Novel fluorescent matrix embedded carbon quantum dots enrouting stable gold and silver hydrosols

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1. Experimental:

1.1. Materials:

Polyethylene glycol (M.W. 200; PEG-200), o-phosphoric acid, acetone, ethanol, silver nitrate and potassium hydroxide were purchased from Merck (India). Polyvinyl alcohol (PVA) of molecular weight 1,25,000 and gold chloride ($HAuCl_4$, $2H_2O$) were obtained from Sigma Aldrich, all the chemicals were of analytical grade and used without further purification.

1.2. Synthesis of matrix embedded carbon quantum dots (MCQD):

5% aqueous solution of polyvinyl alcohol (PVA) solution was prepared initially by slowly adding 5 gm of PVA into 100 mL of water with constant stirring them at a temperature of 80 ^oC to 90 ^oC. This stock solution of 5% PVA was used for the experiment. In brief, 10 mL of PEG 200 was mixed well with 2 mL of 5% PVA solution and then to it 1 mL of o-phosphoric acid was added with stirring prior to microwave irradiation. The resultant mixture was then subjected to microwave irradiation for 55-57 sec at 750 watt until a brown color was obtained. The product was allowed to cool down at room temperature and to it excess of acetone was added and the mixture was shaken well. A brown color precipitate was obtained when the resultant mixture was allowed to settle down. Finally pure MCQDs were separated by centrifugation at 4000 rpm for 15 minutes.

1.3. Synthesis of hexagonal gold nanoparticle (GNPs) by using MCQDs:

A 0.25 m(M) stock solution of gold chloride in milli-Q water was prepared. To the 50 mL of 0.25 m(M) gold chloride solution; 5 mL of MCQD dispersion of concentration 1mg/mL in 3:1 milli-Q water: PEG 200 was added. The resultant mixture was subjected to microwave irradiation for 2 min 40 sec at 450 watt to obtain a wine red color solution of GNPs. In our experiments all possible combinations of gold chloride and MCQDs using heat variations, concentration variations, MCQD concentration variations and time scale variation in synthesis were used. In all the cases 3:1 milli-Q water: PEG 200 dispersion of MCQD was used.

Heat variation. Heat energy in course of the reaction was varied from 100 watt, 300 watt, 450 watt, 600 watt and 750 watt; in brief, to 50 mL of 0.25 m(M) of gold chloride solution 5 mL of MCQD of concentration 1mg/mL was added and the reaction was continued to characteristic wine red color of GNPs in each case.

Substrate concentration variation. Concentration of gold chloride was varied from 0.25 m(M), 0.125 m(M), 0.0625 m(M), 0.03125 m(M) and 0.015625 m(M) respectively. In each variation 50 mL of gold chloride of aforesaid concentration was mixed with 5 mL of MCQD dispersion of concentration 1 mg/mL and the resultant mixture was subjected to microwave irradiation at 450 watt. The reaction was continued until the entire solution became wine red colored.

Catalyst concentration variation. A similar reaction set was repeated by using 50 mL of 0.0625 m(M) gold chloride with 5 mL of MCQD dispersion in 3:1 milli-Q water: PEG 200 where concentration of MCQDs were varied from 0.2 mg/mL, 0.4 mg/mL, 0.6 mg/mL, 0.8 mg/mL, 1mg/mL, 1.2 mg/mL and 1.4 mg/mL respectively. Each set of reaction mixture was subjected to microwave irradiation at 450 watt. The reaction was continued until characteristic color of GNP was obtained.

Time scale variation. A distinct time scale variation in the reaction was carried out by using 0.25 m(M) of gold chloride solution. Briefly, 50 mL of 0.25 m(M) of gold chloride solution was mixed with 5mL of MCQD dispersion of concentration 1mg/mL in 3:1 milli-Q water: PEG 200, the resultant mixture was subjected to microwave irradiation at 450 watt. The reaction was prolonged for a long time and certain amount of aliquot was separated from the reaction after a particular time interval starting from 1 min 30 sec in order to study the formation of GNP as a function of time.

1.4. Catalytic proof of in GNP synthesis by MCQD:

A catalytic proof of MCQD towards GNP synthesis was cross checked by using set variations, these set variations were summarized in table T1. Each sets of the reactions were constituted by using 50 mL 0.25 m(M) gold chloride solution and heating them in a microwave at 450 watt with the variations as shown in table 1 until a characteristic color was obtained. Each of the reaction conditions were adjusted suitably so as to compare with the catalytic activity of the MCQDs. Each of the reaction sets were justified by UV-VIS analysis.

1.5. Room temperature synthesis of silver nanoparticle (AgNPs) by using MCQDs:

In a typical synthesis to 10 mL of 5 m(M) silver nitrate solution, 5 mL of MCQD dispersion of concentration 1mg/mL in 3:1 milli-Q water: PEG 200 was added. The mixture was stirred well followed by addition of 2.5 mL 0.1(M) KOH drop wise with constant stirring until a deep yellow characteristic color of AgNPs were obtained.

In order to study the synthetic pathway towards the formation of AgNPs; to a solution of 10 mL of 5 m(M) silver nitrate solution, 5 mL of MCQD dispersion of concentration 1mg/mL in 3:1 milli-Q water: PEG 200 was added followed by the gradual addition 0.1(M) KOH starting from 500 µL to 3.5 mL. Another variation in set was carried out using appropriate amount of 5% aqueous PVA solution and PEG 200 in mixture to the 10 mL of 5 m(M) silver nitrate solution with stirring followed by the addition of 2.5 mL of 0.1(M) KOH in contrast to original one (where we have used MCQD instead of the mixture).

2. Characterization:

Fourier Transform Infrared Spectroscopy (FT-IR) was conducted by Perkin-Elmer spectrum RX-1 IR spectrophotometer by using methanolic dispersion of MCQD. For absorption and fluorescence measurements we have used Shimadzu absorption spectrophotometer (model no: UV-1700) and Spex-fluorolog-3 spectrofluorimeter (model no: FL3-11), respectively. High-resolution transmission electron microscopy (HRTEM) was carried out by using Phillips CM 200, operating at an acceleration voltage of 200 kV. The field emission scanning electron microscopy (FE-SEM) was also performed by Jeol Model JSM-6340F. For FE-SEM analysis samples were prepared by deposition followed by spin coating of the aqueous dispersion on a glass slide. Again for HR-TEM analysis a very dilute aqueous suspension was prepared, which was then deposited on a copper grid and finally dried in air. During HR-TEM analysis of GNPs and AgNPs, samples were prepared after separation from MCQDs by centrifugation at 14000 rpm for 10 minutes followed by washing several times with water. ^{31}P NMR spectrum was obtained by using Bruker Avance-II 400 MHz instrument operating at a frequency of 400 MHz using D_2O as the solvent. Phase characterization of the sample was carried out by using PW 1840 X-ray diffractometer with Cu-Kα -targets at 2mm slits. EDAX analysis was carried out by using by drop casting of the sample on a glass slide in ZEISS EVO 60 Scanning Electron Microscope with Oxford EDS Detector.

Table 1. Tabular representation of set variation reaction with different reactant conditions.

Set Name	Reactants	Conc. Of gold chloride (mM)	Heat watt	Color
Set 1	MCQD dispersion	0.25	450	Wine red
Set 2	5% PVA solution	0.25	450	Blue
Set 3	10 mL of PEG 200 + 2 mL of 5% PVA solution + 1 mL of o-phosphoric acid	0.25	450	Bluish red
Set 4	PEG-200 and 5% PVA solution	0.25	450	Blackish blue
Set 5	o-Phosphoric acid and PEG-200	0.25	450	No color change

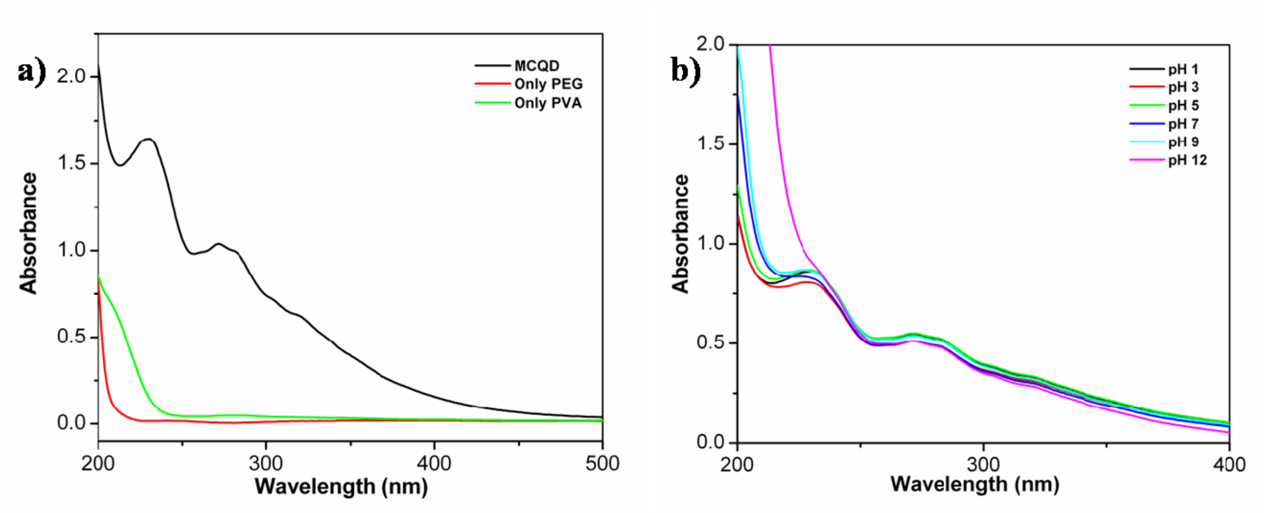

Figure S1. UV-VIS absorbance spectra of (a) MCQD, PEG 200 and PVA respectively; (b) MCQD at different pH varied from pH 1 to pH 12.

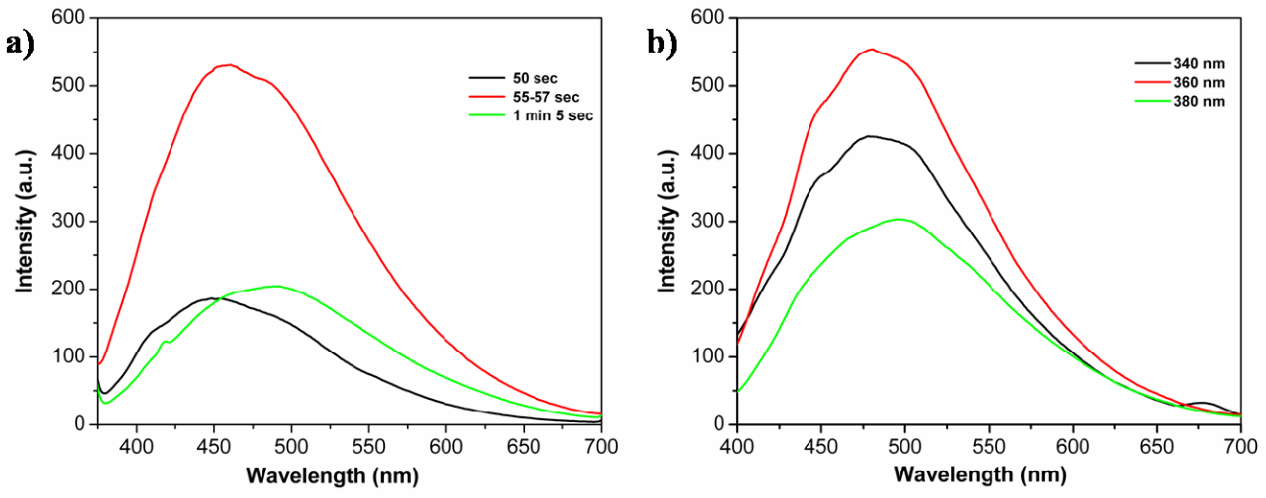

Figure S2. Fluorescence spectra of MCQD (a) At different time interval; (b) At different wavelength.

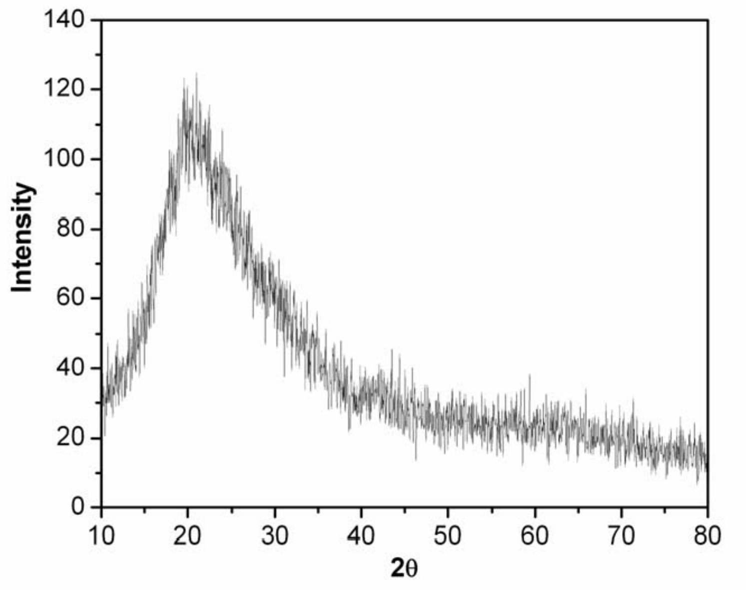

Figure S3. X-ray diffraction pattern of MCQD

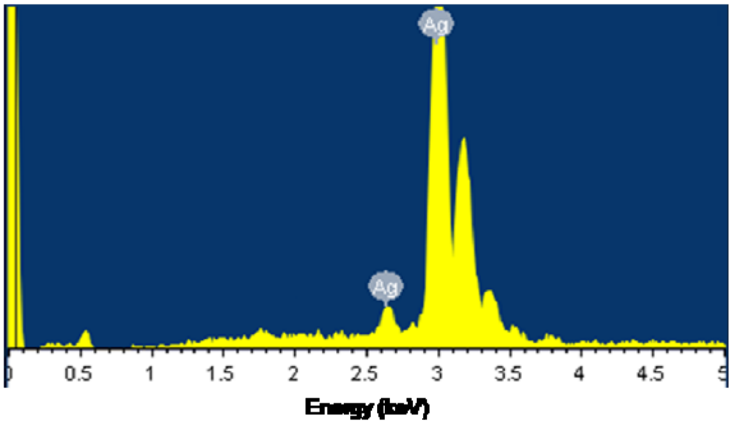

Figure S4. EDAX spectra of AgNPs obtained after separation from MCQDs.

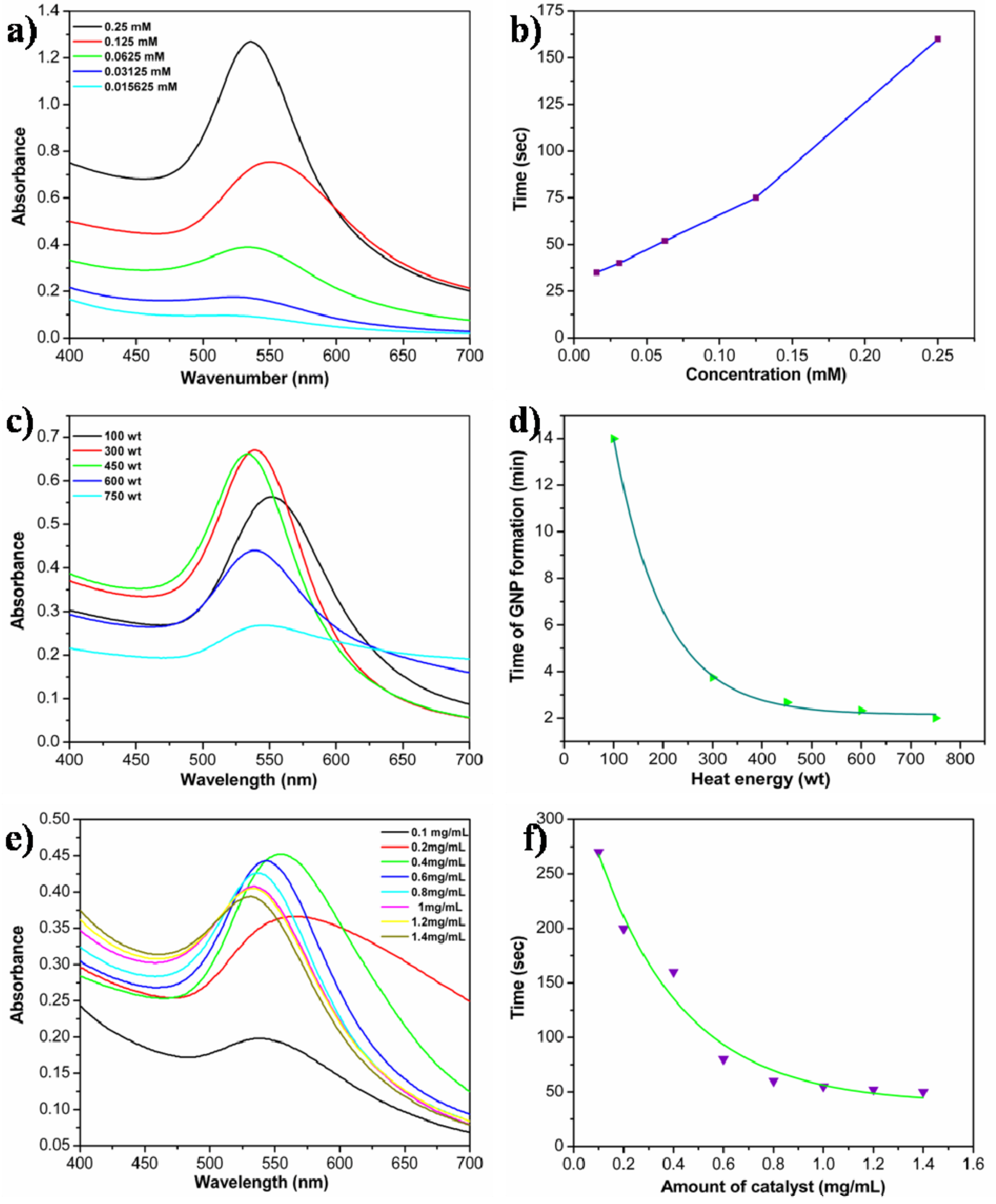

Figure S5. (a) UV-VIS absorbance of GNP formation at different gold chloride concentration, (b) Corresponding time versus concentration plot in course of the reaction; (c) UV-VIS absorbance of GNP formation against different heat energy, (d) Time of GNP formation against heat energy variation illustrating the previous curve which followed a exponentially decay curve; (e) UV-VIS absorbance of GNP formation by the addition of MCQD with increasing concentration, (f) Corresponding time versus amount of catalyst plot which followed a exponentially decreasing curve.

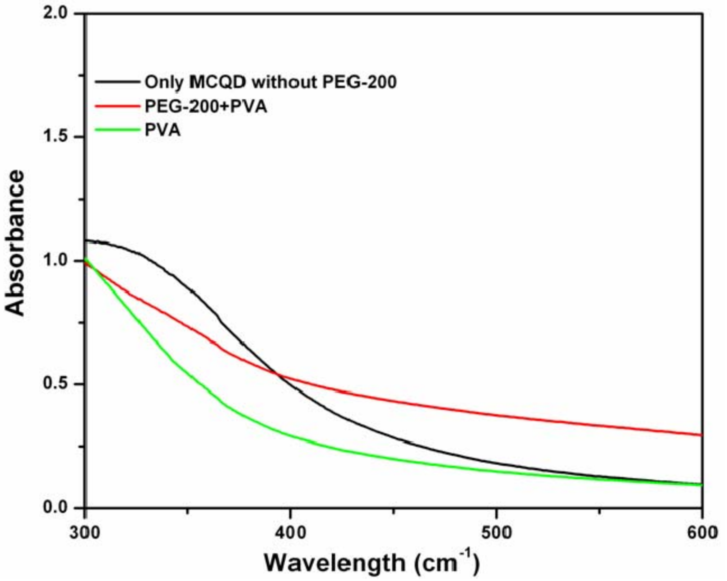

Figure S6. UV-VIS absorbance spectra of sets during AgNPs synthesis with only aqueous dispersion of MCQD, mixture of PEG-200 –PVA and only PVA.