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 polyppyrrrole-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 properties. It has been reported that viologen acts as an
electron relay for photoreduction of hydrogen and electron transfer mediator. Due to the electron relay properties of
viologen salts, they have often been used as redox mediators in enzyme-based biosensors. There are several ways to
modify the electrode surfaces such as incorporation of poly
erm matrix, deposition of chemically preformed polymer,
self-assembly of functionalized alkanethiol monolayer or
multilayer assembly, and electrochemical polymerization
of monomer chemically bound to viologen. Cosnier and
co-workers 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 electro
polymerized film of a pyrrole-derived viologen system
can be used for the determination of cellular S-nitroso-glu	
tathione, explosives like TNT in groundwater and as part
of biosensing devices. It was found that the fluorescence
of a polyanionic-conjugated polymer could be quenched by
extremely low concentrations of cationic electron ace	ceptors in aqueous solutions. For example, N,N'-dimethyl
4,4'-bipyridinium (MV2+)

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 elec
trostatic cross-linker. A series of electrochemical sensors were
built by electrostatic cross-linking of gold nanoparticles
with bipyridinium cyclophanes. The bipyridinium cycloph
anes act as receptors for the association of δ-donor sub
strates associated with the cyclophane units. The resulting
δ-donor–acceptor complexes enables the preconcentration
of the analyte at the conductive surface. A layered
viologen compound shows an efficient photocurrent generation
and fabrication of electrochemical devices. Similarly, the monolayer assembly
of viologen-linked TiO2 electrode can be used for fast
response electrochemical display devices.

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 characteri
zed by UV–visible spectroscopy, cyclic voltammetry and
transmission electron microscopy (TEM).

4-Methyl bipyridyl-1-pentalpyrrole (I) was synthesized
according to the procedure described earlier (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 cooling

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

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immersed in 2–3% solution of 3-aminopropyltrimethoxy-
silane 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 col-
loid pretreatment of the surface, the silylated glass plates
were immersed in Au nanoparticles solution for 30 min
followed by 30 mM of violagen 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 accelerat-
ing 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 respec-
tively. 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 nanoparti-
cles incorporated into the viologen pendant pyrrole mol-
cules. 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
have a strong absorption peak at 520 nm with a characteris-
tic 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 nanoparti-
cles 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 forma-
tion of aggregates of gold colloid with VC5Py. It is ex-
pected 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 citrate-capped gold nanoparticles with VC5Py
was tested in aqueous medium and the extent of aggrega-
tion was determined by UV–visible spectral studies.

The rate of the reaction was tested at different concen-
trations 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 collec-
tive 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 de-
pend 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.](image)

**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 2a. After addition of pyrrole pendant viologen molecules the individual particles form an aggregate (Figure 2b). Due to charge-induced aggregation of colloidal gold solution with VC5Py, a ball-like structure appears (Figure 2b). Similar observations were made in previous studies at different concentration ranges.

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.

UV-visible spectra were recorded for the layer-by-layer assembly of gold nanoparticles followed by a molecular glue of VC5Py on γ-aminopropytriethoxysilicate-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 multilayer 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 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 multiplayer assembly of viologen pendant pyrrole molecular glue with citrate-capped gold nanoparticles.

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 conditions. In the cathodic direction, well-defined redox peaks were observed for the violagen-modified gold nanoparticle surface under the same experimental conditions. These two peaks were assigned to a single electron transfer reaction for the electrostatically bound VCS5Py in 0.1 M H2SO4. In this way a multilayer architecture assembly of electrodes for the various electrocatalytic and photo voltaic applications may be constructed. Due to the electron-donating properties of VCS5Py, the polymerized form of VCS5Py-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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