

Binding of viologen pendant pyrrole with free and bound gold nanoparticles

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Pyrrole derivative of viologen was synthesized using the conventional synthetic methodology. The reactivity of positively charged viologen derivatives with charged gold nanoparticles was studied with UV-visible spectroscopy, electrochemical studies and transmission electron microscopy. The reaction of viologen pendant pyrrole with colloidal gold solution was indicated by a shift in the plasmon peak due to the formation of gold nanoparticles/viologen aggregate. The reaction between them was further confirmed from cyclic voltammetry and electron microscopic studies. The methodology employed in this study can be utilized to design novel building blocks of polypyrrole-derived viologen pendant gold nanoparticles containing nanocomposites on electrode surfaces for various sensor and electrocatalytic applications.

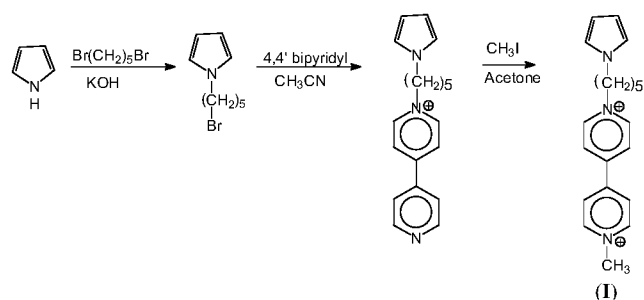
VILOGENS and polyviologens have been widely investigated owing to their photosensitization and electron transfer properties¹⁻³. It has been reported that viologen acts as an electron relay for photoreduction of hydrogen and electron transfer mediator⁴. Due to the electron relay properties of viologen salts, they have often been used as redox mediators in enzyme-based biosensors^{5,6}. There are several ways to modify the electrode surfaces such as incorporation of polymer matrix, deposition of chemically preformed polymer, self-assembly of functionalized alkanethiol monolayer or multilayer assembly^{7,8}, and electrochemical polymerization of monomer chemically bound to viologen. Cosnier and co-workers⁹ have developed a nitrate biosensor, which was prepared by coating a polypyrrole-viologen film on an electrode surface and subsequently immobilizing nitrate reductase. Similar kinds of electrode modified with electropolymerized film of a pyrrole-derived viologen system can be used for the determination of cellular S-nitrosoglutathione¹⁰, explosives like TNT in groundwater¹¹ and as part of biosensing devices¹²⁻¹⁵. It was found that the fluorescence of a polyanionic-conjugated polymer could be quenched by extremely low concentrations of cationic electron acceptors in aqueous solutions. For example, *N,N'*-dimethyl-4,4'-bipyridinium (MV²⁺) (methylviologen) can usually be used as positively charged quencher for reversible fluorescence quenching in both solution and thin-film, which provides the basis for a new class of highly sensitive biological and chemical sensors¹⁶. Recently, it has been reported that a photoelectrochemical device with high surface

area electrodes based on multilayer of gold nanoparticles architecture has been constructed. The multilayer gold nanoparticles superstructure was assembled by stepwise cross-linking of citrate-capped gold nanoparticles with the bis(bipyridyl)Zn(II)protoporphyrin IX dyad acts as electrostatic cross-linker¹⁷. A series of electrochemical sensors were built by electrostatic cross-linking of gold nanoparticles with bipyridinium cyclophanes. The bipyridinium cyclophanes act as receptors for the association of δ -donating substrates in their cavity and the 3D conductivity of the gold nanoparticles array electrochemically senses δ -donor substrates associated with the cyclophane units. The resulting δ -donor-acceptor complexes enables the preconcentration of the analyte at the conductive surface¹⁸⁻²⁰. A layered viologen compound shows an efficient photoinduced charge-transfer separated state, which is long-lived and stable in air. Such an electrode system can be used for the efficient generation of photocurrent and fabrication of electrochromic devices²¹. Similarly, the monolayer assembly of viologen-linked TiO₂ electrode can be used for fast response electrochromic display devices²².

In the present investigation, we have generated multilayer assembly of negatively charged, gold citrate-capped nanoparticles using a molecular glue of viologen pendant pyrrole which will form a conducting polypyrrole nanocomposite either by chemical or electrochemical polymerization of pyrrole on preassembled gold/viologen pendant pyrrole multilayer architecture. The formation of multilayer assembly on ITO substrates and the solution-based aggregates of free gold colloids with viologen pendant pyrrole were characterized by UV-visible spectroscopy, cyclic voltammetry and transmission electron microscopy (TEM).

4-Methyl bipyridyl-1-pentylpyrrole (**I**) was synthesized according to the procedure described earlier²³ (see Scheme 1). Au colloids (12 nm) were synthesized by the addition of HAuCl₄.3H₂O (50 mg) to a refluxing solution of sodium citrate (100 mg) in water (500 ml). The solution turns blue and then pink, indicating the formation of Au colloids. The reaction mixture was refluxed for an additional 15 min before cooling²⁴.

Glass plates were cleaned with distilled water and then with hot piranha solution (7 : 3 molar ratio of conc. H₂SO₄ and 30% H₂O₂). The freshly cleaned glass plates were



Scheme 1.

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immersed in 2–3% solution of 3-aminopropyltrimethoxysilane for 15 min, after which they were washed thoroughly with ethanol, and then heated to 110°C for 10 min. Finally the silylated glass plates were washed with water. For colloid pretreatment of the surface, the silylated glass plates were immersed in Au nanoparticles solution for 30 min followed by 30 mM of viologen salt solution of the cross-linker for 30 min. After each treatment, the glass plates were washed three times with water. Scheme 2 gives the multilayer assembly of viologen pendant pyrrole with gold clusters.

Transmission electron micrographs were obtained using a JEOL TEMSCAN 2000 Ex instrument with an accelerating voltage of 80 keV. Gold nanoparticles were deposited on carbon-coated copper grid by drop-casting method. The UV–visible spectroscopy experiments were carried out using Perkin–Elmer Model 6A, USA. All electrochemical studies were performed using CHI instruments, Model 601, USA. A single-compartment cell set up with a three-electrode assembly was used for cyclic voltammetry studies. The 3-aminopropylsilane modified ITO acts as the working electrode, whereas the platinum wire and Ag/AgCl (3M KCl) function as counter and reference electrodes respectively. All solutions were purged with N₂ gas for 10 min before the starting of all experiments.

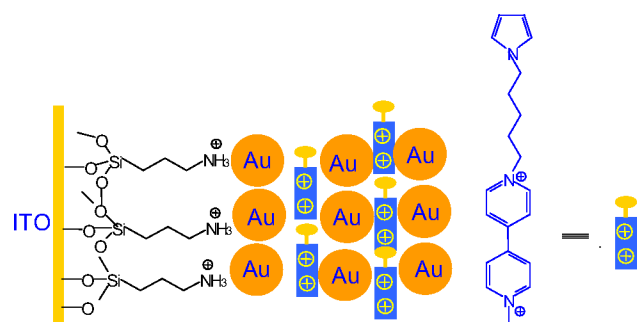
Before characterizing the viologen/Au colloid aggregate, it was necessary to establish whether colloidal gold nanoparticles incorporated into the viologen pendant pyrrole molecules. The negatively charged colloidal gold recognizes and selectively binds viologen molecules when they are free in solution.

The UV–visible absorption spectra of gold nanoparticles, viologen-functionalized pyrrole and an equimolar mixture of gold colloid and viologen-functionalized pyrrole in water were recorded. The citrate-capped gold nanoparticles has a strong absorption peak at 520 nm with a characteristic of plasmon vibration of colloidal gold. Viologen pendant pyrrole (VC5Py) has a prominent absorption band at 370 nm with a characteristic of π – π^* transition. It is expected that an equimolar mixture of citrate-capped gold nanoparticles and the VC5Py could form an aggregate, which gave blue colour to the solution. Consistent with expectations, both the negatively charged gold colloid plasmon band and the

positively charged viologen band were dampened. A new band appearing at higher wavelength is due to the formation of aggregates of gold colloid with VC5Py. It is expected that the gold nanoparticles stabilized with citrate are considered to be relatively weaker than the binding of VC5Py at the surfaces of gold colloids. Accordingly, the reactivity of citrated-capped gold nanoparticles with VC5Py was tested in aqueous medium and the extent of aggregation was determined by UV–visible spectral studies.

The rate of the reaction was tested at different concentrations of reactants. It was expected that the concentration of viologen would affect the rate of the reaction due to the availability of viologen molecules close to the reactive colloidal gold, which could form a cross-linked gold colloid and VC5Py aggregate. When the concentration of VC5Py is around 0.3 mM, nanoparticles form a ball-like aggregate. As expected, the order of addition of viologen to the gold colloid will also affect the rate of the reaction. Thus, it is better if gold nanoparticles are added to VC5Py solution, whereas the reaction is slow when the order of addition is reversed.

It is noted that Au colloid exhibits optical absorption, the so-called plasmon band that has been assigned to collective oscillations of the free electrons. The Au colloid has intense plasmon absorption at 520 nm. The wavelengths at which these absorbances are observed depend on the size and shape of the individual nanoparticles. They also depend on the dielectric constant of the solution, and so the red-shift characteristic of aggregated gold colloid is usually taken into account by an increase in the effective dielectric constant of the surrounding medium. Spectra were recorded immediately after mixing of the dispersions and again after 5 min (Figure 1). A comparison of the spectra after 30 min showed a decrease in intensity of the surface plasmon band at 520 nm, assigned to free gold colloids in suspension. Simultaneously, a new band centred at 650 nm is



Scheme 2.

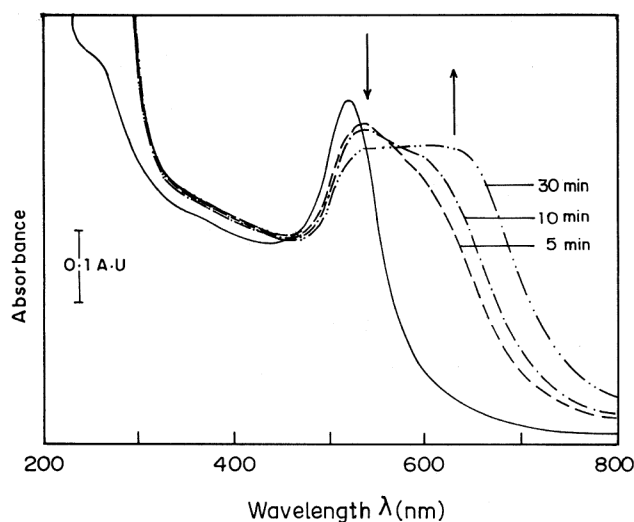


Figure 1. UV–visible spectral studies to monitor reaction between gold nanoparticles and viologen pendant pyrrole at different reaction intervals.

observed. This band is assigned as the intercrystal plasmon band of aggregated metal nanoparticles.

TEM studies have been carried out to investigate the aggregation of VC5Py against the citrate-capped gold clusters. An isolated gold nanoparticle of a diameter 12 nm is shown in Figure 2 *a*. After addition of pyrrole pendant viologen molecules the individual particles form an aggregate (Figure 2 *b*). Due to charge-induced aggregation of colloidal gold solution with VC5Py, a ball-like structure appears (Figure 2 *b*). Similar observations were made in previous studies at different concentration ranges²⁵.

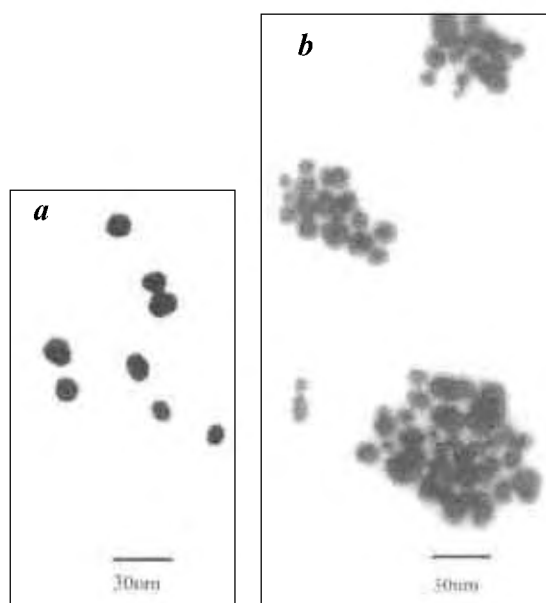


Figure 2. Transmission electron microscopy images for free citrate-capped gold nanoparticles (*a*) and after formation of Au–viologen pendant pyrrole aggregate (*b*).

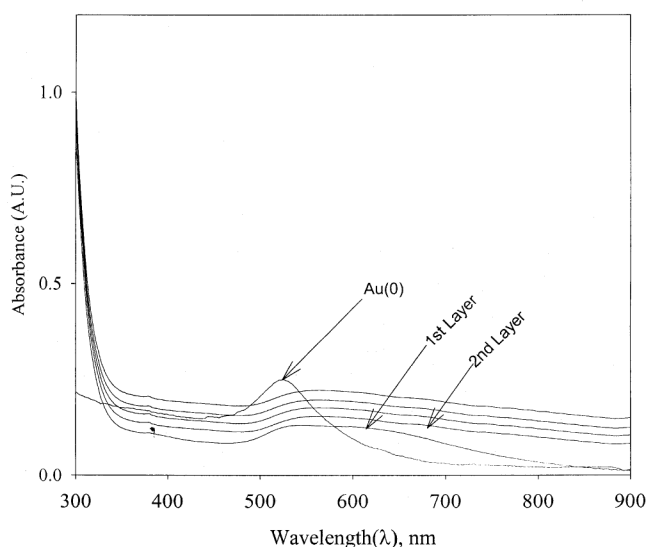


Figure 3. Formation of multi-layer assembly of viologen pendant pyrrole molecular glue with citrate-capped gold nanoparticles.

It has been reported that multilayers of Au nanoparticle assembly on amine-functionalized glass substrates were established by alternate exposure of the substrate to a solution of negatively charged citrate-stabilized nanoparticles and positively charged cyclophanes, which can be used for the construction of sensor devices. It is also known that such multilayer assemblies are highly stable and show strong binding due to the electrostatic interaction between the charged species^{26,27}.

UV–visible spectra were recorded for the layer-by-layer assembly of gold nanoparticles followed by a molecular glue of VC5Py on γ -aminopropyltriethoxysilane-pretreated ITO. The plasmon band at 523 nm is due to the surface-bound Au nanoparticles. This plasmon band becomes flattened after exposing the gold nanoparticles-modified ITO plate to VC5Py solution. Another peak at 630 nm appearing in the visible region is due to the aggregation of gold nanoparticles with VC5Py. For repeated exposure of VC5Py and gold nanoparticles, the absorbance for both peaks increases (Figure 3). Thus this study confirms the construction of a stable multi-layer assembly of gold nanoparticles/VC5Py.

The reactivity of VC5Py against the surface-bound gold nanoparticles has been investigated on solid substrates like glass plate or ITO. The APTMS-pretreated ITO glass substrate was exposed to the citrate-capped gold nanoparticles solution for about 30 min. The complete coverage of colloidal gold cluster was confirmed by both UV–visible and cyclic voltammetry studies. Cyclic voltammogram for the colloidal gold-pretreated ITO glass before and after exposure with viologen derivatives is shown in Figure 4. A broad anodic peak followed by a reduction peak was seen for the monolayer assembly of colloidal gold in 0.1 M H₂SO₄. These peaks were assigned for the oxidation and reduc-

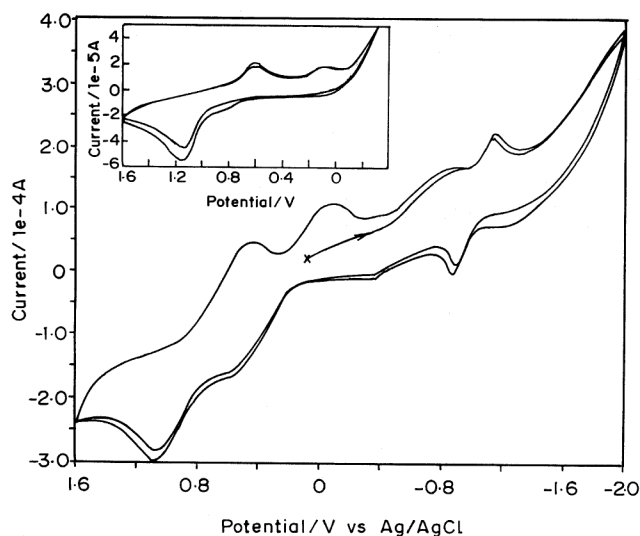


Figure 4. Cyclic voltammetric behaviour of monolayer assembly of pyrrole derivative of viologen pendant on gold nanoparticles preadsorbed on APTMS-modified ITO. 0.1 M H₂SO₄ is the supporting electrolyte with scan rate of 50 mV/s. (Inset) Cyclic voltammogram for gold nanoparticles on amine functionalized monolayer on ITO.

tion of gold nanoparticles. A similar redox behaviour was observed for the surface-bound gold nanoparticles under identical experimental conditions²⁸. In the cathodic direction, well-defined redox peaks were observed for the viologen-modified gold nanoparticle surface under the same experimental conditions. These two peaks were assigned to a single electron transfer reaction for the electrostatically bound VC5Py in 0.1 M H₂SO₄. In this way a multilayer architecture assembly of electrodes for the various electrocatalytic and photovoltaic applications may be constructed. Due to the electron-donating properties of VC5Py, the polymerized form of VC5Py-stabilized noble metal nanoparticles like Au, Pt, Pd, etc. can be utilized for the photoassisted generation of hydrogen as well as various hydrogenation reactions.

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