluorescent gold and silver clusters have been extensively investigated (Zheng *et al.* 2004, Liu *et al.* 2006, Wu *et al.* 2009, Xu and Suslick 2010, Choi *et al.* 2011, Yang *et al.* 2011, Pal and Kryschi 2015, Pyo *et al.* 2015). However, luminescent

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Cu CLs have also attracted increasingly interest in recent years as copper is more abundant. Compared to their noble counterparts (Au, Ag), less expensive Cu clusters possess similar properties, and relevant studies are of fundamental and practical significance.

It is widely accepted that tiny Cu clusters possess an extremely high surface energy and activity, resulting in a great tendency to aggregation and oxidation. Therefore, the synthesis of luminescent Cu clusters with sizes normally less than 3 nm is quite challenging but intriguing (Vazquez-Vazquez *et al.* 2009). A variety of macromolecule-templated and micromolecule-capped Cu clusters had been synthesized and investigated in the past years, emitting from blue to red coloured light (Ghosh *et al.* 2014, Jia *et al.* 2014, Liu and Wang 2014, Zhou *et al.* 2015). The copper clusters can be used as chemical sensors, bio-labelling agents or catalysts, as reported by many researchers (Vilar-Vidal *et al.* 2012, Cao *et al.* 2014, Ghosh *et al.* 2014). However, most of those clusters are inferior in fluorescence quantum yields (QYs), some of which are even instable under ambient condition (Zhang *et al.* 2012). These drawbacks have hampered the Cu clusters from deep fundamental studies and further industrial applications. As a result, to prepare stable and efficient fluorescent Cu clusters is highly desired although it is very challenging.

The synthetic strategies, properties and applications of gold and silver clusters have been intensively reviewed in literature (Shiang *et al.* 2012, Zheng *et al.* 2012, Udayabhaskararao and Pradeep 2013, Qu *et al.* 2015). However, little survey was directed to the synthesis of copper clusters. In this short review, we will focus on the synthetic routes towards the preparation of fluorescent zero-valent Cu clusters, to provide an overall perspective and a guideline on controllably fabricating luminescent Cu clusters.

2. Protecting stabilizers for luminescent Cu clusters

Cu clusters composed of 2~9 atoms were theoretically capable of existing stably (Poater *et al.* 2006). However, in practice, these ultra-small copper particles possess a great tendency to aggregation. Thus stabilizers are generally required in synthesis to prevent nanometer-sized or even smaller clusters from aggregating into larger ones. The often used protecting stabilizers are divided into two major classes: one mainly includes some macromolecules such as dendrimers, polymers, proteins and DNA, which are usually used as templates; and the other one refers to micromolecules like amino acids, peptides and thiols, which are also regarded as small capping ligands.

2.1 Macromolecule-protected Cu clusters

Various template synthetic methods based on macromolecules have been used in the preparation of MCLs (Fig. 1(a)), Normally, these templates require a strong capability of sequestering metal ions from solution. In this regard, dendrimers are the appropriate candidate for producing MCLs (Zheng and Dickson 2002, Zheng *et al.* 2003). Early in 1998, Zhao and colleagues managed to produce different sized zero-valent copper clusters by using poly(amidoamine) (PAMAM) as a template (Balogh and Tomalia 1998). The size of obtained clusters is around 1.8 nm, much smaller than that of common Cu NPs (e.g., ~10 nm), leading to the loss of characteristic plasmon resonance absorption at 560~600 nm. However, unlike gold nanoclusters (QY~40%) (Zheng *et al.* 2003), using dendrimers in fabricating highly fluorescent Cu clusters seems to be less successful. Jie Feng and coworkers applied branched polyethyleneimine

(a) Template-based synthetic methods
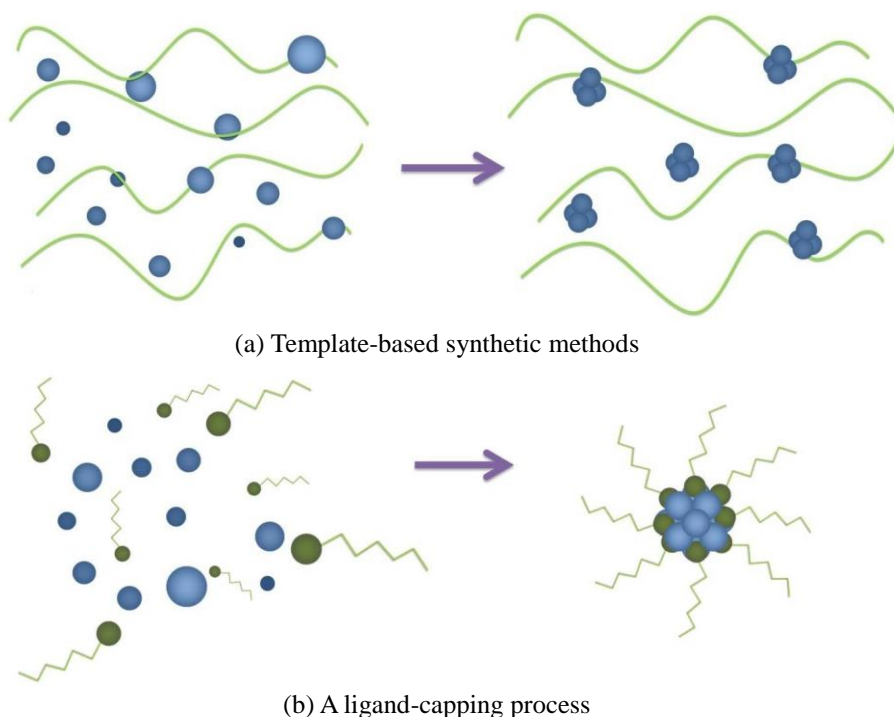

(b) A ligand-capping process

Fig. 1 The preparation of MCLs through different synthetic routes

(BPEI) as capping scaffold to synthesize blue-emitting Cu clusters (Feng *et al.* 2015), reaching a QY of only 2.1%. This is even much lower than that of some micromolecule-capped clusters. Besides dendrimers, polymers like polyethylene glycol (PEG) (Blosi *et al.* 2010, Fernandez-Ujados *et al.* 2013), polyethylene glycolpoly(methacrylic acid) functionalized with pentaerythritol tetrakis 3-mercaptopropionate (PTMP-PMAA) (Zhang *et al.* 2012), polyethyleneimine (PEI) (Ling *et al.* 2014), tannic acid (TA) (Cao *et al.* 2014, Cao *et al.* 2015), are reported to be effective in improving the emission of Cu clusters. PEG-capped Cu clusters were obtained by two different novel strategies, giving significantly different QYs of 0.65 % (Blosi *et al.* 2010) and 3.6 % (Fernandez-Ujados *et al.* 2013), respectively (Table 1), TA-protected Cu clusters (Cao *et al.* 2014) are blue emitting (emission centered at 430 nm, QY=17%) while PEI-encapsulated ones are green fluorescent (emission centered at 480 nm, QY=3.8%), And their luminescence can be quenched by Fe^{3+} ions. In addition, some biological macromolecules like DNA (Jia *et al.* 2012) and proteins (Goswami *et al.* 2011, Ghosh *et al.* 2014) have also been applied as templates. Those successful attempts have rendered macromolecule encapsulated Cu clusters' promising applications in biological field (Liu 2014). It is noteworthy that the QYs of those proteins-templated Cu clusters are quite high. For example, BSA-capped Cu clusters' QY was reported to be 15%, with an emission band centered at 406 nm (Goswami *et al.* 2011), applicable in sensing Pb^{2+} (Fig. 2(a)) . In addition, lysozyme-templated Cu clusters are also highly fluorescent (Ghosh *et al.* 2014), giving a QY as high as 18%. And more interestingly, these lysozyme-templated clusters' emission shows a wavelength-dependent character. However, macromolecule-protected MCLs generally have a large hydrodynamic layer (~3 nm, as shown in Table 1), which may bring limitation to their potential applications (Adhikari and Banerjee 2010)，such as catalysts. In contrast to those "large" particles,
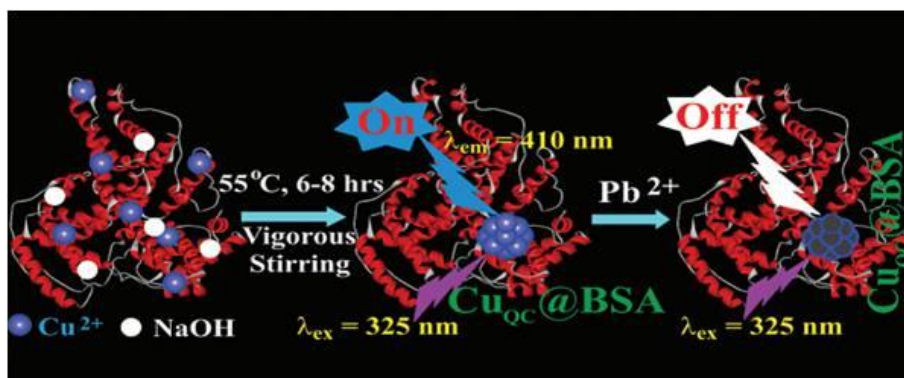
(a) BSA-encapsulated Cu clusters applied as sensing Pb^{2+} ions in aqueous environment. (Reprinted with permission from (Goswami *et al.* 2011). Copyright 2011 American Chemical Society.)
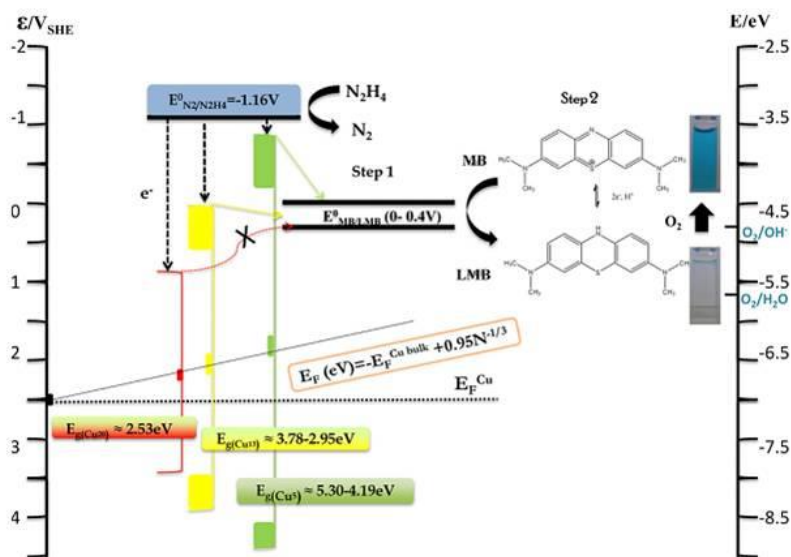
(b) TBA-capped Cu_{13} clusters used as a catalyst in the reduction of methylene blue by N_2H_4. (Reprinted with permission from (Vilar-Vidal *et al.* 2012). Copyright 2012 American Chemical Society)

Fig. 2 The applications of both macromolecule and micromolecule-capped Cu clusters

micromolecule-capped MCLs with much smaller hydrodynamic radius have attracted continuously increasing attention in recent years, due to their inimitable and excellent optical, electronic and catalytic features.

2.2 Micromolecule-capped Cu clusters

Different from macromolecules, applying micromolecular stabilizers in the synthesis of luminescent MCLs normally refer to a ligand-capping process (some amino acids and peptides can also act as templates), in which monolayer-protected clusters are usually produced (Fig. 1(b)), Thiols are found to have a quite strong affinity with transition metal like gold and silver. Thus thiols-based compounds are effective and most applied in producing fluorescent MCLs (Jin 2010).

Table 1 Cu clusters obtained by various "bottom-up" synthetic strategies according to recent reports

Stabilizer	Method	$\lambda_{ex}/\lambda_{em}$ (nm)	QY (%)	Size (nm)	Reductant	Ref
TBA	ED	300/410	13	0.61	-	(Vilar-Vidal *et al.* 2010)
TA	HBS	360/430	14	2.2	AA	(Cao *et al.* 2014)
PEG	MA	355/475	0.65	2.3	-	(Blosi *et al.* 2010)
PEG	HBS	320/416	3.6	2.5	$NaBH_4$	(Fernandez-Ujados *et al.* 2013)
DPA	BR	345/418,640	14.1	1.0	-	(Jia *et al.* 2014)
PTMP-PMAA	PR	360/630	2.2	0.7	-	(Zhang *et al.* 2012)
BSA	BR	325/406	15	2.8	-	(Goswami *et al.* 2011)
SDS	MP	290/333	-	< 0.8	$NaBH_4$	(Vazquez-Vazquez *et al.* 2009)
BTA	HBS	-	-	-	$NaBH_4$	(Salorinne *et al.* 2012)
MPP	HBS	364/425,593	3.5,0.9	-	$NaBH_4$	(Wei *et al.* 2011)
PAMAM	HBS	-	-	< 1.8	$NaBH_4$	(Balogh and Tomalia 1998)
TGA	HBS	305/491	3.7	2.3	$N_2H_4 \cdot H_2O$	(Liu and Wang 2014)
dsDNA	HBS	344/593	-	1.69	AA	(Jia *et al.* 2012)
L-histidine	BR	350/456	1.6	-	-	(Zhao and Huang 2014)
PET	Solid-phase	403/615	-	1.4	$NaBH_4$	(Ganguly *et al.* 2013)
DHLA	HBS	342/590	-	1.8	THPC	(Zhou *et al.* 2015)
lysozyme	HBS	375/450	18	2.3	$N_2H_4 \cdot H_2O$	(Ghosh *et al.* 2014)
L-cysteine	BR	375/480	14.3	2~3	-	(Yang *et al.* 2014)
PEI	HBS	355/480	3.8	1.8	$N_2H_4 \cdot H_2O$	(Ling *et al.* 2014)
BPEI	HBS	360/430	2.1	1	AA	(Feng *et al.* 2015)
GSH	BR	380/600	3.6	1~3	-	(Luo *et al.* 2015)
GSH	HBS	390/617	-	-	$N_2H_4 \cdot H_2O$	(Gao *et al.* 2015)

However, unlike gold, copper possesses a weaker interaction with the mercapto group (Udayabhaskararao and Pradeep 2013). Because of this, it remains possible for ultra small thiols-capped copper clusters to unceasingly grow into large particles, thus losing their luminescence property. With the development of techniques, however, more and more fluorescent thiols-capped copper clusters have been successfully prepared. Red emitting Cu clusters capped by D-penicillamine (DPA, QY=14.1%) (Jia *et al.* 2014), glutathione (GSH, QY=3.6%) (Luo *et al.* 2015), 2-phenylethanethiol (PET) (Ganguly *et al.* 2013), and orange emitting Cu clusters protected by dihydrolipoic acid (DHLA) (Zhou *et al.* 2015), were recently reported. Among them, DPA and DHLA-protected Cu clusters were very stable and capable of detecting H_2O_2, while GSH-capped Cu clusters were found to be sensible to pH change and vitamin B1. It is worth mentioning that aggregation induced emission was observed from DPA-capped Cu clusters, evinced by PL and TEM measurements (Jia *et al.* 2014). Such process usually occurs as the cluster size becomes extremely small, and similar phenomena have also been reported by other researchers (Jia *et al.* 2013, Liu and Wang 2014). Besides thiols, amine compounds are found to be effective as well.

Through a particular electrochemical method, Vilar-Vidal's group prepared blue emitting Cu clusters using tetrabutylammonium (TBA) as capping agent (Vilar-Vidal *et al.* 2010). The as-prepared clusters turned out to be quite versatile, useful in chemical sensing (Vilar-Vidal *et al.* 2014), catalytic (Fig. 2(b)) (Vilar-Vidal *et al.* 2012) and photocatalytic reactions (Vilar-Vidal *et al.* 2014). In addition, L-histidine was used as template to synthesize green emitting Cu clusters (Zhao and Huang 2014), which were found to be capable of sensing guanosine 5'-triphosphate (GTP),

Note that most of stabilizers normally possess a carbon chain composed of more than 5 carbon atoms. Although extreme short carbon chain may bring difficulties in producing luminescent MCLs, there are still a few of successful cases using short carbon-chain compounds as capping ligands. A water soluble, green light-emitting Cu_5 cluster (QY=3.7%) capped by thioglycollic acid (TGA) had been successfully synthesized (Liu and Wang 2014). It's a stabilizer with the shortest carbon chain (two-carbon) reported so far. Furthermore, *L*-cysteine (Yang *et al.* 2014, Cui *et al.* 2015), an amino acid with a three-carbon chain, was also applied in synthesizing green fluorescent Cu clusters, with an unusual high QY of 14.3% (Yang *et al.* 2014). Therefore, the carbon-chain length of micromolecular stabilizers plays an important role in preparing luminescent Cu clusters, and systematic studies in this regard are necessary.

3. The synthetic routes of luminescent Cu clusters

Besides the stabilizers, the routes of synthesizing copper clusters can be generally classified as two categories, namely "bottom-up" and "top-down" routes.

3.1 "Bottom-up" synthetic route

"Bottom-up" synthetic approach, the earliest developed and widely adopted one, is a "size-up" route where "bottom" refers to the atomic metals while "up" to the resulted clusters. For preparing fluorescent Cu clusters, various "bottom-up" synthetic methods have been exploited in recent years, such as homogeneous Brust-Schiffrin method (HBS) (Balogh and Tomalia 1998, Wei *et al.* 2011), blend and reflux (BR) (Goswami *et al.* 2011, Zhao and Huang 2014), photoreduction (PR) (Zhang *et al.* 2012), electrochemical deposition (ED) (Vilar-Vidal *et al.* 2010), microwave-assisted method (MA) (Kawasaki *et al.* 2011), multiphase synthetic route (MP) (Vazquez-Vazquez *et al.* 2009) and so on. Table 1 gives an overview of Cu clusters prepared by various "bottom-up" strategies.

3.1.1 Homogeneous "Brust-Schiffrin" method
Wet chemical reduction is the most frequently and commonly adopted strategy because of its operational simplicity and facile preparation conditions. In a typical wet chemical reduction process, metal-stabilizer complex is primarily generated and then further reduced by reductants to form MCLs in an appropriate solvent. The initial success in synthesis of stable MCLs with this wet chemical reduction strategy could date back to 1995 when one-phase "Brust-Schiffrin" method was reported (Brust *et al.* 1995). Since then, various luminescent gold and silver clusters have been prepared through such or analogous strategies (Shang *et al.* 2011, Udayabhaskararao and Pradeep 2013).

As for the synthesis of luminescent copper clusters, the wet chemical reduction method is

equally popular. By using a modified "Brust–Schiffrin" method, Wei and coworkers (Wei *et al.* 2011) obtained an ethanol soluble Cu clusters (mainly Cu_8) with dual emissions at 492 nm (QY=3.5%) and 593 nm (QY=0.9%) by reduction with $NaBH_4$. By reducing $CuSO_4$ with ascorbic acid, Cao and colleagues obtained tannic acid-capped copper clusters (QY=17%) (Cao *et al.* 2014). Using the same reductant, Jia and coworkers prepared DNA-hosted copper clusters by reducing $Cu(NO_3)_2$ in the presence of DNA duplex (Jia *et al.* 2012). Some other copper clusters by applying this approach can also be found, as shown in Table 1.

As an indispensable element in a typical wet chemical system, the employed reductant's reduction capacity may greatly influence the formation of products. Various compounds have been chosen as reductants in the preparation of copper nanoclusters, such as $NaBH_4$, hydrazine hydrate, ascorbic acid (AA) and so on (Table 1), Note that $NaBH_4$ is the most popular reducing agent used in synthesizing MCLs due to its strong reducing capacity. But mild reductants are sometimes more preferred in consideration of obtaining a monodisperse, size-selective system, as reported in Ghosh's previous work (Ghosh *et al.* 2012). Lisieck found that, as a reducing agent, hydrazine is more effective than $NaBH_4$ in producing copper clusters (Lisieck and Pileni 1993). And in some situations such as template-based synthesis, mild reducing agent is necessarily demanded in the presence of strong stabilizer, since low reducing rate will favor the sequestering process by stabilizers and generation of luminescent clusters (Qu *et al.* 2015). Therefore, a suitable reducing agent is a key factor to select when applying wet reduction method to synthesize Cu clusters.

On the other hand, the addition of extra reducing agent will inevitably introduce impurities into the resultant system, although the reductant is sometimes necessary in preparing a metal cluster. The existence of impurities will inevitably complicate the purification procedure, thus synthesizing metal clusters in the absence of extra reductants appears more favorable.

3.1.2 Blend and reflux method

In many cases, stabilizers themselves possess a certain reducing capacity. Jia and coworkers obtained highly fluorescent Cu clusters by simply blending DPA and $Cu(NO_3)_2$ in water under vigorous stirring (Jia *et al.* 2014). Similar work using blend strategy was also reported by Goswami's group (Goswami *et al.* 2011). In some situation, stabilizers fail to fully reduce the metal precursor mainly due to inappropriate preparation conditions, for instance, under the ambient condition. Stabilizers may require high temperature to overcome the energy barrier to completely reduce metal ions. Therefore, a protocol like reflux method would be suitable. Zhao and colleagues successfully obtained aqueous-soluble copper clusters (Cu_3~Cu_8, QY=1.6%) after refluxing the solution of $CuCl_2$ and histidine for 12 h at 70°C (Zhao and Huang 2014). In this process, histidine acted as both stabilizer and reducing agent. Taking advantage of the appropriate reducing capacity of the imidazole group from histidine, Cu^{2+} ions were reduced and luminescent copper clusters were formed (Yang *et al.* 2011). The reflux method offers a relatively high temperature for the formation of Cu clusters, which also avoids the introduction of extra reducing agent. However, specific reaction conditions need to be discreetly controlled in this kind of synthesis, to prevent any possible aggregation or overreaction.

3.1.3 Microwave-assisted method

Another applicable synthetic protocol without additional reducing agents is microwave-assisted method. It has been previously utilized in fabricating carbon quantum dots (Yang *et al.* 2013), and also increasingly adopted in the synthesis of MCLs. Hideya Kawasaki and coworkers reported a microwave-assisted synthetic method to prepare blue-fluorescent Cu clusters (~2 nm, QY=0.65%)

(Kawasaki *et al.* 2011) after they successfully obtained platinum and palladinum nanoclusters through almost the same route (Kawasaki *et al.* 2010, Hyotanishi *et al.* 2011). The peak reaction temperature using this method was as high as 185℃, without the presence of additional reducing agents.

3.1.4 Photoreduction method

Even if the used protecting stabilizer doesn't have enough reducing capability, or the preparative condition such as temperature of the system is too mild to trigger the desired reaction, MCLs can still be synthesized without additional reductant. Zhang's group reported a facile one-step method to prepare polymer ligands-capped Cu clusters (Cu_5, QY=2.2%) through a simple, fast photo-reduction method (Zhang *et al.* 2012), where Au (Au_5, QY=5.3%), Ag (Ag_5, QY=6.8%) clusters were also produced by the same approach. The thioether polymer ligand was firstly synthesized by functionizing poly (methacrylic acid) with pentaerythritol tetrakis 3-mercaptopropionate, and then mixing with $Cu(NO_3)_2$ solution to produce luminescent copper clusters under ultraviolet irradiation. The introduction of UV light drives the polymer ligands' sequestering process of the metal ions, lowering down the required preparative temperature and thereby accelerating the reaction process. However, over-long period of irradiation would lead to the quenching of the formed clusters' fluorescence (Zhang *et al.* 2012).

The quantum yields of some clusters prepared through these reductant-free methods described above, however, are relative low (QY< 5%), To tackle this issue, it's imperative to introduce a quite different synthetic protocol, named as electrochemical synthetic approach. Unlike traditional chemical synthesis, similarly extra reducing agent-free electrochemical synthetic route may bring more superiority in producing highly fluorescent copper clusters.

3.1.5 Electrochemical synthetic method

Reetdz and coworkers firstly reported on a simple electrochemical method that has been widely applied in the synthesis of various nanoparticles or clusters (Reetz and Helbig 1994, Chang *et al.* 1999, Morales and Santos 1999). By simply adjusting the current density, the size of the as-prepared particles can be controlled (Rodríguez-Sánchez *et al.* 2000, Rodríguez-Sánchez *et al.* 2005). Using a modified Reetdz's method, Vilar-Vidal (2010) obtained tetrabutylammonium nitrate-capped Cu_n clusters (~Cu_{14}) with a fluorescence quantum yield as high as 13%, remarkably higher compared to many Cu clusters prepared by wet chemical synthetic methods. During the synthesis process, Cu^{2+} ions were at first produced by the electrolysis of Cu anode and then reduced and capped at the Pt cathode under a certain current density. The current here, an external driving force similar to what the photons act in the photoreduction method, play an extremely significant role as both oxidizing and reducing agent towards controlling the final dimensions of resultant copper nanoclusters. In addition, the number of Cu core (Cu_5, Cu_{20}) can also be regulated by utilizing different purification and heat treatments (Vilar-Vidal *et al.* 2012).

3.1.6 Multiphase synthetic method

For the regular wet chemical reduction methods discussed above, they mostly involve a one-phase environment, where the metal's reducing reactions take place homogeneously. But heterogeneous synthetic routes are found to be also effective. Researchers have managed to develop a variety of multiphase methods to prepare fluorescent MCLs in recent years. The Brust-Schiffrin method, known as the most influential one, is based on a two-phase strategy (Brust *et al.* 1994). Heterogeneous environment, like interfaces and micelles, provides "templates" or

"nano-cages" for the nucleation and growth of MCLs (Capek 2004). As early as in 1993, Lisieck and colleagues obtained copper clusters with sizes varying from 2 to 10 nm by applying a reverse micelle method (Lisieck and Pileni 1993). And in 2009，Vazquez and coworkers prepared size-tunable copper clusters with a microemulsion technique (Vazquez-Vazquez *et al.* 2009). They found that different dosage of reductant would lead to various sized Cu particles, and only Cu_n ($n \leq 13$) would possess the property of photoluminescence by using the least reducing agent. This kind of water-in-oil microemulsion method have been discovered to be capable of precisely controlling the resultant nanoparticles' size and shape (López-Quintela 2003, López-Quintela *et al.* 2004).
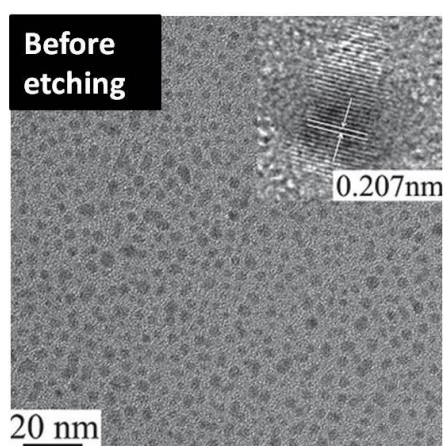
3.2 "Top-down" synthetic route

Ultra small clusters can also be prepared by etching large particles. And this is widely accepted as a "up-bottom" or "top-down" synthetic route, a newly developed and exploited strategy. "Etching" is the core concept of this synthetic protocol. Ligand-exchange method and phase transfer method are two mainly applied approaches in the synthesis of fluorescent copper clusters.

### 3.2.1 Ligand-exchange method

It can be literally understood that this method involves a process of ligand exchange, in which excessive etchant etches the surface of metal nanoparticles, producing etchant-capped MCLs with a relatively smaller size. Etchants can be small molecules (thiols) (Muhammed *et al.* 2008, Lin 2009) or macromolecules (e.g., BSA), and various etching routes have been developed to produce fluorescent Au and Ag nanoclusters.

Glutathione (GSH), a tripeptide with a mercapto group, is intensively applied as a protecting stabilizer in the "bottom-up" synthesis of luminescent MCLs. Moreover, GSH is also a frequently-used etchant (Lin 2009). Jia and colleagues recently etched non-fluorescent, ascorbic acid reduced and capped Cu nanoparticles into fluorescent, subnanometer-sized Cu nanoclusters by utilizing GSH as a etchant (Jia *et al.* 2013). During the etching process, the size of copper
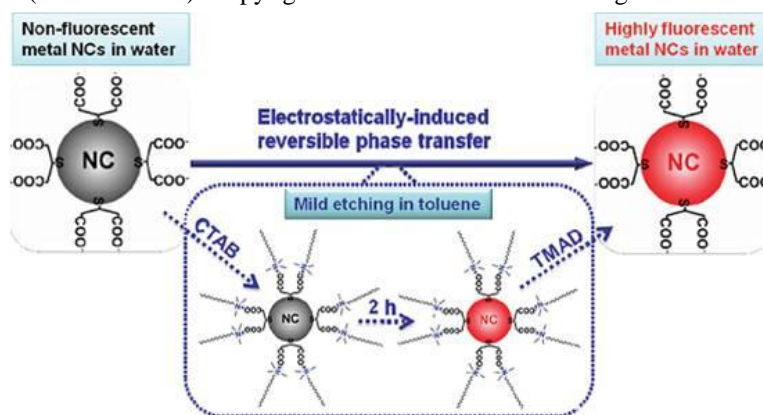

(a) HRTEM image of Cu NPs before etching in a ligand-exchange process. (Reprinted with permission from (Jia *et al.* 2013). Copyright 2013 WILEY‑VCH Verlag GmbH & Co. KGaA.)

Fig. 3 The "top -down" synthetic strategies
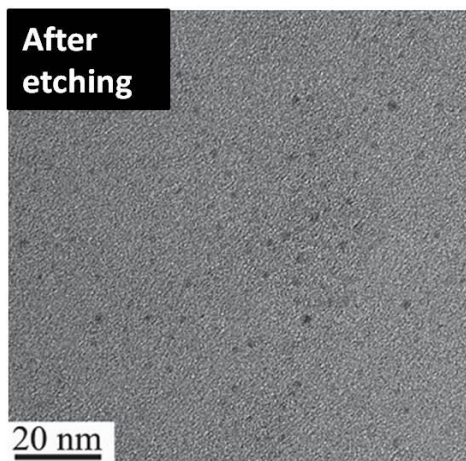
(b) HRTEM image of Cu clusters after etching in a ligand-exchange process. (Reprinted with permission from (Jia *et al.* 2013). Copyright 2013 WILEY‑VCH Verlag GmbH & Co. KGaA.)

(c) The Schematic illustration of etching non-fluorescent Cu clusters into fluorescent ones through a phase transfer method. (Reprinted with permission from (Yuan *et al.* 2011). Copyright 2011 American Chemical Society.)

Fig. 3 Continued

particles underwent a drastic decrease, from ~4.2 nm down to ~0.2 nm (Figs. 3(a)-(b)), The as-prepared copper clusters were found to possess a core composed of only two atoms, exhibiting an aggregation-induced fluorescence (QY=0.45% in water and 6.6% in ethanol), To use such "size-focusing" method synthesizing luminescent copper clusters, some amino acids like penicillamine and cysteine as the etchant are also applicable.

3.2.2 Phase transfer method

In some circumstances, however, the initially formed metal clusters may not be able to fluoresce. At this point, the phase transfer method may be of some help. Previous studies demonstrated that phase transfer strategy owned a conspicuous enhancing effect on the photoluminescence of non-luminescent silver clusters (Díez *et al.* 2010, Rao 2010). However, successful attempts on the fabrication of luminescent copper clusters through phase transfer

method are still limited. Yuan and coworkers reported a fast and versatile phase transfer method to change polydisperse, unstable, non-luminescent Cu clusters into monodisperse, highly stable, fluorescent ones, by which Au, Ag and Pt clusters were also successfully produced (Yuan *et al.* 2011). In their work, cetyltrimethylammonium bromide (CTAB) was added to transfer the GSH-protected MCLs from aqueous phase to toluene phase, where the etching process occurred. And then the fluorescent MCLs were delivered back to aqueous phase with the original capping ligands by adding hydrophobic tetramethylammonium decanoate (TMAD), in such a reversible phase transfer process, CTAB and TMAD played an important role. The electrostatic interaction between CTA^+ and COO^- (from GSH) enables the aqueous-organic phase transfer, while TMAD's combination with CTA^+ drives the as-etched copper clusters back to water. And in the etching process, excess amount of etchant (CTAB) and mild etching environment (the toluene phase) are two vital factors. Insufficient etchant would only lead to formation of large non-luminescent particles, and mild etching environment might favor the generation of fluorescent copper clusters with a well-defined structure.

Generally speaking, the stabilizers applied in the preparation of gold or silver nanoclusters are also possibly available to that of Cu clusters, and so are the preparing methods. Rao and colleagues applied a novel solid state route to synthesize Ag_9 quantum cluster (Rao *et al.* 2010), and Ganguly's group subsequently reported on preparing thiols-protected copper clusters (~Cu_{38}) through a similar solid phase-based approach (Ganguly *et al.* 2013). Therefore anterior research work on the synthesis of Au and Ag clusters may be a helpful resource to Cu clusters. However, the specific synthetic conditions or procedures may be of some difference due to the remarkable distinction in the interaction between stabilizers and metal atoms, as mentioned previously.

4. Characterization of copper clusters

Characterization of copper clusters is critical to understanding metal clusters' unique physical and chemical properties. Generally, both Cu clusters and nanoparticles share the basic characterization methods, like UV-vis absorption spectroscopy, X-Ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), surface enhanced Raman scattering spectroscopy (SERS) and so forth (Jin 2010, Wei *et al.* 2011, Liu 2014, Luo *et al.* 2015). But there are still some differences in characterization due to the particularities of various materials. Some regular characterization methods for metal nanoparticles or bulk metal, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), seem to be less effective in characterizing copper clusters because of their poor crystallinity and tiny size. And photoluminescence (PL) spectroscopy, a most extensively used method in copper clusters, is seldom applied in Cu nanoparticles and bulk copper as they rarely possess PL property (Zheng *et al.* 2012).

It has been established that Mie theory is no longer available in copper clusters due to their ultra-small dimension (Jia *et al.* 2012), which leads to the absence of characteristic plasmon resonance peak (~560 nm) in their UV-vis absorption spectra that is commonly seen in copper nanoparticles. Instead, with respect to copper nanoparticles, Cu clusters' absorption peak will drastically shift to the UV region (Goswami *et al.* 2011), where in some cases more than one absorption peak may emerge (Wei *et al.* 2011, Vilar-Vidal *et al.* 2014), exhibiting a molecular-like feature. These behaviors mentioned above are most likely attributed to the strong quantum confinement effect, according to previous reports (Vilar-Vidal *et al.* 2010, Salorinne *et al.* 2012). Therefore, the generation of copper clusters can be initially verified by ruling out the presence of

plasma peak in their UV-vis absorption spectra.

To reveal the micro morphologies of copper clusters, high resolution transmission electron microscopy (HR-TEM) is normally required, since the clusters generally have an average diameter less than 3 nm (Table 1), However, HRTEM sometimes fails to present the morphology as the copper clusters are generally too small to be observed (Zhao and Huang 2014). In this regard, mass spectroscopy (MS) appears to be more effective in investigating the clusters' nature, which helps researchers to better understand the composition of a copper cluster (Wei *et al.* 2011, Gao *et al.* 2015). Specific charge peaks in the mass spectra provide the molecular weight information, which may be ascribed to certain Cu clusters generated during the synthetic process. Nowadays a combination of both HRTEM and MS methods is increasingly adopted, thus the formation and composition of copper clusters can be well confirmed (Jia *et al.* 2013, Jia *et al.* 2014). And some surface analysis measurements such as XPS, FITR and SERS can also be applied to further understand the elements' valence states and surface-capped functional groups of the as-synthesized copper clusters (Luo *et al.* 2015, Zhou *et al.* 2015).

5. Summary and outlook

A variety of synthetic methods for preparing luminescent zero covalent copper have been surveyed, which are mostly derived from the synthetic protocols previously applied for producing fluorescent Au and Ag clusters. These as-reported fluorescent Cu clusters generally have relatively low quantum yields (<5%), averagely lower than those of their gold and silver counterparts. Furthermore, the instability is another apparent drawback as the newly-prepared fluorescent copper clusters often progressively lose their photoluminescence property and other superior performance due to the effect of gradual aggregation and oxidation. And this defect has also inhibited fluorescent zero covalent Cu clusters from being successfully synthesized and investigated, inferred from the shortage of relevant reports in literature. Finally, undesired polydisperse systems are usually obtained by using these presently available synthetic methods, especially for thiols-capped Cu clusters (Jia *et al.* 2013). This is certainly unfavorable to either fundamental studies or further applications. To resolve these issues, the current synthetic routes may still require remarkable improvement. And considerable efforts need to be made to develop novel and particular synthetic strategies, if possible, for monodisperse, highly fluorescent and stable copper clusters.

With regard to fundamental research, luminescence mechanism of copper clusters has so far been scarcely investigated, which has been a big challenge remaining in the field. But recent studies on Au nanoclusters' PL origin have provided referential explanations to copper clusters' luminescence (Wei *et al.* 2011, Zheng *et al.* 2012), since the properties of these two metal clusters are quite similar. But in order to better understand the electron behavior and electronic structure of copper clusters, specific studies on luminescence origin of copper clusters are of significant necessity.

As for application, the previous attempts on utilizing luminescent copper clusters mainly refer to sensing some chemical compounds or ions, such as metal ions, GTP, H_2O_2 and so forth. Less attention has been directed to copper clusters' catalytic performance and other potential properties so far. Theoretically, copper clusters are supposed to be an excellent catalyst. They contain a large percent of surface atoms with unsaturated coordination, resulting in an extreme tendency to combine with other substance, which makes them appropriate for catalytic reactions. Once the

stability of Cu clusters is improved, and facile and cost-effective synthetic methods are available, these versatile copper clusters will certainly be a promising material in future.

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References

Adhikari, B. and Banerjee, A. (2010), "Facile synthesis of water-soluble fluorescent silver nanoclusters and HgII Sensing", *Chem. Mater.*, **22**(15), 4364-4371.

Aiken, J.D. and Finke, R.G. (1999), "A review of modern transition-metal nanoclusters: their synthesis, characterization, and applications in catalysis", *J. Mol. Catal. A-Chem.*, **145**(1-2), 1-44.

Balogh, L. and Tomalia, D.A. (1998), "Poly(amidoamine) dendrimer-templated nanocomposites. 1. synthesis of zerovalent copper nanoclusters", *J. Am. Chem. Soc.*, **120**, 7355-7356.

Blosi, M., Albonetti, S., Dondi, M., Martelli, C. and Baldi, G. (2010), "Microwave-assisted polyol synthesis of Cu nanoparticles", *J. Nanopar. Res.*, **13**(1), 127-138.

Brust, M., Fink, J., Bethella, D., Schiffrina, D.J. and Kielyb, C. (1995), "Synthesis and reactions of functionalised gold nanoparticles", *J. Am. Chem. Soc.*, 1655-1656.

Brust, M., Walker, M., Bethell, D., Schiffrin, D.J. and Whyman, R. (1994), "Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system", *J. Am. Chem. Soc.*, 801-802.

Cao, H., Chen, Z. and Huang, Y. (2015), "Copper nanocluster coupling europium as an off-to-on fluorescence probe for the determination of phosphate ion in water samples", *Talanta*, **143**, 450-456.

Cao, H., Chen, Z., Zheng, H. and Huang, Y. (2014), "Copper nanoclusters as a highly sensitive and selective fluorescence sensor for ferric ions in serum and living cells by imaging", *Biosens. Bioelectron.*, **62**, 189-195.

Capek, I. (2004), "Preparation of metal nanoparticles in water-in-oil (w/o) microemulsions", *Adv. Colloid. Interfac.*, **110**(1-2), 49-74.

Chakraborty, P. (1998), "Metal nanoclusters in glasses as non-linear photonic materials", *J. Mater. Sci.*, **33**(9), 2235-2249.

Chang, S.S., Shih, C.W., Chen, C.D., Lai, W.C. and Chris Wang, C.R. (1999), "The shape transition of gold nanorods", *Langmuir*, **15**(3), 701-709.

Choi, S., Yu, J., Patel, S.A., Tzeng, Y.L. and Dickson, R.M. (2011), "Tailoring silver nanodots for intracellular staining", *Photochem. Photobiol. Sci.*, **10**(1), 109-115.

Cui, M., Song, G., Wang, C. and Song, Q. (2015), "Synthesis of cysteine-functionalized water-soluble luminescent copper nanoclusters and their application to the determination of chromium(VI)", *Microchim. Acta.*, **182**(7-8), 1371-1377.

Díez, I., Jiang, H. and Ras, R.H.A. (2010), "Enhanced smission of silver nanoclusters through quantitative phase transfer", *Chem. Phys. Chem.*, **11**, 3100-3104.

Feng, J., Ju, Y., Liu, J., Zhang, H. and Chen, X. (2015), "Polyethyleneimine-templated copper nanoclusters via ascorbic acid reduction approach as ferric ion sensor", *Anal. Chim. Acta.*, **854**, 153-160.

Fernandez-Ujados, M., Trapiella-Alfonso, L., Costa-Fernandez, J.M., Pereiro, R. and Sanz-Medel, A. (2013), "One-step aqueous synthesis of fluorescent copper nanoclusters by direct metal reduction", *Nanotechnology*, **24**(49), 495601.

Ganguly, A., Chakraborty, I., Udayabhaskararao, T. and Pradeep, T. (2013), "A copper cluster protected with phenylethanethiol", *J. Nanopart. Res.*, **15**(4), 1522-1529.

Gao, X., Lu, Y., Liu, M., He, S. and Chen, W. (2015), "Sub-nanometer sized $Cu_6(GSH)_3$ clusters: one-step synthesis and electrochemical detection of glucose", *J. Mater. Chem. C*, **3**(16), 4050-4056.

Ghosh, A., Udayabhaskararao, T. and Pradeep, T. (2012), "One-step route to luminescent $Au_{18}SG_{14}$ in the condensed phase and its closed shell molecular ions in the gas phase", *J. Phys. Chem. Lett.*, **3**(15), 1997-2002.

Ghosh, R., Sahoo, A. K., Ghosh, S. S., Paul, A. and Chattopadhyay, A. (2014), "Blue-emitting copper nanoclusters synthesized in the presence of lysozyme as candidates for cell labeling", *ACS Appl. Mater. Inter.*, **6**(6), 3822-3828.

Goswami, N., Giri, A., Bootharaju, M.S., Xavier, P.L., Pradeep, T. and Pal, S.K. (2011), "Copper quantum clusters in protein matrix: potential sensor of Pb^{2+} ion", *Anal. Chem.*, **83**(24), 9676-9680.

Hyotanishi, M., Isomura, Y., Yamamoto, H., Kawasaki, H. and Obora, Y. (2011), "Surfactant-free synthesis of palladium nanoclusters for their use in catalytic cross-coupling reactions", *Chem Commun*, **47**, 5750-5752.

Jia, X., Li, J. and Wang, E. (2013), "Cu nanoclusters with aggregation induced emission enhancement", *Small*, **9**(22), 3873-3879.

Jia, X., Li, J., Han, L., Ren, J., Yang, X. and Wang, E. (2012), "DNA-hosted copper nanoclusters for fluorescent identification of single nucleotide polymorphisms", *ACS Nano*, **6**(4), 3311-3317.

Jia, X., Yang, X., Li, J., Li, D. and Wang, E. (2014), "Stable Cu nanoclusters: from an aggregation-induced emission mechanism to biosensing and catalytic applications", *Chem. Commun.*, **50**(2), 237-239.

Jin, R. (2010), "Quantum sized, thiolate-protected gold nanoclusters", *Nanoscale*, **2**, 343-362.

Jin, R., Zhu, Y. and Qian, H. (2011), "Quantum-sized gold nanoclusters: bridging the gap between organometallics and nanocrystals", *Chem. Eur. J.*, **17**, 6584-6593.

Kawasaki, H., Kosaka, Y., Myoujin, Y., Narushima, T., Yonezawa, T. and Arakawa, R. (2011), "Microwave-assisted polyol synthesis of copper nanocrystals without using additional protective agents", *Chem. Commun.*, **47**(27), 7740-7742.

Kawasaki, H., Yamamoto, H., Fujimori, H., Arakawa, R. and Iwasakia, M.I.Y. (2010), "Surfactant-free solution synthesis of fluorescent platinum subnanoclusters", *Chem. Commun.*, **46**, 3759-3761.

Lin, C. (2009), "Synthesis, characterization, and bioconjugation of fluorescent gold nanoclusters toward biological labeling applications", *ACS Nano*, **3**(2), 395-401.

Ling, Y., Zhang, N., Qu, F., Wen, T., Gao, Z.F., Li, N.B. and Luo, H.Q. (2014), "Fluorescent detection of hydrogen peroxide and glucose with polyethyleneimine-templated Cu nanoclusters", *Spectrochim. Acta. A: Mol. Biomol. Spectrosc.*, **118**, 315-320.

Lisieck, I. and Pileni, M.P. (1993), "Synthesis of copper metallic clusters using reverse micelles as microreactors", *J. Am. Chem. Soc.*, **115**, 3887-3896.

Liu, H. and Wang, C.Y. (2014), "Luminescent Cu(0)@Cu(I)–TGA core–shell nanoclusters via self-assembly", *Synthetic. Met.*, **198**, 329-334.

Liu, J. (2014), "DNA-stabilized, fluorescent, metal nanoclusters for biosensor development", *TrAC-Trend. Anal. Chem.*, **58**, 99-111.

Liu, Z., Peng, L. and Yao, K. (2006), "Intense blue luminescence from self-assembled Au-thiolate clusters", *Mater. Lett.*, **60**(19), 2362-2365.

López-Quintela, M.A. (2003), "Synthesis of nanomaterials in microemulsions: formation mechanisms and growth control", *Curr. Opin. Colloid. In.*, **8**(2), 137-144.

López-Quintela, M.A., Tojo, C., Blanco, M.C., García Rio, L. and Leis, J.R. (2004), "Microemulsion dynamics and reactions in microemulsions", *Curr. Opin. Colloid. In.*, **9**(3-4), 264-278.

Luo, Y., Miao, H. and Yang, X. (2015), "Glutathione-stabilized Cu nanoclusters as fluorescent probes for sensing pH and vitamin B1", *Talanta*, **144**, 488-495.

Mathew, A. and Pradeep, T. (2014), "Noble metal clusters: applications in energy, environment, and biology", *Part. Part. Syst. Char.*, **31**(10), 1017-1053.

Morales, J. and Santos, J. (1999), "Electrical transport and magnetic properties of misfit layered compounds

intercalated with cobaltocene", *Chem. Mater.*, **11**(10), 2737-2742.

Muhammed, M.A.H., Ramesh, S., Sinha, S., Pal, S.K. and Pradeep, T. (2008), "Two distinct fluorescent quantum clusters of gold starting from metallic nanoparticles by pH-dependent ligand etching", *Nano. Res.*, **1**(4), 333-340.

Pal, N.K. and Kryschi, C. (2015), "A facile synthesis of highly stable and luminescent Ag clusters: a steady-state and time-resolved spectroscopy study", *Phys. Chem. Chem. Phys.*, **17**(3), 1957-1965.

Poater, A., Duran, M., Jaque, P., Toro-Labbé , A. and Solà, M. (2006), "Molecular structure and bonding of copper cluster monocarbonyls Cu_nCO (n =1-9)", *J. Phys. Chem. B*, **110**, 6526-6536.

Pyo, K., Thanthirige, V.D., Kwak, K., Pandurangan, P., Ramakrishna, G. and Lee, D. (2015), "Ultrabright luminescence from gold nanoclusters: rigidifying the Au(I)-thiolate shell", *J. Am. Chem. Soc.*, **137**(25), 8244-8250.

Qu, X., Li, Y., Li, L., Wang, Y., Liang, J. and Liang, J. (2015), "Fluorescent gold nanoclusters: synthesis and recent biological application", *J. Nanomater.*, **2015**, 1-23.

Rao, T. (2010), "Luminescent Ag_7 and Ag_8 slusters by interfacial synthesis", *Angew. Chem. Int. Ed.*, **49**, 3925-3929.

Rao, T., Nataraju, B. and Pradeep, T. (2010), "Ag_9 quantum cluster through a solid-State route", *J. Am. Chem. Soc.*, **132**(46), 16304-16307.

Reetz, M. T. and Helbig, W. (1994), "Size-selective synthesis of nanostructured transition metal clusters", *J. Am. Chem. Soc.*, **116**(16), 7401-7402.

Rodríguez-Sánchez, L., Blanco, M.C. and López-Quintela, M.A. (2000), "Electrochemical synthesis of silver nanoparticles", *J. Phys. Chem. B*, **104**(41), 9683-9688.

Rodríguez-Sánchez, M.L., José Rodríguez, M. and Arturo López-Quintela, M. (2005), "Kinetics and mechanism of the formation of Ag nanoparticles by electrochemical techniques: a plasmon and cluster time-resolved spectroscopic study", *J. Phys. Chem. B*, **109**(3), 1183-1191.

Salorinne, K., Chen, X., Troff, R.W., Nissinen, M. and Hakkinen, H. (2012), "One-pot synthesis and characterization of subnanometre-size benzotriazolate protected copper clusters", *Nanoscale*, **4**(14), 4095-4098.

Shang, L., Dong, S. and Nienhaus, G.U. (2011), "Ultra-small fluorescent metal nanoclusters: synthesis and biological applications", *Nano Today*, **6**(4), 401-418.

Shiang, Y.C., Huang, C.C., Chen, W.Y., Chen, P.C. and Chang, H.T. (2012), "Fluorescent gold and silver nanoclusters for the analysis of biopolymers and cell imaging", *J. Mater. Chem.*, **22**(26), 12972-12982.

Udayabhaskararao, T. and Pradeep, T. (2013), "New protocols for the synthesis of stable Ag and Au nanocluster molecules", *J. Phys. Chem. Lett.*, **4**(9), 1553-1564.

Vazquez-Vazquez, C., Banobre-Lopez, M., Mitra, A., Lopez-Quintela, M.A. and Rivas, J. (2009), "Synthesis of small atomic copper clusters in microemulsions", *Langmuir*, **25**(14), 8208-8216.

Vilar-Vidal, N., Carmen Blanco, M., López-Quintela, M.A., Rivas, J. and Serra, C. (2010), "Electrochemical synthesis of very stable photoluminescent copper clusters", *J. Phys. Chem. C*, **114**, 15924-15930.

Vilar-Vidal, N., Rey, J.R. and Lopez Quintela, M.A. (2014), "Green emitter copper clusters as highly efficient and reusable visible degradation photocatalysts", *Small*, **10**(18), 3632-3636.

Vilar-Vidal, N., Rivas, J. and López-Quintela, M.A. (2012), "Size dependent catalytic activity of reusable subnanometer copper(0) clusters", *ACS Catal.*, **2**(8), 1693-1697.

Vilar-Vidal, N., Rivas, J. and Lopez-Quintela, M.A. (2014), "Copper clusters as novel fluorescent probes for the detection and photocatalytic elimination of lead ions", *Phys. Chem. Chem. Phys.*, **16**(48), 26427-26430.

Wei, W., Lu, Y., Chen, W. and Chen, S. (2011), "One-pot synthesis, photoluminescence, and electrocatalytic properties of subnanometer-sized copper clusters", *J. Am. Chem. Soc.*, **133**(7), 2060-2063.

Widegren, J.A. and Finke, R.G. (2003), "A review of soluble transition-metal nanoclusters as arene hydrogenation catalysts", *J. Mol. Catal. A-Chem.*, **191**(2), 187-207.

Wilcoxon, J.P. and Abrams, B.L. (2006), "Synthesis, structure and properties of metal nanoclusters", *Chem. Soc. Rev.*, **35**(11), 1162-1194.

Wu, Z., Suhan, J. and Jin, R. (2009), "One-pot synthesis of atomically monodisperse, thiol-functionalized Au$_{25}$ nanoclusters", *J. Mater. Chem.*, **19**(5), 622-626.

Xu, H. and Suslick, K.S. (2010), "Sonochemical synthesis of highly fluorescent Ag nanoclusters", *ACS Nano*, **4**(6), 3209-3214.

Yang, X., Feng, Y., Zhu, S., Luo, Y., Zhuo, Y. and Dou, Y. (2014), "One-step synthesis and applications of fluorescent Cu nanoclusters stabilized by L-cysteine in aqueous solution", *Anal. Chim. Acta.*, **847**, 49-54.

Yang, X., Shi, M., Zhou, R., Chen, X. and Chen, H. (2011), "Blending of HAuCl4 and histidine in aqueous solution: a simple approach to the Au$_{10}$ cluster", *Nanoscale*, **3**(6), 2596-2601.

Yang, Z., Li, Z., Xu, M., Ma, Y., Su, Y., Gao, F., Wei , H. and Zhang, L. (2013), "Controllable synthesis of fluorescent carbon dots and their detection application as nanoprobes", *Nano-Micro. Lett.*, **5**(4), 247-259.

Yuan, X., Luo, Z., Zhang, Q., Zhang, X. and Xie, J. (2011), "Synthesis of highly fluorescent metal (Ag, Au, Pt, and Cu) nanoclusters by electrostatically induced reversible phase transfer", *ACS Nano*, **5**(11), 8800-8808.

Zhang, H., Huang, X., Li, L., Zhang, G., Hussain, I., Li, Z. and Tan, B. (2012), "Photoreductive synthesis of water-soluble fluorescent metal nanoclusters", *Chem. Commun.*, **48**(4), 567-569.

Zhang, L. and Wang, E. (2014), "Metal nanoclusters: new fluorescent probes for sensors and bioimaging", *Nano Today*, **9**(1), 132-157.

Zhao, X.J. and Huang, C.Z. (2014), "Water-soluble luminescent copper nanoclusters reduced and protected by histidine for sensing of guanosine 5′-triphosphate", *New. J. Chem.*, **38**(8), 3673-3677.

Zheng, J. and Dickson, R.M. (2002), "Individual water-soluble dendrimer-encapsulated silver nanodot fluorescence", *J. Am. Chem. Soc.*, **124**(47), 13982-13983.

Zheng, J., Petty, J.T. and Dickson, R.M. (2003), "High quantum yield blue emission from water-soluble Au$_8$ nanodots", *J. Am. Chem. Soc.*, **125**(26), 7780-7781.

Zheng, J., Zhang, C. and Dickson, R.M. (2004), "Highly fluorescent, water-soluble, size-tunable gold quantum dots", *Phys. Rev. Lett.*, **93**(7), 077402.

Zheng, J., Zhou, C., Yu, M. and Liu, J. (2012), "Different sized luminescent gold nanoparticles", *Nanoscale,* **4**(14), 4073-4083.

Zhou, T., Yao, Q., Zhao, T. and Chen, X. (2015), "One-pot synthesis of fluorescent DHLA-stabilized Cu nanoclusters for the determination of H$_2$O$_2$", *Talanta*, **141**, 80-85.

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