# Surfactant-Free Synthesis and Functionalization of Highly Fluorescent Gold Quantum Dots

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# Abstract

A novel route has been developed for surfactant-free synthesis of highly fluorescent gold quantum dots (GQDs) in *N*,*N*-dimethylformamide (DMF). The as-prepared GQDs show instinctive fluorescence and good solubility in water. The formation mechanism and functionalization of GQDs were investigated by UV-vis spectra, fluorescence excitation and emission spectra, mass spectra, and TEM observation. Ligand-dependent optical properties of functionalized GQDs were found to be dramatically different. The approach provides a facile method of functionalization of bare GQDs for further applications, such as fluorescent biolabels, energy transfer units, and light-emitting devices.

# Introduction

- Quantum clusters of gold have size less than 1 nm and hence posses molecule-like properties
- They act as link between the nanoparticle and molecular behavior
- Several methods have been developed for the synthesis of quantum clusters using thiols, dendrimers, DNA, phosphines etc.
- Exhibit strong fluorescence
- Several nanostructures have been synthesized using DMF as solvent as well as reducing agent
- First report of the synthesis of quantum clusters using DMF

# **Experimental**

### **Preparation of Bare GQDs**

A solution of 100  $\mu$ L of 0.1 M aqueous HAuCl<sub>4</sub> in 10 mL of DMF was stirred at room temperature for 10 min before being reacted at 140 °C for 4 h under vigorous stirring. After cooling to room temperature, the mixture was centrifuged three times at 12 000 rpm to remove any larger gold nanoparticles. It thus afforded a light brown and clear solution. After evaporating off the solvent under vacuum, the residue was passed through a silica gel column with methanol as eluent. The gold atomic cluster solutions were then collected and evaporated to dryness, then redissolved in a small amount of methanol as stock solution for further modification. The concentration of the obtained GQDs solutions was calculated as 1.42 ×  $10^{-3}$  M

## SCHEME 1: Chemical Structures of Different Capping Ligands Polyvinyl pyrrolidone



## Purification and Functionalization of As-Prepared Bare GQDs with Various Ligands

#### (A) For TA, MUA, DT, DA, PVP, TPP, and PAMAM functionalized GQDs

To a stirred 3 mL of stock solution of GQDs in methanol was added 100  $\mu$ Lof the corresponding ligand in methanol (4.3 × 10<sup>-2</sup> M) dropwise. The mixture was stirred and maintained in the dark for more than 24 h for completion of the ligand capping process. After removal of the solvent, the residue was redissolved in 3 mL of methanol.

#### (B) For TCB functionalized GQDs:

To a stirred 1 mL solution of 10 mg of S-acetylthiocholine bromide in methanol was added 0.5 mL of HCI (2 M aqueous) dropwise. The mixture was stirred and maintained in the dark at room temperature overnight. The acetyl group was expected to be deprotected to give free thiol as thiocholine bromide (TCB). Then, 3 mL of stock solution was added via syringe. The mixture was stirred further for more than 24 h. After removal of the solvent, the residue was redissolved in a small amount of water and passed through a dialytic memberane with a molecular weight cutoff of 2 kD. The TCB functionalized GQDs was then resuspended in deioned water

# **Results & Discussion**

- GQD were synthesized by reducing AuCl<sub>4</sub><sup>-</sup> in DMF at 140 °C
- Pale yellow-colour less-light brown,  $Au(III) \rightarrow Au(I) \rightarrow Au(0)$
- DMF acts as reducing agent as well as solvent at high temperature
- Reaction was complete in 4 h
- Solution was centrifuged at 12000 rpm
- Supernatant showed absorption peak at 294 nm
- Supernatant showed strong blue fluorescence under uv light



Figure 1. Optical absorption spectra of as-prepared bare GQDs in methanol (red curve), original AuCl4<sup>-</sup> ions in water (green curve), and fluorescence emission spectrum of as-prepared bare GQDs in methanol (blue curve).

## **<u>Time-dependent formation of GDQ</u>**

- Reaction was monitored at regular intervals by Uv-vis and fluorescence
- While heating, intensity of peak at 324 decreased and new peak at 294 nm appeared



- Fluorescence increases with time at reaches maximum after 4 h
- NaBH<sub>4</sub> was added at regular intervals Different amount of gold nanoparticles were formed- No gold nanoparticles after 4 h
- Below 140 °C, no fluorescence intensity and large number of nanoparticles were formed
- Clusters formed were very stable even to acid or base treatment



## **Functionalization of bare GQD**

- Functionalized GQD exhibit different optical behaviors
- TAA stabilized GQD showed enhanced absorption
- PAMAM and TPP stabilized GQD showed new peaks at 486 and 541 nm due to electronic transition between ligand and metal core



- Most of the ligands did not influence fluorescence
- TPP stabilized GQD-quenching of fluorescence due to electronic transition between TPP and gold core-colour change
- TA- self quenching by agglomeration due to carboxyl group





Figure S1. ESI mass spectrum of TCB stabilized GQDs dissolved in  $H_2O$ , the main peak corresponds to  $[Au_{11}(SCH_2CH_2Me_3N)_2(H_2O)_2]^{2+}$ .

## Effect of ligand concentration

- Under same condition-various amounts of PVP-different clusters
- Emission wavelength related to PVP concentration



- No change in emission wavelength higher than 5x10<sup>-2</sup> M
- PVP provide a cross-linking environment for gold cluster agglomeration
- With increase in PVP concentration, agglomeration enhances
- After PVP functionalization , the ligand protects cluster from quenching





# PVP provides a pathway for agglomeration, thus clusters can be visualized under TEM



Figure 5. TEM images of as-prepared bare GQDs (A) and PVP encapsulated GQDs (B). (C) High-resolution TEM image of PVP cross-linked GQDs

## **Tunable Optical Properties**

- PVP functionalized clusters can be chemically reduced to exhibit blue-shifted emission
- QY increases by treatment with reducing agent



TABLE 1:	Photophysics	of Different	Samples	of	Gold
Quantum <b>D</b>	ots <sup>a</sup>				

	before reduction				after reduction			
sample no.	Ex. (nm)	Em. (nm)	fwhm (nm)	QY (%)	Ex. (nm)	Em. (nm)	fwhm (nm)	QY (%)
1	372	446	99	4.49	347	423	93	11.21
2	384	468	105	6.32	349	427	96	13.63
3	396	481	108	8.65	353	436	103	14.28

 $^{a}$ Ex. = Excitation wavelength. Em. = Emission wavelength. fwhm = full width at half maximum. QY = quantum yield, determined through comparison with quinine sulfate.

# Conclusion

A facile and novel pathway for surfactant-free synthesis of highly fluorescent GQDs is developed which can be further functionalized with various ligands to show tunable optical behavior. Requiring neither complicated synthesis with toxic precursors nor difficult overcoating with surface passivation and solubilization chemistry, such welldefined, size-tunable discrete excitation and emission suggests that these nanomaterials may find potential utility as energy transfer units and novel light emitting devices. Furthermore, surfactant-free synthesis of GQDs provides a better platform for further functionalization with various capping ligands, which have great potential for use in sensing platforms and novel biomarkers.